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GEOCHEMICAL CHARACTERISTICS OF THE BOCHNIA EVAPORITES MEMBER, WITH NEW ASPECTS IN Br/Cl RATIO DETERMINATIONS

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Abstract. The Bochnia Evaporites member (3rd cyclothem) is the thickest set of strata among 5 cyclothem representing Miocene evaporites in the southern part of Poland. Sediments of the 3rd cyclothem may be subdivided into 2 subcycles, *A* nad *B*, reflecting two different conditions of sedimentation. Geochemical study of the member in question was carried out on the ground of numerous samples collected from the whole stratigraphic sequence. As much as 58 samples from the Wieliczka and Bochnia salt mines were subjected to chemical analyses.

From the calculated values for K^+ , Mg^{2+} , and Ca^{2+} , as well as the ratios of $Mg:Cl$ and $K:Cl$, one may conclude that close to the top of the member favourable conditions for deposition of $K-Mg$ salts have been initiated. Bromine analysis in relation to palaeosalinity does confirm this conclusion.

Besides colourimetric method in bromine analysis, a new, practical, and accurate method has been applied, using SEMQ electron microprobe. This method emphasizes the significance of small distance of sampling sites, within the range 2-10 cm.

INTRODUCTION

The Miocene evaporites are widespread almost all over the southern part of Poland, displaying facies variation, ranging from carbonatic to chloridic (Fig. 1). In the late Miocene these deposits were folded and thrust from the south towards the north by the Carpathian movements, leading to various degrees of deformation, from severely deformed deposits, passing northward to less deformed ones. As a result of the work of Garlicki (1968), five sedimentary cyclothem were distinguished. These five cyclothem were stratigraphically considered as five members belonging to Wieliczka Formation or to the salt bearing formation (Garlicki *in press*), where Bochnia Evaporites member represents the 3rd member or the 3rd cyclothem.

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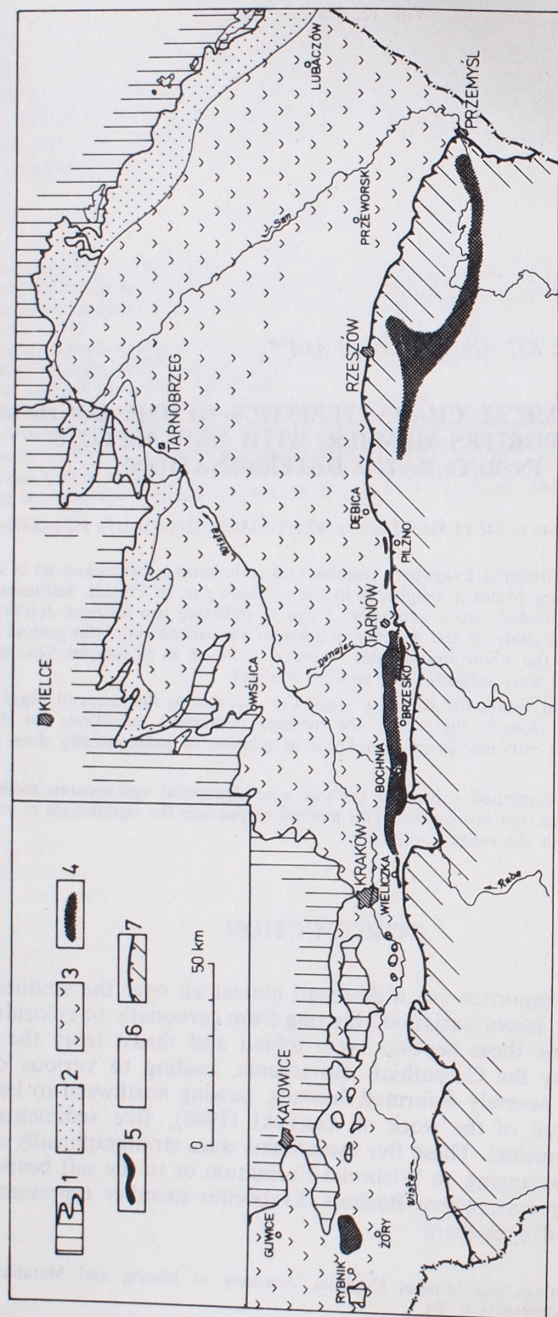


Fig. 1. Distribution of Badenian evaporites in the Carpathian foreland of Poland

1 - outcrops of sediments older than Miocene, 2 - carbonate-littoral facies, 3 - sulfate facies, 4 - chloride facies, 5 - salt deposits within the folded and overthrust unit, 6 - area without evaporites, 7 - margin of the Flysch Carpathians overthrust

Stratigraphically, the member in question consists of five green salt layers, separated by intercalations, and is overlain by Shaft salts and Lower Spiza salts. The whole sequence is initiated with terrigenous sediments and ended with layers of salt. This facilitates further stratigraphic subdivision of the member into two subcycles.

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STRATIGRAPHIC SETTING

Bochnia Evaporites member consists of two subcycles, A and B, reflecting different physico-chemical conditions governing in the basin (Fig. 2).

The lower subcycle A in non-deformed portions of the basin comprises 5 green salt layers separated by 4 intercalations. The green salt layers could be considered as a prograding phase towards the maturity of evaporating process, which took place within the middle cycle of the 5 minor ones. The deposit of the minor cycle no 3 is the thickest and the purest one, whereas those of minor cycles nos 1 and 2, 4 and 5 represent aggrading and retrograding phases respectively. Intercalations, alternating with 5 green salt layers are represented mainly by terrigenous material, composed of anhydritic claystones and silt-

MEMBER	SUBCYCLE	MINOR CYCLE	LITHOLOGICAL UNITS
BOCHNIA EVAPORITES Mbr	Subcycle B	7	Lower Spiza Salts
			I
	Subcycle B	6	Shaft Salts
			I
	Subcycle A	5	1 st green Salt
			I
		4	2 nd green Salt
			I
		3	3 rd green Salt
			I
		2	4 th green Salt
			I
		1	5 th green Salt
			I

Fig. 2. Stratigraphic subdivision of Bochnia Evaporites Member

stones with shales. All intercalations are thinly bedded, reflecting quiet conditions of sedimentation.

The upper subcycle B represents the maturation phase of evaporation process. It contains the thickest salt layers as well as the purest ones, being the products of two minor sedimentary cycles (numbered as 6 and 7). Shaft salts represent minor cycle no 6 and are developed as pure salts displaying bituminous odour. They reflect the first relatively longer period of evaporation. Lower Spiza salts represent minor cycle no 7 which is considered as the culmination of evaporation process. This cycle is made up of the purest and thickest salt layers among those constituting the member. The subcycle B begins with the thickest intercalation, reflecting the longest period of terrigenous influxes to the basin. A second intercalation recorded separates both Shaft and Lower Spiza salts.

