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

PART II. CHEMICAL AND SPECTROGRAPHIC ANALYSIS, STRUCTURAL FORMULA

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Abstract. This paper presents chemical investigations of 15 samples of Ordovician glauconite. The results served as a basis for calculation of structural formulae for the glauconites. The chemical composition and crystallochemical formulae were compared with the corresponding data published by other authors for Ordovician glauconites and glauconites of different ages.

INTRODUCTION

This paper presents the results of further studies of 15 samples of Ordovician (Arenigian) glauconites derived from NE Poland. Preliminary investigations of these samples, comprising the separation of glauconite grains, their morphology, the determination of density and cation-exchange capacity, as well as thermal analysis, were published in a separate paper (Chabło, 1979).

EXPERIMENTAL AND RESULTS

Chemical analysis

Silica content in the glauconites was determined by gravimetric method. After SiO_2 determination, the solution was used for the complexometric determination of aluminium (Flaschka, Abdine, 1956; Chabło, 1964) and the sum of calcium, magnesium and manganese after prior precipitation of R_2O_3-type oxides with pyridine (Ponomariov, 1961). Colorimetric analysis with hydrogen peroxide (H_2O_2) was employed to determine titanium. The contents of potassium, sodium and calcium were determined in the solutions obtained through the decomposition of

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Table 1

Chemical analysis of glauconite from Ryboły borehole (in wt. %)

Component	1	2	3	4	5	6	7	Average results $\bar{x}$
SiO_2	51.29	51.34	51.43	51.38	51.41	51.24	51.27	51.34
TiO_2	0.44	0.42	0.40	0.41	0.43	0.44	0.42	0.42
Al_2O_3	12.00	12.10	12.20	12.20	12.01	12.08	12.18	12.11
Fe_2O_3	14.88	14.71	14.72	14.92	14.87	15.00	15.01	14.88
FeO	2.42	2.51	2.54	2.41	2.49	2.39	2.41	2.45
MnO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	3.61	3.62	3.55	3.62	3.58	3.57	3.52	3.58
CaO	0.55	0.55	0.51	0.55	0.48	0.48	0.48	0.51
Na_2O	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.
K_2O	7.56	7.58	7.51	7.60	7.76	7.66	7.79	7.64
P_2O_5	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
H_2O^+	5.15	5.09	5.23	5.27	5.50	5.39	5.36	5.28
H_2O^-	1.43	1.57	1.43	1.35	1.35	1.31	1.34	1.40
Total	99.38	99.54	99.57	99.76	99.93	99.61	99.83	99.66

tr. – trace, n.d. – not detected,

glauconites with hydrofluoric and perchloric acids. The concentration of sodium and potassium was measured using flame photometry, that of calcium by atomic absorption. Magnesium percentage was calculated subtracting the determined calcium content from the sum of calcium, magnesium and manganese. Manganese determination gave negative results because the content of this element in the analys-

Table 2

Statistical data for the chemical analysis of glauconite from Ryboły borehole (acc. to data of Table 1)

Component	Number of determinations	Arithmetic average $\bar{x}$	Median	Range	Confidence interval $n = 7$ $\beta_r = 0.51$ for confidence level 0.99		$R \cdot K_r$ for $n = 7$ $K_r = 0.37$	Standard deviation s
					$\bar{x} - R \cdot \beta_r$	$\bar{x} + R \cdot \beta_r$		
SiO_2	7	51.34	51.34	0.19	51.24	51.44	0.070	0.073
TiO_2	7	0.42	0.42	0.04	0.40	0.44	0.015	0.015
Al_2O_3	7	12.11	12.10	0.20	12.01	12.21	0.074	0.086
Fe_2O_3	7	14.88	14.88	0.19	14.78	14.98	0.070	0.068
FeO	7	2.45	2.42	0.15	2.37	2.53	0.056	0.059
MgO	7	3.58	3.58	0.10	3.53	3.63	0.037	0.038
CaO	7	0.51	0.51	0.07	0.47	0.55	0.026	0.035
K_2O	7	7.64	7.60	0.28	7.50	7.78	0.104	0.105
P_2O_5	7	0.05	0.05	–	–	–	–	–
H_2O^+	7	5.28	5.26	0.24	5.16	5.40	0.089	0.076
H_2O^-	7	1.40	1.35	0.26	1.27	1.53	0.096	0.089
		99.66						

ed samples was too small for the colorimetric method to be effective. For phosphorus and manganese determinations glauconites were decomposed with hydrofluoric and nitric acids. The contents of total and ferrous iron were determined by titration with potassium dichromate in the presence of an indicator (sodium diphenylamine-sulphonate aqueous solution) of glauconite samples decomposed with hydrofluoric and sulphuric acids. The content of H_2O^- was determined drying the glauconites at 105° whereas that of H_2O^+ by Penfield's method.

In order to check whether the results were reproducible, the analysis of Ryboły sample was repeated seven times. The resulting data (Tab. 1) served for statistical estimation of the adopted procedure (Tab. 2). It appeared that standard deviations calculated for respective components were lower than given by other authors, e.g. for diabase W-1 (Stevens *et al.*, 1960). Chemical analyses of all the glauconites studied are presented in Table 3; for Ryboły sample average percentages of the respective components have been given according to Table 1.