RESEARCH MATERIALS AND GEOCHEMICAL ANALYSES

58 samples covering the Bochnia Evaporites member from the Wieliczka and Bochnia salt mines were collected for geochemical study at 0.3–1.2 m intervals across the total thickness of each salt bed. The interval was depending on the uniformity of salt and the position of non-halite intercalations. The samples were obtained using hand pick method in order to get the purest halite specimens.

The main constituents of the samples were determined as follows:

chlorine (wt. %) – by argentometric method,

sulphate (wt. %) – the samples were treated with dil. hydrochloric acid and sulphate precipitated from the obtained solution as BaSO₄, filtered, burned and weighed,

insoluble residue (wt. %) – the initial sample was dissolved in distilled water, filtered off, washed, dried and weighed.

Moreover, Na, K, Mg, Fe, Zn, Cu, Mn, Pb, Ni, Co, Sr, Cd were determined as wt. %, using PYE UNICAM, SP 90 Atomic Absorption Spectrophotometer. In addition boron was determined by spectrochemical method.

The results of the above mentioned analyses are presented in Tables 1–4 and Figs. 3–6. In addition the concentration logarithms of K⁺, Mg²⁺, Ca²⁺, and Cl⁻ (in ppm) have been calculated (Tables 5 and 6), as well as the functional ratios of K:Cl and Mg:Cl presented in Figs 7, 8, 9 and 10.

BROMINE PROFILE

The geochemistry of bromine in the marine evaporites was studied already by Boeke (1908), and recently developed by many authors (Kühn 1955a, b, 1968, Valyashko 1956, Schwerdtner and Wardlaw 1963, Holser 1966, 1970, 1979, Raup 1966, Zak 1969, 1974, Hite 1970, 1974, Raup and Hite 1978, Garlicki and Wiewiórka 1981). General distribution of bromine in rocks and waters was presented by Holser (1966), where by the author introduced the distribution coefficient. From this coefficient one can calculate the concentration of bromine during crystallization of the first halite, and then, as evaporation proceeds, its concentration in the brine and succeeding crystals.

Samples collected from Wieliczka salt mine (58 in number), with 0.2–0.5 m interval, were analysed using colourimetric procedure. In addition 25 samples

Table 1

Results of chemical analyses, V¹th level, Wieliczka (wt. %)

Symbol	Sample no	Insoluble residue	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	CaSO ₄	MgSO ₄	Na ₂ SO ₄	KCl	MgCl ₂	CaCl	NaCl	wt %
W-6-1*	1	18.60	28.34	0.044	2.48	0.015	43.26	7.64	8.43	0.076	1.93	0.092	—	—	71.18	100.31
W-6-2	2	5.68	34.09	0.017	1.72	0.014	53.19	3.32	4.69	—	—	0.036	0.053	0.920	86.65	98.37
W-6-6	3	1.19	38.09	0.008	0.47	0.009	57.96	1.98	1.59	0.044	1.60	0.017	—	—	95.56	100.01
W-6-7	4	5.81	34.05	0.017	2.38	0.013	52.48	6.23	8.08	0.064	0.08	0.036	—	—	86.50	100.4
W-6-8	5	2.24	37.76	0.012	0.49	0.013	57.51	2.32	1.65	0.063	1.64	0.026	—	—	94.81	100.4
W-6-9	6	4.05	37.14	0.015	0.77	0.016	54.96	4.07	2.63	0.079	3.18	0.031	—	—	90.57	100.4
W-6-12	7	5.12	34.61	0.017	2.38	0.012	53.06	6.14	7.08	0.058	0.58	0.036	—	—	87.45	100.2
W-6-13	8	4.04	35.73	0.013	1.69	0.013	51.58	4.89	5.75	0.066	1.15	0.028	—	—	89.30	100.3
W-6-14	9	1.25	38.03	0.011	0.76	0.019	54.17	4.44	2.58	0.096	1.58	0.022	—	—	94.87	100.3
W-6-17	10	1.08	37.18	0.009	0.80	0.086	58.15	1.13	1.59	—	—	0.019	0.335	0.919	94.49	98.45
W-6-18	11	2.79	37.30	0.009	0.80	0.005	56.74	2.86	2.70	0.023	1.39	0.021	—	—	93.53	100.4
W-6-19	12	5.79	35.09	0.014	1.49	0.012	53.37	4.64	5.07	0.059	1.49	0.293	—	—	87.97	100.3
W-6-20	13	1.44	38.07	0.011	0.24	0.009	57.83	1.89	0.82	0.043	1.89	0.023	—	—	95.34	99.56
W-6-21	14	1.50	38.25	0.011	0.28	0.006	58.51	2.43	0.98	0.029	0.98	0.023	—	—	96.46	99.97
W-6-22	14	1.51	38.78	0.011	0.25	0.005	58.86	1.45	0.84	0.025	1.23	0.022	—	—	97.04	100.4
W-6-23	16	1.33	38.84	0.009	0.19	0.006	59.57	0.90	0.65	0.028	0.65	0.019	—	—	98.21	100.4
W-6-24	17	1.97	38.51	0.011	0.20	0.005	58.51	2.21	0.69	0.025	1.52	0.023	—	—	96.45	100.5
W-6-25	18	1.66	38.72	0.010	0.28	0.005	58.69	1.46	0.97	0.026	1.15	0.021	—	—	96.75	100.4
W-6-26	19	1.51	38.39	0.009	0.21	0.005	58.69	1.64	0.72	0.029	1.63	0.020	—	—	96.17	100.08
W-6-27	20	1.58	38.62	0.011	0.26	0.006	58.33	1.38	0.87	0.023	1.15	0.023	—	—	96.75	100.3
W-6-28	21	0.92	38.03	0.009	0.24	0.005	58.69	0.51	0.73	—	—	0.020	0.018	0.075	96.65	98.7
W-6-29	22	0.91	38.76	0.006	0.07	0.003	59.22	0.84	0.24	0.014	0.97	0.012	—	—	97.64	99.78
W-6-30	23	32.01	25.19	0.058	0.98	0.093	35.99	5.84	3.36	0.461	4.59	0.122	—	—	59.24	99.78

* Wieliczka, level number, sample number in the profile.