On the basis of the results obtained, the average chemical composition of Polish Ordovician glauconites was calculated and compared with the average composition of Ordovician glauconites of Sweden, the platform of the European part of the USSR, and the Siberian platform. Also the average chemical composition of Ordovician glauconite was calculated and compared with the average data for glauconites of different ages (Tab. 4).

Spectrographic analysis

Spectrographic analysis of the samples was carried out with Zeiss Q-24 and PGS-2 spectrographs, using boron-free carbon electrodes and standards made on silicate rock matrix. The standards contained admixtures of Li, Ba, Sr, Zn, Cu, Ni, Co, Pb, Ga, Zr, Cr, Sn (0.0005 – 0.2%) and 0.00005 – 0.02% of boron.

Since the silicate matrix of the standards differs significantly from glauconite both in the composition and structure, the data presented in Table 5 are to be treated as estimated.

Calculation of the structural formula for glauconite

Structural formulae for the glauconites studied were calculated on the assumption that positive charges of the cations should balance 10 O^{2-} + 2 OH^-, i.e. 22 negative charges (Hendricks, Ross, 1941; Harvey, 1943; Smulikowski, 1954). With this assumption it is not necessary to take into account the water content. In the calculations the amount of calcium was decreased by its part combined with phosphorus in $Ca_3(PO_4)_2$, and the content of iron in Podborowisko sample was lowered by the part combined with sulphur in pyrite (FeS_2). In the parent glauconitites phosphates were found to be present, and the glauconitite from Podborowisko contained partly oxidized pyrite (Langier-Kuźniarowa, 1967, 1971).

Calculation of the number of cations per 1/2 unit cell is presented in Table 6. The crystallochemical formulae for the Polish glauconites (Tab. 7) were compared with the corresponding average formulae for glauconites of different ages (Tab. 8).

The average crystallochemical formula for Ordovician glauconite (Tab. 8) was calculated from 15 chemical analyses made by the present author (Tab. 3) and 17 analyses published by other authors (Tab. 4, explanations).

Table 3

Chemical analysis of glauconites from NE Poland (in wt. %)

Component	Bartoszyce	Gołdap	Kętrzyn IG 1	Krzywa	Krzyże	Łochów IG 1	Mielnik	Olsztyn IG 2	Podborowisko	Rajsk	Ryboły	Strabla variety		Tłuszcz	Waśki
												light	dark		
SiO_2	50.03	51.09	50.95	51.69	51.36	50.59	51.57	51.15	50.86	52.06	51.34	51.49	51.34	51.90	52.20
TiO_2	0.25	0.40	0.39	0.15	0.30	0.21	0.16	0.36	0.32	0.21	0.42	0.23	0.26	0.14	0.19
Al_2O_3	12.54	13.05	12.54	10.38	11.01	10.78	9.43	13.54	10.83	11.53	12.11	11.07	9.46	12.03	11.26
Fe_2O_3	16.10	15.78	15.04	18.45	16.66	17.91	18.79	14.71	15.49	15.15	14.88	14.72	16.34	15.28	14.51
FeO	1.86	1.61	1.91	1.70	1.85	2.36	2.85	1.65	2.37	2.43	2.45	2.86	3.27	2.16	2.74
MgO	3.36	3.46	3.60	3.00	3.40	3.13	3.08	3.31	3.24	3.41	3.58	3.19	3.18	3.20	3.65
CaO	0.41	0.41	0.44	0.52	0.57	0.46	0.43	0.51	0.58	0.56	0.51	0.54	0.53	0.43	0.54
Na_2O	tr.	n.d.	n.d.	0.07	0.17	0.07	tr.	tr.	0.22	n.d.	tr.	tr.	tr.	0.07	0.12
K_2O	8.47	7.98	8.07	7.55	7.62	8.16	7.98	8.04	7.79	7.66	7.64	7.74	7.92	7.98	7.66
P_2O_5	0.04	0.14	0.13	0.08	0.08	0.12	0.04	0.04	0.07	0.08	0.05	0.12	0.12	0.09	0.08
H_2O^+	5.03	4.78	5.85	4.93	5.27	4.90	5.19	5.25	5.08	5.27	5.28	5.32	5.32	5.09	5.28
H_2O^-	1.85	1.68	1.80	1.56	1.68	1.42	1.16	1.25	3.27	1,39	1.40	3.32	2.86	1.33	1.47
S	–	–	–	–	–	–	–	–	0.06	–	–	–	–	–	–
Total	99.94	100.38	100.72	100.08	99.97	100.11	100.68	99.81	100.18	99.75	99.66	100.60	100.60	99.80	99.70

Table 4

The average chemical composition of Ordovician glauconites and glauconites of different ages (in wt. %)