Table 2
Results of chemical analyses, V^{IIIa} level, Wieliczka (wt %)

Symbol	Sample no	Inso- luble residue	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	CaSO ₄	MgSO ₄	Na ₂ SO ₄	KCl	MgCl ₂	CaCl ₂	NaCl	wt %
<i>W-8-1</i>	24	0.09	38.40	0.006	0.10	0.003	59.04	0.52	0.35	0.015	0.34	0.014	—	—	97.36	98.20
<i>W-8-2</i>	25	9.74	33.15	0.017	1.44	0.006	51.06	3.43	4.85	—	—	0.037	0.024	0.036	84.09	98.79
<i>W-8-3</i>	26	1.47	37.28	0.008	0.59	0.009	56.74	1.63	2.02	0.048	0.24	0.017	—	—	94.54	98.35
<i>W-8-4</i>	27	22.16	28.44	0.021	1.78	0.008	41.67	6.18	6.03	0.037	2.81	0.043	—	—	68.67	99.74
<i>W-8-6</i>	28	9.05	34.51	0.022	0.73	0.008	51.19	1.69	2.48	0.040	0.03	0.046	—	—	87.71	99.35
<i>W-8-8</i>	29	5.83	35.43	0.017	0.69	0.014	54.79	1.77	2.51	—	—	0.035	0.056	0.149	90.06	98.84
<i>W-8-9</i>	30	1.90	36.39	0.011	1.11	0.012	56.21	2.53	3.59	—	—	0.022	0.047	0.059	92.52	98.27
<i>W-8-11</i>	31	1.92	36.76	0.009	0.89	0.010	55.67	3.05	3.01	0.050	1.31	0.020	—	—	91.77	98.19
<i>W-8-12</i>	32	2.91	36.11	0.009	1.44	0.011	55.61	4.33	4.89	0.055	0.06	0.019	—	—	91.73	99.32
<i>W-8-14</i>	33	1.12	37.50	0.008	0.69	0.009	57.98	1.39	1.97	—	—	0.017	0.038	0.208	95.32	98.67
<i>W-8-15</i>	34	1.28	37.76	0.008	0.53	0.008	57.98	1.61	1.81	0.041	0.45	0.016	—	—	95.59	99.19
<i>W-8-16</i>	35	0.87	38.21	0.006	0.20	0.003	58.33	0.71	0.69	0.014	0.31	0.012	—	—	96.78	98.67
<i>W-8-17</i>	36	1.26	37.61	0.009	0.71	0.011	58.45	1.13	1.59	—	—	0.019	0.042	0.678	95.59	99.19
<i>W-8-18</i>	37	0.34	38.07	0.008	0.32	0.006	58.87	0.67	0.95	—	—	0.016	0.023	0.015	96.76	98.21
<i>W-8-19</i>	38	0.70	37.72	0.007	0.40	0.004	58.16	1.82	1.36	0.019	0.02	0.015	—	—	95.89	98.21
<i>W-8-20</i>	39	0.92	37.79	0.007	0.45	0.005	58.16	1.25	1.54	0.025	0.21	0.015	—	—	95.89	98.64
<i>W-8-21</i>	40	4.61	35.13	0.009	1.29	0.004	54.23	3.02	4.28	—	—	0.020	0.017	0.088	89.29	98.31
<i>W-8-22</i>	41	0.85	37.62	0.007	0.48	0.003	58.16	0.96	1.36	—	—	0.015	0.013	0.224	95.63	98.15
<i>W-8-23</i>	42	15.16	32.79	0.014	0.20	0.008	50.55	0.75	0.68	0.044	0.05	0.029	—	—	83.33	99.31
<i>W-8-24</i>	43	8.64	33.76	0.017	1.39	0.008	51.55	3.96	4.73	0.044	0.87	0.036	—	—	84.98	99.39

Table 3

Results of chemical analyses, V^{IIIa} level, Bochnia (wt %)

Symbol	Sample no	Inso- luble residue	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	CaSO ₄	MgSO ₄	Na ₂ SO ₄	KCl	MgCl ₂	CaCl ₂	NaCl	wt %
<i>B-5-4*</i>	44	7.45	35.59	0.048	0.38	0.012	54.61	1.31	1.31	0.060	0.49	0.100	—	—	89.90	99.37
<i>B-5-5</i>	45	21.07	28.84	0.054	1.74	0.014	42.20	5.63	5.93	0.069	2.06	0.115	—	—	69.49	98.73
<i>B-5-6</i>	46	7.83	35.08	0.048	0.42	0.012	54.08	1.11	1.44	0.059	0.07	0.101	—	—	89.17	98.67
<i>B-5-18</i>	47	18.85	29.48	0.022	1.78	0.048	45.44	5.65	6.03	0.238	0.28	0.046	—	—	74.93	100.37
<i>B-5-19</i>	48	17.67	29.23	0.025	1.79	0.045	45.05	4.57	6.07	0.223	0.16	0.052	—	—	74.24	98.43
<i>B-5-20</i>	49	17.36	29.81	0.022	1.59	0.017	45.20	4.75	5.41	0.086	1.25	0.046	—	—	74.49	98.65
<i>B-5-21</i>	50	14.62	27.80	0.024	1.44	0.026	47.52	4.85	4.89	0.131	1.90	0.051	—	—	78.28	99.88

Table 4

Results of chemical analyses, IX^{th} level, Bochnia (wt %)

Symbol	Sample no	Inso- luble residue	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	CaSO ₄	MgSO ₄	Na ₂ SO ₄	KCl	MgCl ₂	CaCl ₂	NaCl	wt %
<i>B-9-A</i>	51	2.32	37.38	0.007	0.15	0.002	57.62	0.66	0.49	0.011	0.45	0.014	—	—	95.01	98.38
<i>B-9-B</i>	52	1.77	37.92	0.006	0.18	0.003	58.15	0.78	0.59	0.015	0.52	0.012	—	—	95.89	98.79
<i>B-9-C</i>	53	1.53	37.94	0.006	0.15	0.003	38.33	0.63	0.49	0.013	0.39	0.012	—	—	96.18	98.63
<i>B-9-D</i>	54	1.51	37.35	0.007	0.61	0.004	57.27	1.92	2.06	0.019	0.67	0.014	—	—	94.42	98.69
<i>B-9-E</i>	55	1.09	37.61	0.008	0.72	0.004	57.98	1.96	2.45	0.019	0.02	0.016	—	—	95.59	99.19
<i>B-9-F</i>	56	3.69	36.19	0.009	0.88	0.008	55.79	2.12	2.97	0.027	—	0.019	0.009	—	91.99	98.72
<i>B-9-G</i>	57	0.87	38.39	0.005	0.25	0.007	58.69	1.29	0.84	0.036	0.99	0.010	—	—	96.76	99.51
<i>B-9-H</i>	58	2.44	36.61	0.010	0.80	0.004	56.32	2.11	2.73	0.021	0.25	0.022	—	—	92.85	98.33

* Bochnia, level number, sample number in the profile.

Table 5

Concentration logarithms of K^+ , Mg^{2+} , Ca^{2+} , and the relations
of $K:Cl$, $Mg:Cl$, VI^{th} level, Wieliczka

Symbol	Sample no	K^+ wt %	Mg^{2+} wt %	Ca^{2+} wt %	Cl^- wt %	K^+ Log ppm	Mg^{2+} Log ppm	Ca^{2+} Log ppm	$\frac{K \cdot 10^3}{Cl}$	$\frac{Mg \cdot 10^3}{Cl}$
W-6-1	1	0.044	0.015	2.48	43.26	2.64	2.18	4.39	1.006	0.353
W-6-2	2	0.017	0.014	1.72	53.19	2.23	2.13	4.23	0.322	0.254
W-6-6	3	0.008	0.009	0.47	57.96	1.91	1.95	3.67	0.139	0.152
W-6-7	4	0.017	0.013	2.38	52.48	2.23	2.11	4.38	0.322	0.247
W-6-8	5	0.013	0.013	0.49	57.51	2.09	2.10	3.69	0.217	0.219
W-6-9	6	0.015	0.016	0.77	54.96	2.17	2.20	3.89	0.269	0.289
W-6-12	7	0.017	0.012	2.38	53.06	2.23	2.07	4.38	0.319	0.222
W-6-13	8	0.014	0.013	1.69	51.58	2.13	2.12	4.23	0.261	0.257
W-6-14	9	0.011	0.019	0.76	54.17	2.02	2.29	3.88	0.195	0.358
W-6-17	10	0.009	0.086	0.80	58.15	1.96	2.93	3.90	0.155	1.472
W-6-18	11	0.010	0.005	0.80	56.74	1.99	1.67	3.90	0.176	0.083
W-6-19	12	0.014	0.012	1.49	53.37	2.14	2.08	4.17	0.261	0.226
W-6-20	13	0.011	0.009	0.24	57.83	2.04	1.93	3.38	0.339	0.145
W-6-21	14	0.011	0.006	0.29	58.51	2.04	1.78	3.46	0.189	0.103
W-6-22	15	0.011	0.005	0.25	58.86	2.02	1.69	3.39	0.179	0.085
W-6-23	16	0.009	0.006	0.19	59.57	1.97	1.75	3.28	0.158	0.094
W-6-24	17	0.011	0.005	0.20	58.51	2.04	1.69	3.31	0.189	0.085
W-6-25	18	0.010	0.005	0.28	58.69	2.00	1.73	3.45	0.172	0.091
W-6-26	19	0.010	0.005	0.21	58.69	1.98	1.69	3.33	0.164	0.085
W-6-27	20	0.011	0.006	0.26	58.33	2.05	1.77	3.41	0.191	0.101
W-6-28	21	0.010	0.005	0.24	58.69	1.98	1.67	3.38	0.164	0.080
W-6-29	22	0.006	0.003	0.07	59.22	1.75	1.45	2.85	0.096	0.047
W-6-30	23	0.058	0.093	0.99	35.99	2.76	2.97	3.99	1.613	2.584

Table 6

Concentration logarithms of K^+ , Mg^{2+} , Ca^{2+} , and the relations
of $K:Cl$, $Mg:Cl$, IX^{th} level Bochnia

Symbol	Sample no	K^+ wt %	Mg^{2+} wt %	Ca^{2+} wt %	Cl^- wt %	K^+ Log ppm	Mg^{2+} Log ppm	Ca^{2+} Log ppm	$\frac{K \cdot 10^3}{Cl}$	$\frac{Mg \cdot 10^3}{Cl}$
B-9-A	51	0.007	0.002	0.14	57.62	1.83	1.34	3.16	0.117	0.038
B-9-B	52	0.006	0.003	0.17	58.15	1.76	1.49	3.24	0.099	0.053
B-9-C	53	0.006	0.003	0.14	58.33	1.76	1.43	3.16	0.099	0.046
B-9-D	54	0.007	0.004	0.61	57.27	1.83	1.58	3.78	0.118	0.067
B-9-E	55	0.008	0.004	0.72	57.98	1.89	1.58	3.86	0.133	0.066
B-9-F	56	0.009	0.008	0.88	55.79	1.97	1.91	3.94	0.169	0.145
B-9-G	57	0.005	0.007	0.25	58.69	1.68	1.86	3.39	0.082	0.124
B-9-H	58	0.010	0.004	0.80	56.32	2.02	1.63	3.90	0.186	0.075

Table 7

Results of trace chemical analyses, VI^{th} , $VIII^{th}$ levels, Wieliczka. N* below detection limit