Component	Ordovician							Of different ages		Explanations
	Sweden	Poland own analyses	USSR platform		available in literature	other publications and own analyses $n = 32$		Smulikowski (1954) "typical" glauconites	Weaver, Pollard (1973)	
			European	Siberian		number of determinations	average composition			
	$n = 6$	$n = 15$	$n = 7$	$n = 4$	$n = 17$			$n = 22$	$n = 69$	
SiO_2	50.26	51.31	49.43	48.67	49.51	32	50.27	49.58	49.215	Sweden: Hadding (1932), p. 124 analyses: 47, 49, 50, 51, 52 Burst (1958) analysis no. 4 Platform of the European part of the USSR: Nikołajewa, Borodajewska *et al.* (1971), p. 73, Tab. 4 analyses: Adze, Engure. E-1/1 E-7/4, E-9/2a, Poland: Fenoszina *et al.* (1966) analysis of sample 307 Siberian Platform: Nikołajewa, Borodajewska *et al.* (1971) p. 72, Tab. 3, analyses: 148, 10/XII, 5/XII, 7/9
TiO_2	–	0.27	0.15	0.31	0.21	25	0.24	–	–	
Al_2O_3	11.37	11.44	9.91	8.61	10.12	32	10.74	8.41	9.148	
Fe_2O_3	15.06	15.99	17.02	19.33	16.87	32	16.46	18.81	17.951	
FeO	2.27	2.27	2.75	2.45	2.51	32	2.40	2.78	3.427	
MnO	–	tr.	0.0145	0.062	0.03	9	0.03	–	–	
MgO	2.90	3.33	3.88	3.58	3.47	32	3.40	3.75	3.584	
CaO	0.74	0.50	0.44	0.79	0.63	32	0.57	0.51	0.644	
Na_2O	0.53	0.12	0.17	0.11	0.28	22	0.24	0.55	0.460	
K_2O	8.34	7.88	7.70	7.99	7.99	32	7.94	7.11	6.884	
P_2O_5	–	0.09	0.182	0.072	0.16	24	0.12	–	–	
H_2O^+	5.10	5.19	–	–	5.10	20	5.17	H_2O 8.12	8.482	
H_2O^-	4.57	1.83	2.39	1.72	2.79	30	2.31	–	–	
Heating loss	–	–	5.76	6.45	6.07	12	6.07	–	–	
Li_2O	–	–	0.035	0.0296	0.033	8	0.033	–	–	

n = number of analyses

Table 5

Spectrophotometric analysis of glauconites from NE Poland
(weight %)

Locality of sample	Sn	Zn	Cu	Ni	Cr	V	Ga	Li	B	Co	Mn	Ba	As	Be	Ge
Bartoszyce	0.0002	0.002	0.002	0.001	0.004	0.0065	0.01	0.003	>0.01	+	+	+	+	+	+
Gołdap	n.d.	0.002	0.001	0.0015	0.007	0.0065	0.005	0.003	>0.01	+	+	+	+	+	+
Kętrzyn IG 1	0.0002	0.002	0.001	0.001	0.007	0.012	0.008	0.005	0.02	+	+	+	+	+	+
Krzywa	n.d.	0.01	0.001	0.001	0.007	0.0065	0.005	0.002	0.01	+	+	+	+	+	+
Krzyże	n.d.	0.002	0.001	0.0002	0.004	0.001	0.0003	0.005	< 0.01	+	+	+	+	+	+
Łochów IG 1	n.d.	0.002	0.001	0.0015	0.007	0.015	0.005	0.002	0.02	+	+	+	+	+	+
Mielnik	n.d.	0.003	0.001	0.001	0.002	0.0065	0.005	0.002	0.01	+	+	+	n.d.	+	+
Podborowisko	n.d.	0.005	0.001	0.001	0.007	0.003	0.005	0.004	>0.01	+	+	+	n.d.	+	+
Olsztyn IG 2	n.d.	0.002	0.001	0.001	0.007	0.012	0.005	0.002	<0.01	+	n.d.	+	n.d.	+	+
Rajsk	n.d.	0.004	0.001	0.001	0.01	0.015	0.008	0.006	0.02	+	+	+	+	+	+
Ryboły	0.0002	0.01	0.001	0.001	0.013	0.009	0.01	0.006	0.02	+	+	+	+	+	+
Strabla light variety	0.0002	0.002	0.001	0.0002	0.007	0.012	0.0025	0.006	0.01	+	+	+	+	+	+
Strabla dark variety	n.d.	0.002	0.001	0.0004	0.013	0.012	0.0025	0.006	0.01	+	+	+	+	+	+
Tłuszcz	n.d.	0.002	0.002	0.001	0.01	0.015	0.005	0.002	0.01	+	+	+	+	+	+
Waśki	n.d.	0.005	0.001	0.0006	0.01	0.0065	0.005	0.006	0.01	+	+	+	+	+	+

+ qualitative detection, n.d. – not detected.