Symbol	Sample no	Fe	Zn	Cu	Mn	Pb	Ni	Co	Sr	Cd	B
W-8-1	24	0.005	0.0001	0.001	0.0002	N*	N	N	0.005	0.0006	<0.001
W-8-3	25	0.010	0.0003	0.002	0.0006	<N	N	N	0.014	0.0004	<0.001
W-6-1	1	0.001	0.0002	0.004	0.0001	0.0002	0.0006	0.0002	0.016	0.0002	<0.001
W-6-2	2	0.120	0.0001	0.001	0.0030	0.0002	0.0006	<N	0.009	0.0002	0.001
W-6-6	3	0.008	0.0001	0.002	0.0001	0.0002	0.0002	<N	0.008	0.0002	<0.001
W-6-7	4	0.410	0.0016	0.002	0.0110	0.0008	0.0007	0.0015	0.016	0.0002	0.001
W-6-8	5	0.016	0.0001	0.001	0.0003	0.0002	0.0002	0.0002	0.006	0.0002	<0.001
W-6-9	6	0.040	0.0001	0.002	0.0020	<N	N	N	0.008	N	<0.001
W-6-12	7	0.011	0.0006	0.002	0.0003	<N	N	N	0.007	N	<0.001
W-6-13	8	0.068	0.0001	0.002	0.0002	<N	N	N	0.011	N	<0.001
W-6-14	9	0.051	0.0004	0.002	0.0001	<N	N	N	0.006	0.0006	<0.001
W-6-17	10	0.008	0.0002	0.002	0.0001	<N	N	N	0.005	0.0008	<0.001
W-6-18	11	0.008	0.0001	0.002	0.0001	<N	N	N	0.006	<0.0002	<0.001
W-6-19	12	0.126	0.0004	0.002	0.0014	<N	N	N	0.016	<0.0002	<0.001
W-6-20	13	0.008	0.0002	0.001	0.0006	<N	N	N	0.009	0.0004	<0.001
W-6-21	14	0.028	0.0003	0.002	0.0008	<N	N	N	0.007	0.0006	<0.001
W-6-22	15	0.026	0.0004	0.002	0.0007	<N	N	N	0.006	0.0004	<0.001
W-6-23	16	0.014	0.0002	0.002	0.0002	<N	N	N	0.008	0.0003	<0.001
W-6-24	17	0.021	0.0005	0.001	0.0012	<N	N	N	0.005	0.0004	<0.001
W-6-25	18	0.028	0.0003	0.001	0.0006	<N	N	N	0.008	0.0008	<0.001
W-6-26	19	0.016	0.0002	0.001	0.0002	<N	N	N	0.008	0.0004	<0.001
W-6-27	20	0.018	0.0002	0.002	0.0003	<N	N	N	0.006	0.0004	<0.001
W-6-28	21	0.016	0.0003	0.001	0.0004	<N	N	N	0.005	0.0004	<0.001
W-6-29	22	0.003	0.0012	0.002	0.0001	<N	N	N	0.006	0.0006	<0.001
W-6-30	23	0.015	0.0001	0.002	0.0001	<N	N	N	0.005	0.0005	<0.001

were obtained from the third green salt layer, where spacing between samples was ranging between 2–10 cm, in order to throw the light on Br/Cl ratio changes within close intervals. These samples were analysed using Scanning Electron Microprobe Quantimeter, type SEMQ-ARL. The obtained values of Br and Cl contents were not absolute ones, but referred to two standards containing pure Br and Cl (NaCl and KBr pure crystals) with 60.66 wt. % and 67.15 wt. % for Cl and Br respectively. The results of both analyses have been presented in Figs 11 and 12.

DISCUSSION AND INTERPRETATION OF RESULTS

The content of NaCl (in weight percent) ranges from 52 to 98, and its observed increase in positively correlated upwards with stratigraphic sequence. This is presented in Table 1 and Fig. 3, where in the Lower Spiza salts (samples nos 14–22 and 23) the relative increase of NaCl content rises up to its maximum within sample no 21, while within sample no 23 the percent of insoluble residue is higher, indicating the end of the evaporation period. In the third green salt layer, a duplication phenomenon within one evaporative period restricted to one lithological type was established. Sample no. 4 represents a short period of decrease of NaCl content. This is consistent with macroscopic observations, which show a clayey layer intercalated with salt.

Recently Dean *et al.* (1978), and Holser (1979) were the first to point atten-

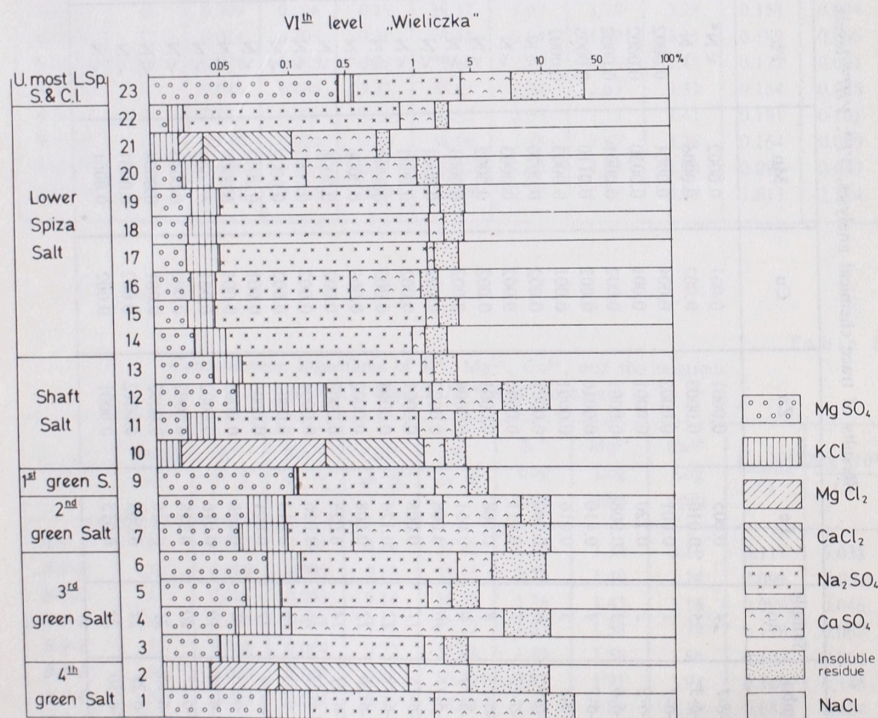


Fig. 3. Petrochemical diagram, VIth level, 320 m SE of Shaft Kinga, Wieliczka mine

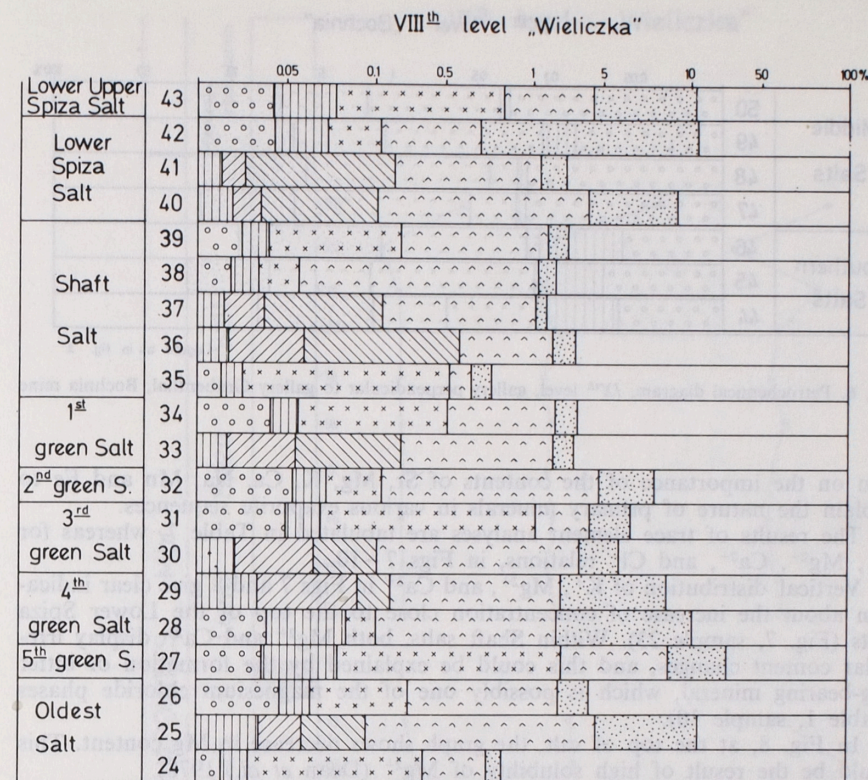


Fig. 4. Petrochemical diagram, VIIIth level, 1100 m E of Shaft Kinga, Wieliczka mine

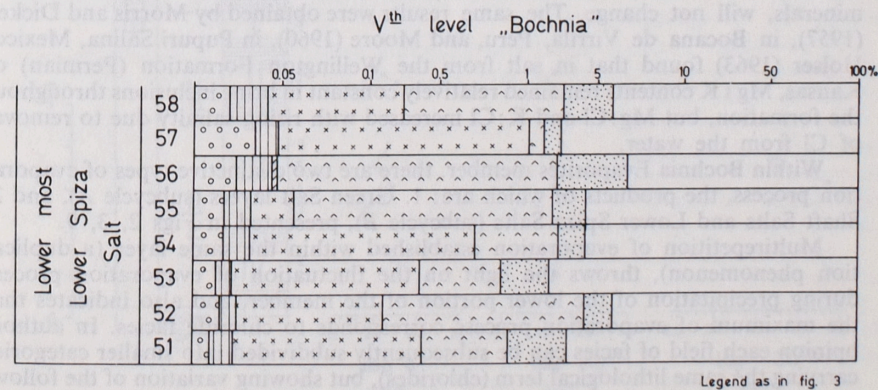
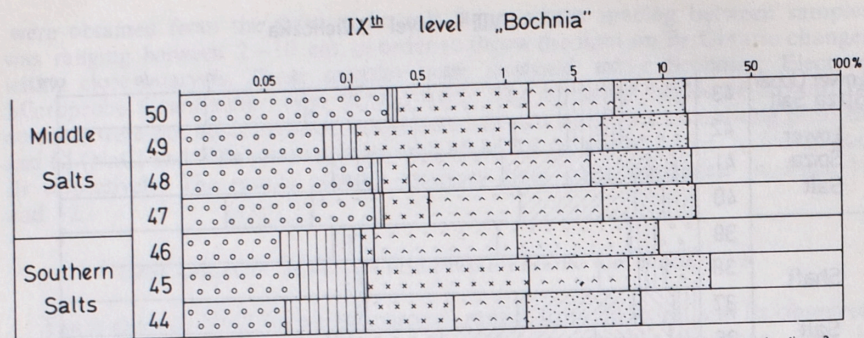


Fig. 5. Petrochemical diagram, Vth level, gallery Pachman, Bochnia mine



Legend as in fig. 3

Fig. 6. Petrochemical diagram, IXth level, gallery perpendicular to gallery Grubenthal, Bochnia mine

tion on the importance of the contents of Sr, Mg, K, Ca, Na, Mn and Fe to explain the nature of primary minerals in various evaporite sequences.

The results of trace element analyses are tabulated in Table 7, whereas for K^+ , Mg^{2+} , Ca^{2+} , and Cl^- relations, in Figs 7–10.

Vertical distribution of K^+ , Mg^{2+} , and Ca^{2+} in Figs 7 and 8 give clear indication about the increase of concentration close to the top of the Lower Spiza salts (Fig. 7, sample 23). Within Shaft salts, both Mg^{2+} and Ca^{2+} display irregular content changes, and this could be explained by the formation of bitter Mg-bearing mineral, which is possibly one of the magnesium chloride phases (Table 1, sample 10).

In Fig. 8, at the top of salt, the graph shows decrease in Mg content. This could be the result of high solubility of Mg^{2+} (Dean *et al.*, 1978).

In Figs 9 and 10, the functional ratio of K:Cl and Mg:Cl shows rapid increase close to the top of both Shaft and Lower Spiza salts (or Middle Salts), where during the process of evaporation, the concentration of K^+ , Mg^{2+} , and Na^+ will not change till the point of halite formation, when Na^+ concentration in sea water will decrease. On the other hand, the relative concentration of K^+ and Mg^{2+} , which is considered as indicator for the appearance of potash facies minerals, will not change. The same results were obtained by Morris and Dickey (1957), in Bocana de Virrila, Peru, and Moore (1960), in Pupuri Salina, Mexico. Holser (1963) found that in salt from the Wellington Formation (Permian) of Kansas, Mg:K contents remained relatively constant in brine inclusions throughout the formation, but Mg:Cl and K:Cl increased with rising salinity due to removal of Cl from the water.

Within Bochnia Evaporites member, there are two distinctive types of evaporation process, the products of which are: 1. Green Salt layers (subcycle A), and 2. Shaft Salts and Lower Spiza Salts (subcycle B), presented in Figs 2, 3, 9.

Multirepetition of evaporation established within the same layer (a duplication phenomenon), throws the light on the fluctuation of evaporation process during precipitation of the lower portion of the member, and also indicates that the maximum of evaporation process corresponds to chloride facies. In authors opinion each field of facies can be subsequently subdivided into smaller categories carrying the same lithological term (chlorides), but showing variation of the following parameters:

a) degree of crystallinity,

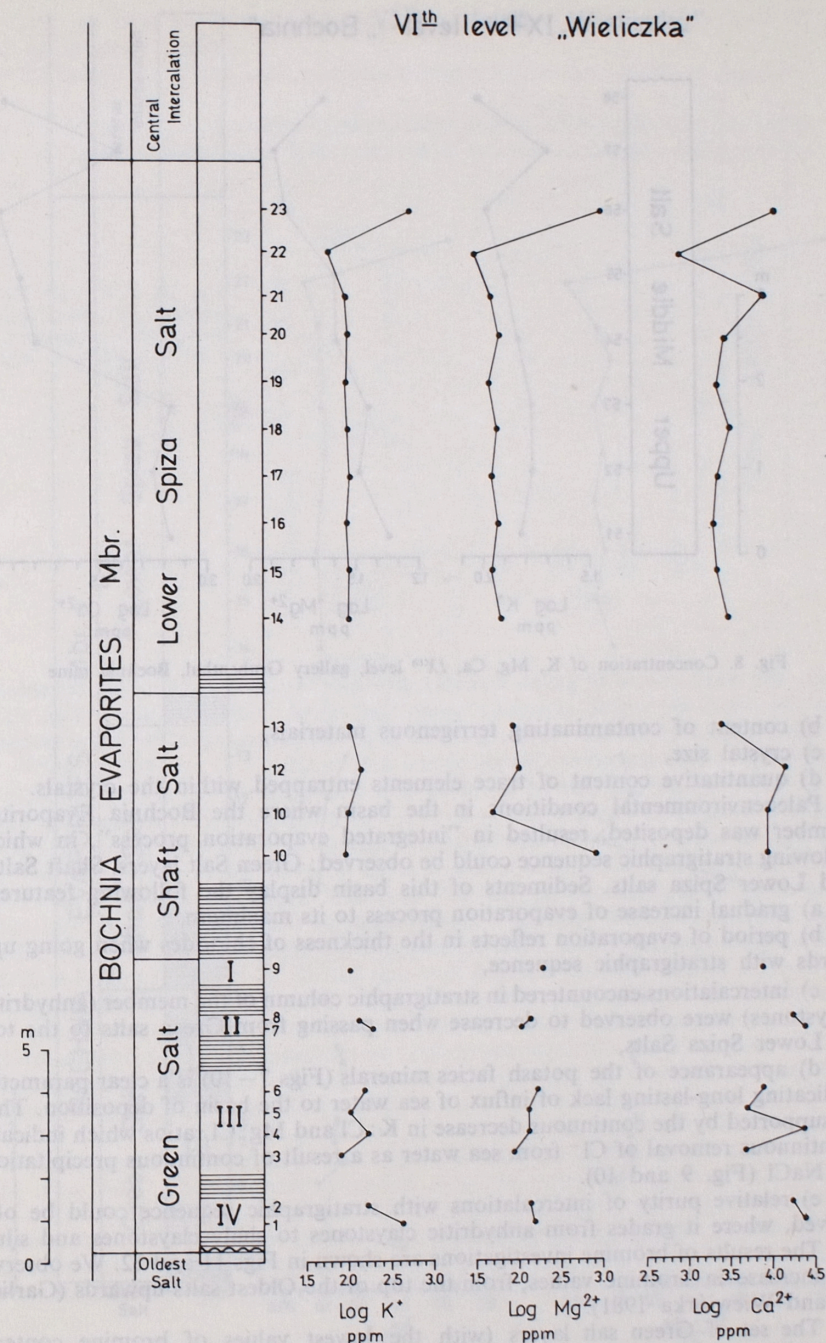


Fig. 7. Concentration of K, Mg, Ca, VIth level, 320 m SE of Shaft Kinga, Wieliczka mine

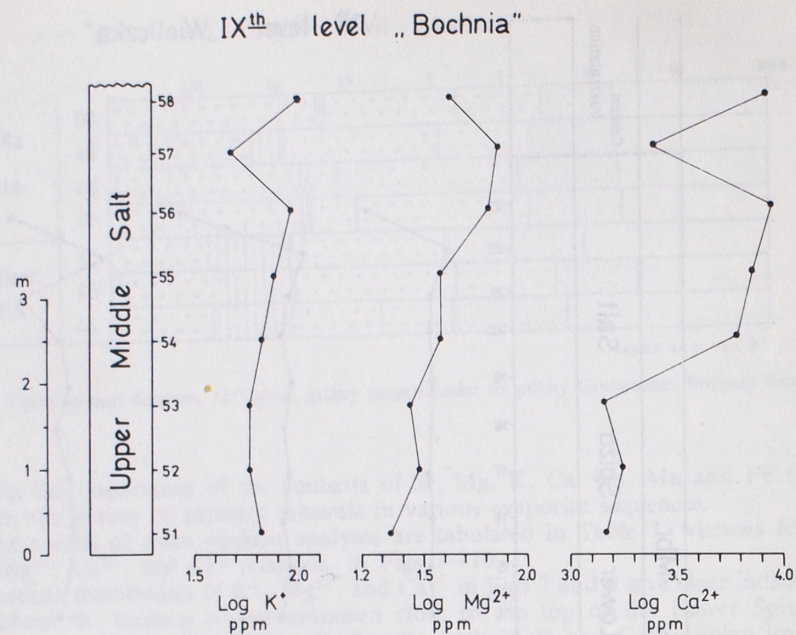


Fig. 8. Concentration of K, Mg, Ca, IXth level, gallery Grubenthal, Bochnia mine

- b) content of contaminating terrigenous materials,
- c) crystal size,
- d) quantitative content of trace elements entrapped within the crystals.

Paleoenvironmental conditions in the basin where the Bochnia Evaporites member was deposited, resulted in "integrated evaporation process", in which following stratigraphic sequence could be observed: Green Salt layers, Shaft Salts, and Lower Spiza salts. Sediments of this basin display the following features:

- a) gradual increase of evaporation process to its maximum,
- b) period of evaporation reflects in the thickness of chlorides when going upwards with stratigraphic sequence,
- c) intercalations encountered in stratigraphic column of the member (anhydritic claystones) were observed to decrease when passing from Green salts to the top of Lower Spiza Salts,
- d) appearance of the potash facies minerals (Figs 7–10) is a clear parameter indicating long-lasting lack of influx of sea water to the basin of deposition. This is supported by the continuous decrease in K:Cl and Mg:Cl ratios which indicate continuous removal of Cl⁻ from sea water as a result of continuous precipitation of NaCl (Fig. 9 and 10).

e) relative purity of intercalations with stratigraphic sequence could be observed, where it grades from anhydritic claystones to shaly claystones and silts.

The results of bromine investigations are shown in Figs 11 and 12. We observe an increase in bromine values, from the top of the Oldest salts upwards (Garlicki and Wiewiórka 1981).