Table 6

Calculation of the crystallochemical formula for glauconite from Ryboły borehole

Component	Percentage	Mole ratio	Atomic ratio I	Cation valency	Number of charges	Number of cations $I\frac{22}{5.136}$	Component	Percentage	Mole ratio	Atomic ratio I	Cation valency	Number of charges	Number of cations $I\frac{22}{5.136}$
SiO_2	51.34	0.855	0.855	4	3.420	3.66	Na_2O	–	–	–	1	–	–
TiO_2	0.42	0.005	0.005	4	0.020	0.02	K_2O	7.64	0.081	0.162	1	0.162	0.69
Al_2O_3	12.11	0.119	0.238	3	0.714	1.02	P_2O_5	0.05					
Fe_2O_3	14.88	0.093	0.186	3	0.558	0.80	H_2O^+	5.28					
FeO	2.45	0.034	0.034	2	0.068	0.15	H_2O^-	1.40					
MgO	3.58	0.089	0.089	2	0.178	0.38							
CaO	0.51	0.008*	0.008	2	0.016	0.03	Total	99.66	–	–	–	5.136	–

* Calcium percentage was diminished by the part combined with phosphorus in $Ca_3(PO_4)_2$

Table 7

Crystallochemical formulae for glauconites of NE Poland

Locality of sample	K	Na	Ca	X	Mg	Fe^{2+}	Fe^{3+}	Al^{VI}	Ti	Y	OH	Si	Al	Z	O
Bartoszyce	0.78	–	0.03	0.81	0.36	0.11	0.87	0.65	0.02	2.01	2.00	3.59	0.41	4.00	10.00
Gołdap	0.72	–	0.02	0.74	0.37	0.09	0.84	0.70	0.02	2.02	2.00	3.61	0.39	4.00	10.00
Kętrzyn IG 1	0.74	–	0.02	0.76	0.38	0.11	0.81	0.69	0.02	2.01	2.00	3.64	0.36	4.00	10.00
Krzywa	0.69	0.01	0.03	0.73	0.32	0.10	0.99	0.56	0.01	1.98	2.00	3.69	0.31	4.00	10.00
Krzyże	0.70	0.03	0.04	0.77	0.36	0.11	0.93	0.60	0.02	2.02	2.00	3.67	0.33	4.00	10.00
Łochów IG 1	0.75	0.02	0.02	0.79	0.34	0.14	0.97	0.55	0.01	2.01	2.00	3.64	0.36	4.00	10.00
Mielnik	0.73	–	0.03	0.76	0.33	0.17	1.01	0.48	0.01	2.00	2.00	3.69	0.31	4.00	10.00
Olsztyn IG 2	0.72	–	0.03	0.75	0.35	0.10	0.78	0.75	0.02	2.00	2.00	3.63	0.37	4.00	10.00
Podborowisko	0.73	0.03	0.04	0.80	0.35	0.14	0.84	0.63	0.02	1.98	2.00	3.70	0.30	4.00	10.00
Rajsk	0.70	–	0.03	0.73	0.36	0.15	0.81	0.67	0.01	2.00	2.00	3.70	0.30	4.00	10.00
Ryboły	0.69	–	0.03	0.72	0.38	0.15	0.80	0.68	0.02	2.03	2.00	3.66	0.34	4.00	10.00
Strabla light variety	0.72	–	0.03	0.75	0.34	0.17	0.80	0.67	0.01	1.99	2.00	3.72	0.28	4.00	10.00
Strabla dark variety	0.73	–	0.03	0.76	0.35	0.20	0.89	0.55	0.02	2.01	2.00	3.74	0.26	4.00	10.00
Tłuszcz	0.73	0.02	0.02	0.77	0.35	0.13	0.82	0.68	0.01	1.99	2.00	3.67	0.33	4.00	10.00
Waśki	0.70	0.02	0.03	0.75	0.39	0.16	0.78	0.67	0.01	2.01	2.00	3.72	0.28	4.00	10.00

Table 8

Comparison of the average crystallochemical formulae for glauconites
n = number of analyses

K	Na	Ca	X	Mg	Fe^{2+}	Fe^{3+}	Al	Ti	Y	OH^-	Si	Al	Z	O
Ordovician glauconites from NE Poland $n = 15$														
0.72	0.01	0.03	0.76	0.36	0.14	0.86	0.64	0.02	2.02	2.00	3.67	0.33	4.00	10.00
Ordovician glauconites $n = 32$														
0.73	0.03	0.04	0.80	0.37	0.14	0.90	0.58	0.01	2.00	2.00	3.66	0.34	4.00	10.00
Glauconites of different ages (Hendricks, Ross, 1941) $n = 32$														
K	Na	Ca	0.84	0.40	0.19	0.97	0.47	—	2.03	2.00	3.65	0.35	4.00	10.00
Smulikowski (1954) $n = 60$														
0.67	0.08	0.08	0.83	0.41	0.17	1.05	0.40	—	2.03	2.00	3.66	0.34	4.00	10.00
Weaver, Pollard (1973) $n = 82$														
0.66	0.06	0.07	0.79	0.39	0.20	1.01	0.45	—	2.05	2.00	3.65	0.35	4.00	10.00

DISCUSSION

The chemical composition of glauconites in variable. The noted differences are due to the nature of the initial material, regional conditions, sample record, the degree of homogeneity of the structure, as well as to the presence of admixtures that can be difficult to detect, separate or determine.

A study of the chemical composition of a large number of glauconite samples has revealed that the essential differences regard mainly some components whilst other constituents show certain stability (Hendricks, Ross, 1941; Smulikowski, 1954; Borchert, Braun, 1963; Weaver, Pollard, 1973). This observation is in accordance with recent, mainly X-ray, investigations from which it appears that typical of glauconite is the 10Å mica structure, and that the essential variations in composition, involving a change in the proportion of aluminium and ferric iron, occur within this structure.

Considering the amounts of aluminium and iron in the structure, glauconites can be divided into those showing the prevalence of aluminium, intermediate, and glauconites with predominant iron, the latter being the commonest (Smulikowski, 1954; Borchert, Braun, 1963). Changes in the aluminium and iron content are not expected to be attended by any significant changes in the content of potassium. Several studies (Manghnani, Hower, 1964; Cimbálniková, 1971) show that a decrease in potassium percentage in glauconites is due to the increase in the content of the expanding component and, therefore, to the lower degree of homogeneity of the structure. But then, the presence of the expanding component changes the proportions of aluminium, ferric iron and other constituents.

It is feasible that one of the factors responsible for the variations in the chemical composition of glauconite is some undetected admixtures of iron compounds (Bentor, Kastner, 1965) and amorphous silica (Smulikowski, 1954). The origin of these admixtures is obscure. Zumpe's studies (1971) revealed changes in the distribution of Si, K, Ca and Fe concentrations in different zones of a glauconite grain, which seem to be brought about by the process of crystallization of glauconite. Thence a tentative hypothesis can be advanced that under certain circumstances, the excess of some components precipitates as various mineral phases.

The average chemical composition of NE Polish glauconites was compared with their Ordovician equivalents from Sweden (Hadding, 1932), the platform of the European part of the USSR and the Siberian platform (Nikolayeva, Borodayevskaya *et al.*, 1971). The analyses were chosen following Smulikowski's instructions (1954). Incomplete analyses, as well as those which gave total determinations of some components, e.g. iron, without comments, were not taken into account. Table 4 presents the average chemical composition of Ordovician glauconites, along with the number of analyses (n) from which the average percentages of components were calculated. In the case when certain determinations were missing, the averages were calculated from a smaller number of analyses. Thus, although the average composition of Ordovician glauconite was calculated from 32 analyses, the number of determinations from which the average percentages were calculated was given for each component.

The average perçentage of silica is the highest for the Polish glauconites, amounting to 51.31%. The average content of ferric iron shows a slight regular increase from the west (Sweden 15.06% Fe_2O_3) to the east (Siberian platform 19.33% Fe_2O_3) (Tab. 4). Simultaneously, a less pronounced decrease in aluminium percentage has been noted in the same direction. The same or similar FeO contents in the Ordovician glauconites of the compared areas are not fortuitous and testify to similar, rather moderate, oxidation-reduction conditions.

Average percentages of FeO and Fe_2O_3 in the Ordovician glauconites are lower than average percentages of these components in glauconites of different ages. The average Al_2O_3 percentage is somewhat higher in the Ordovician glauconites. The content of potassium (K_2O) for the glauconites studied averages 7.88%, being lower than in the Ordovician glauconites of Sweden and differing only slightly from the percentage of this element in the glauconites of the platform of the European part of the USSR or the Siberian platform. In general, potassium percentage in the Ordovician glauconites is higher than in glauconites of different ages (Tab. 4).

On the basis of 78 chemical analyses of glauconites, Borchert and Braun (1963) confirmed the observation that the increase in Fe^{3+} content in glauconite is attended by a decrease in the amount of aluminium. Considering the Fe^{3+} to Al ratio, they distinguished three types of glauconite: glauconites showing marked prevalence of Fe^{3+} over Al, those containing on the average 19% Fe_2O_3 and 8% Al_2O_3, and aluminium glauconites containing 10% Fe_2O_3 and 15% Al_2O_3.

The content of ferrous iron is similar, averaging 3.5% FeO in glauconites with the marked prevalence of Fe^{3+}, 3.0% in average ones, and 3.5% FeO in aluminium glauconites. Magnesium percentage is also similar (3.0%, 3.5%, 3.5% MgO). Very characteristic is the same potassium percentage for all the three types of glauconite, averaging 7.5% K_2O. As appears from these data, the average composition of the glauconites studied approximates to that of the average group (15.99% Fe_2O_3, 11.44% Al_2O_3, 3.33% MgO), tending towards aluminium glauconite. The percentage of ferrous iron is lower than calculated by Borchert and Braun.

Individually, samples Krzywa, Łochów and Mielnik correspond to average glauconite while the others are intermediate between average and aluminium glauconites (Tab. 3). Basing on the division of Borchert and Braun, it can be demonstrated (Tab. 4) that the Ordovician glauconites show regular variability of Fe_2O_3 and Al_2O_3 percentages from nearly average for the Siberian platform (19.33% Fe_2O_3, 8.61% Al_2O_3) to aluminium glauconite westwards.

Spectrographic analysis was performed to supplement chemical analyses of glauconites. From the results (Tab. 5), as well as from the data published elsewhere, it appears that manganese content in glauconites is low and, therefore, it should be classed among trace elements. Colorimetric determinations of manganese were made in all the samples, but its amount appeared to be too small to be detected by this method. In 1966 Jasyrev found the following trace elements in glauconites of different ages (Ordovician, Upper Jurassic, Lower and Middle Cretaceous) of the platform of the European part of the USSR: Be, Sc, V, Cr, Co, Ni, Cu, Zn, Y, Zr, Nb, Ta, Mo, Th, U, Li, B, Ti, Mn. Bentor and Kastner (1965) found that Sr, Ba, Cr, V, Cs and Rb were present in glauconite. According to these authors, the presence of Sr, Ba and V is due to the occurrence of expanding components in glauconite grains. Jasyrev (1966) is of the opinion that the majority of trace elements are not inherent in the structure of glauconite but got into the grains by way of sorption, or accompany the admixtures of other minerals contaminating glauconite grains.

The estimated lithium content in the analysed samples varies from 0.002% to 0.006% Li. Jasyrev (1966) gives a figure of 0.01% Li for the Ordovician glauconites whereas more recent data (Nikolayeva, Borodayevskaya *et al.*, 1971) referring to the Ordovician glauconites are similar, varying from 0.032 to 0.04% Li_2O for the platform of the European part of the USSR and from 0.02 to 0.052% Li_2O for the Siberian platform. The same authors give figures between 0.030 and 0.047% Li_2O for the present-day glauconites of the West African shelf.

In Jasyrev's opinion, the percentage of lithium is in intimate association with that of ferrous iron and, indeed, it has been found to be higher in dark-green grains.

This fact substantiates the hypothesis that Li together with Fe^{2+} occupies the octahedral sites. During the oxidation of Fe^{2+} lithium is released from the lattice, and this accounts for the low Li content in oxidized samples. It can remain in the form of adsorbed ion, which accounts for exchangeability of Li^+ cation. Treating with caution the non-quantitative data from Table 5, it can be inferred that lower Li percentages in the analysed samples are due to average Fe^{3+} content rather than to the advanced oxidation process.

In the analysed samples an increased boron content, estimated at hundredth parts of a per cent, was detected (Tab. 5). According to Jasyrev (1966), boron enters into the structure of glauconite substituting for silicon in the silicon-oxygen tetrahedra. He estimates the percentage of boron in the glauconites of the platform of the European part of the USSR at 0.064%, whereas Nikolayeva, Simonova and Borodayevskaya (1971) give values of 0.010–0.180% for the Ordovician glauconites of the same area and 0.037–0.200% for the Siberian platform. According to the cited authors, the average boron percentage in the Ordovician glauconites of the platform of the European part of the USSR and the Siberian platform is 0.076% and 0.058% respectively.

The crystallochemical formulae for the glauconites studied (Tab. 7) differ primarily in the amount of iron and aluminium at the octahedral sites. In the Ordovician glauconites of north-eastern Poland the Fe^{3+}/Al_{VI} ratio varies from the equilibrium state ($Fe^{3+}/Al_{VI} = 1.04$) in samples Olsztyn IG-2 and Dobre (Turnau-Morawska, Łącka, Wiewióra, 1975) to 2.10 in Mielnik sample. The average Fe^{3+}/Al_{VI} ratio for the 15 analysed samples is 1.34 while for 32 Ordovician glauconites from various areas it is 1.55. The corresponding values of the Fe^{3+}/Al_{VI} ratio in the average crystallochemical formulae for glauconites of different ages (Tab. 8) vary from 2.06 to 2.62. The glauconites under study show slight prevalence of iron over aluminium at the octahedral sites (average Fe^{3+}/Al_{VI} ratio = 1.34), attaining in the extreme case of Mielnik sample a value of 2.10, which corresponds to the lower limit of the Fe^{3+}/Al_{VI} ratio in the average crystallochemical formulae for glauconites of different ages.

Variations in the content of the other components of glauconites are insignificant, concerning mainly ferrous iron and potassium (Tab. 7). Compared with the average crystallochemical formulae for glauconites of different ages (Tab. 8), there is in general less Fe^{2+} and more K per unit crystallochemical formula. Magnesium content is little differentiated (Tab. 7), and the amount of Mg^{2+} ions at the octahedral sites is somewhat less than reported for glauconites of different ages. From the data in Table 8 it can be inferred that the average silicon percentage in glauconite is virtually constant and little dependent on the geological age of the sample.

All the samples in question are in the field of Cambrian and Ordovician glauconites in the diagram of Shutov *et al.* (1973, p. 275, Fig. 3) which determines the relationship between the percentage of Al^{3+}_{VI} and $Fe^{3+}/(Fe^{3+}+Al_{VI})$ in glauconites of different ages.

REFERENCES

BENTOR Y.K., KASTNER M., 1965: Notes on the mineralogy and origin of glauconite. *Jour. Sed. Petrology*. 35, 1, 155–166. Menasha, Wisconsin.

BORCHERT H., BRAUN H., 1963: Zum Chemismus von drei Glaukonittypen. *Chemie der Erde*, 23, 1, 83–90. Jena.

BURST J.F., 1958: Mineral heterogeneity in "glauconite" pellets. *Amer. Mineral.*, 43, 5–6, 481–497. Menasha, Wisconsin.

CIMBÁLNIKOVÁ A., 1971: Chemical variability and structural heterogeneity of glauconites. *Amer. Mineral.*, 56, 7–8, 1385–1392. Menasha, Wisconsin.
CHABŁO A., 1964: Próba oceny kompleksometrycznych metod oznaczania glinu w krzemianach. *Chemia Analityczna* 9, 501–508. Warszawa.
CHABŁO A., 1979. Studies of the chemical composition of glauconite from the Ordovician sediments of NE Poland. Part I. Separation of glauconite grains and their morphology, determination of density and cation-exchange capacity, thermal analysis. Mineralogia Polonica, 10, No 1, 49–61. Warszawa.
[FIENOSZINA U.I., GERENCZUK N.K., CWIK S.M.] ФЕНОШИНА У.И., ГЕРЕНЧУК Н.К., ЦВИК С.М., 1966: О разложении глауконита органическими кислотами. Вопросы минералогии осадочных образований, книга 7, с. 66—73. Изд. Львовского Университета. Львов.
FLASCHKA H., ABDINE H., 1956: Zur komplexometrischen Titration von Aluminium und Eisen und der Summe beider. *Z. anal. Chem.* 152, 77–80. Berlin.
HADDING A., 1932: The pre-Quaternary sedimentary rocks of Sweden, part IV:Glauconite and glauconitic rocks. *Medd. Lunds Geol.-Min. Inst.* 51, 175, Lund.
HARVEY C.O., 1943: Some notes on the calculation of molecular formulae for glauconite. *Amer. Mineral.*, 28, 9–10, 541–543. Menascha, Wisconsin.
HENDRICKS S.B., ROSS C.S. 1941: Chemical composition and genesis of glauconite and celadonite. *Amer. Mineral.*, 26, 12, 683–708. Menasha, Wisconsin.
[JASYREW A.P.] ЯСЫРЕВ А.П., 1966: Распределение микроэлементов в глауконитах Русской платформы. *Докл. АН СССР*, 168, 4, 914—916. Москва.
LANGIER-KUZNIAROWA A., 1967: Petrografia ordowiku i syluru na Niżu Polski. *Biul. Inst. Geol.* 197, 115–327. Warszawa.
LANGIER-KUŹNIAROWA A., 1971: Nowe dane do petrografii ordowiku i syluru na Niżu Polskim. *Biul. Inst. Geol.* 245, 253–351. Warszawa.
MANGHNANI M.H., HOWER J., 1964: Glauconites: cation exchange capacities and infrared spectra. Part I. The cation exchange capacity of glauconites. *Amer. Mineral.*, 49, 5–6, 586–598. Menasha, Wisconsin.
[NIKOŁAJEWA I.W., BORODAJEWSKA Z.W., SUCHARENKO A.W., GOŁUBOWA G.A., ZIERKAŁOWA M.I.] НИКОЛАЕВА И.В., БОРОДАЕВСКАЯ Э.В., СУХАРЕНКО А.В., ГОЛУБОВА Г.А., ЗЕРКАЛОВА М.И., 1971: Минералы группы глауконита в ордовикских отложениях юга Сибирской и северо-запада Русской платформы. *Тр. Института геол. и геофиз. АН СССР (Сибирское отделение)*, 144, 52—80. *Наука* Москва.
[NIKOŁAJEWA I.W., SIMONOWA W.I., BORODAJEWSKA Z.W.] НИКОЛАЕВА И.В., СИМОНОВА В.И., БОРОДАЕВСКАЯ З.В., 1971: Бор в ордовикских минералах группы глауконита. *Тр. Института геол. и геофиз. АН СССР (Сибирское отделение)*, 144, 124—131. Изд. *Наука* Москва.
[PONOMARIOW A.I.] ПОНОМАРЕВ А.И., 1961: Методы химического анализа силикатных и карбонатных горных пород. Изд. АН СССР. Москва.
SHUTOV V.D., KATZ M.Y.A., DRITS V.A., SOKOLOVA A.L., KOZAKOV G.A., 1973: Crystallochemical heterogeneity of glauconite as depending on the conditions of its formation and post-sedimentary changes. *Proceedings of the International Clay Conference* 1972, 269–279. Madrid.
SMULIKOWSKI K., 1954: The problem of glauconite. *Arch. Min.* 18, 1, 21–120. Warszawa.
STEVENS R.E., and others, 1960: Second report on a cooperative investigation of the composition of two silicate rocks. *Geological Survey Bulletin* 1113, 126. Washington.
TURNAU-MORAWSKA M., ŁĄCKA B., WIEWIÓRA A., 1975: Charakterystyka krystalochemiczna glaukonitu ze skał ordowiku obniżenia podlaskiego na tle litologii i genezy. *Kwart. geol.* 19, 4, 829–843. Warszawa.
WEAVER Ch.E., POLLARD L.D., 1973: Developments in sedimentology 15. The chemistry of clay minerals, 25–44. Elsevier, Amsterdam.
ZUMPE H.H., 1971: Microstructures in Cenomanian glauconite from the Isle of Wight, England. *Min. Mag.*, 38, 294, 215–224. London.

Adam CHABŁO

BADANIA SKŁADU CHEMICZNEGO GLAUKONITÓW Z UTWORÓW ORDOWIKU PÓŁNOCNO-WSCHODNIEJ POLSKI

CZĘŚĆ II. ANALIZA CHEMICZNA I SPEKTROGRAFICZNA, WZÓR KRYSTALOCHEMICZNY

Streszczenie

Wyniki 15 analiz chemicznych próbek ordowickich glaukonitów z obszaru północno-wschodniej Polski (tab. 3) porównano z odpowiednimi danymi dla glaukonitów ordowickich i różnowiekowych Szwecji, platformy europejskiej części ZSRR i platformy syberyjskiej (tab. 4). Glaukonity badane wykazują średnio największą zawartość krzemionki tak w stosunku do glaukonitów ordowickich porównywanych obszarow, jak i różnowiekowych. Ogólnie glaukonity ordowickie zawierają średnio więcej potasu niż różnowiekowe. Zawartość żelaza trójwartościowego (Fe_2O_3) wzrasta w nich w kierunku wschodnim (tab. 4). Na podstawie średnich zawartości glinu i trójwartościowego żelaza, badane próbki glaukonitu zaliczono do glaukonitów o przeciętnej zawartości tych pierwiastków według podziału Borcherta i Brauna (1963), z tendencją w kierunku glaukonitu glinowego.

Analiza spektrograficzna wykazała obecność niewielkich ilości pierwiastków śladowych, których szacunkowe zawartości przedstawiono w tabeli 5. Na podkreślenie zasługuje podwyższona zawartość boru. Fakt ten jest zgodny z wynikami uzyskanymi dla glaukonitów ordowickich pochodzących z porównywanych obszarów ZSRR.

W tabeli 7 przedstawiono wzory krystalochemiczne (strukturalne) badanych glaukonitów, a na tej podstawie obliczono ich średni wzór krystalochemiczny (tab. 8). Obliczono też wzór krystalochemiczny z 32 analiz własnych i zaczerpniętych z piśmiennictwa dla glaukonitu ordowickiego (tab. 8). Wzory te porównano ze średnimi wzorami krystalochemicznymi dla glaukonitów różnowiekowych (Hendricks, Ross, 1941; Smulikowski, 1954; Pollard, 1973). Glaukonity ordowickie zawierają więcej glinu, a nieco mniej żelaza trójwartościowego w pozycji oktaedrycznej przy prawie takiej samej zawartości krzemu i glinu w pozycji tetraedrycznej jak glaukonity różnowiekowe.

Адам ХАБЛО

ИССЛЕДОВАНИЕ ХИМИЧЕСКОГО СОСТАВА ГЛАУКОНИТОВ ИЗ ОБРАЗОВАНИЙ ОРДОВИКА СЕВЕРО-ВОСТОЧНОЙ ПОЛЬШИ

ЧАСТЬ II. ХИМИЧЕСКИЙ И СПЕКТРОГРАФИЧЕСКИЙ АНАЛИЗ, КРИСТАЛЛОХИМИЧЕСКАЯ ФОРМУЛА

Резюме

Результаты химического анализа 15 проб ордовицких глауконитов из северо-восточной Польши (таб. 3) сравнивались с соответствующими данными ордовицких и разновозрастных глауконитов Швеции, платформы

европейской части СССР и сибирской платформы (таб. 4). Исследованные глаукониты имеют (средне) самое большое содержание кремнезёма как по отношению к ордовицким сравниваемых территорий, так и разновозрастных. Вообщем, ордовицкие глаукониты содержат в среднем большее количество калия, чем разновозрастные. Содержание трёхвалентного железа (Fe_2O_3) в них возрастает в восточном направлении (таб. 4). На основании среднего содержания алюминия и трёхвалентного железа исследованные пробы глауконита отнесены к глауконитам со средним содержанием этих элементов согласно классификации Борхарта и Брауна (1963), с тенденцией в направлении алюминиевого глауконита.

Спектрографический анализ показал наличие небольших количеств микроэлементов, приблизительное содержание которых представлено в таблице 5. Необходимо подчеркнуть повышенное содержание бора. Этот факт соответствует результатам, полученным для ордовицких глауконитов со сравниваемых территорий СССР.

В таблице 7 представлены кристаллохимические (структурные) формулы исследованных глауконитов, а на этом основании подсчитана средняя кристаллохимическая формула (таб. 8). Подсчитана была также кристаллохимическая формула на основе 32 анализов собственных и взятых с литературных данных для ордовицкого глауконита (таб. 8). Эти формулы сравнивались со средними кристаллохимическими формулами для разновозрастных глауконитов (Гендрикс. Росс, 1941 ; Смуликовски, 1954 ; Поллард, 1973). Ордовицкие глаукониты содержат немного больше алюминия, а несколько меньше трёхвалентного железа в октаэдрическом слое, при почти таком же самом содержании кремния и алюминия в тетраэдрическом слое, как разновозрастные глаукониты.