The set of Green salt layers (with the lowest values of bromine content 22–38 ppm) represents the low quality chloridic phase. Within fourth Green salt

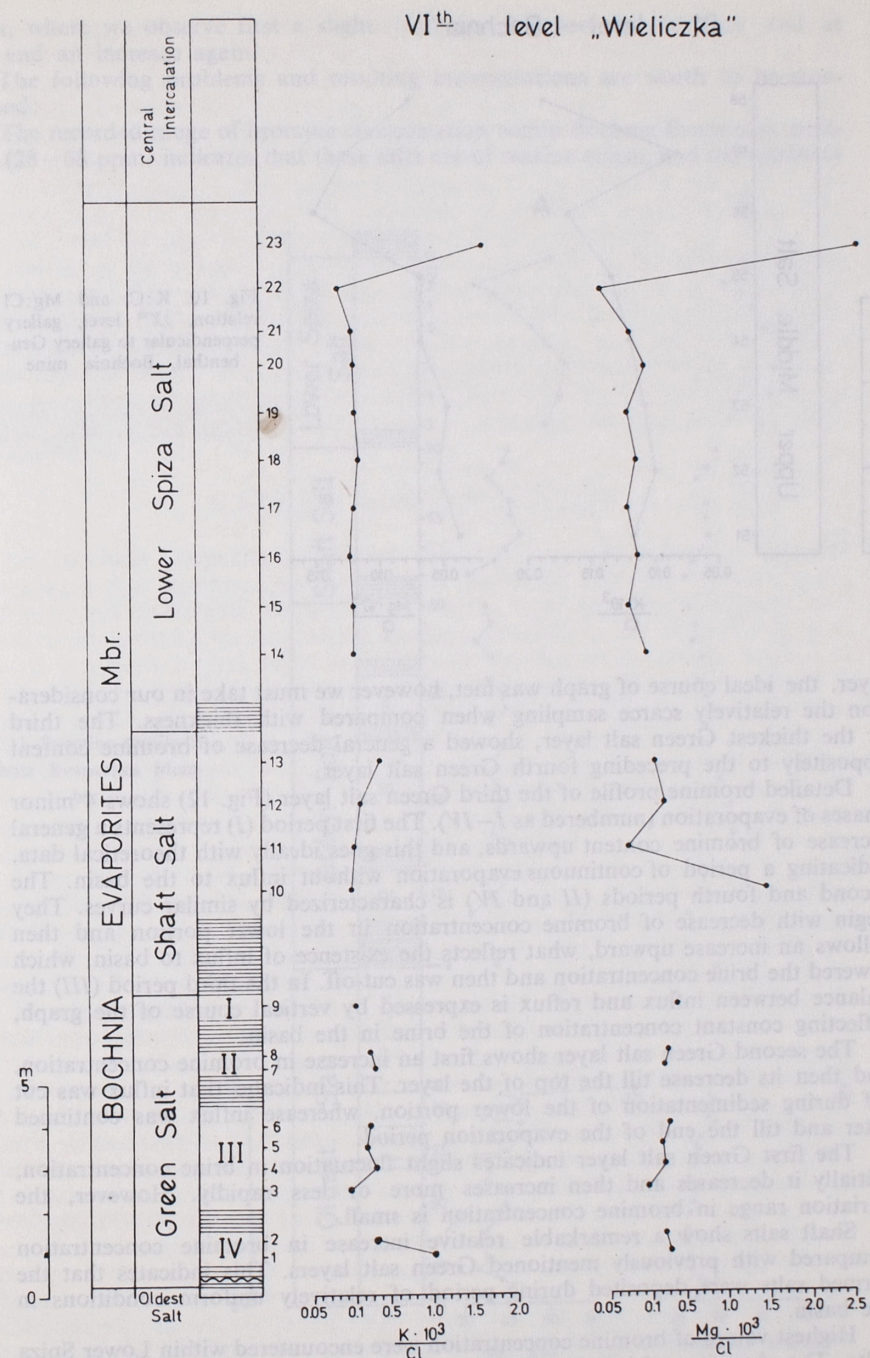


Fig. 9. K:Cl and Mg:Cl relation, VIth level, 320 m SE of Shaft Kinga, Wieliczka mine

IX level „Bochnia”

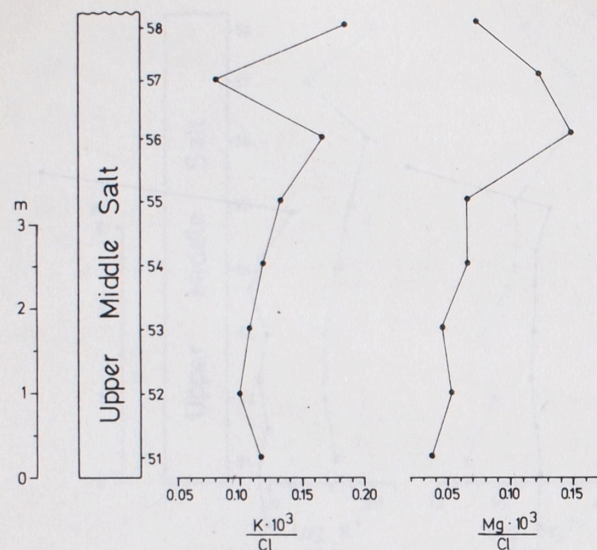


Fig. 10. K:Cl and Mg:Cl relation, IXth level, gallery perpendicular to gallery Grubenthal, Bochnia mine

layer, the ideal course of graph was met, however we must take in our consideration the relatively scarce sampling when compared with thickness. The third or the thickest Green salt layer, showed a general decrease of bromine content oppositely to the preceding fourth Green salt layer.

Detailed bromine profile of the third Green salt layer (Fig. 12) shows 4 minor phases of evaporation (numbered as I–IV). The first period (I) represents a general increase of bromine content upwards, and this goes ideally with theoretical data, indicating a period of continuous evaporation without influx to the basin. The second and fourth periods (II and IV) is characterized by similar curves. They begin with decrease of bromine concentration in the lower portion and then follows an increase upward, what reflects the existence of influx to basin, which lowered the brine concentration and then was cut-off. In the third period (III) the balance between influx and reflux is expressed by vertical course of the graph, reflecting constant concentration of the brine in the basin.

The second Green salt layer shows first an increase in bromine concentration, and then its decrease till the top of the layer. This indicates that influx was cut off during sedimentation of the lower portion, whereas influx was continued after and till the end of the evaporation period.

The first Green salt layer indicates slight fluctuation in brine concentration, initially it decreases and then increases more or less rapidly. However, the variation range in bromine concentration is small.

Shaft salts show a remarkable relative increase in bromine concentration compared with previously mentioned Green salt layers. This indicates that the formed salts were deposited during period of relatively uniform conditions in the basin.

Highest values of bromine concentration were encountered within Lower Spiza salts. The character of bromine profile in general is similar to that of Shaft

salts, where we observe first a slight increase, followed by decrease and at the end an increase again.

The following problems and resulting interpretations are worth to be mentioned:

The recorded range of bromine concentration within Bochnia Evaporites member (28–68 ppm) indicates that these salts are of marine origin, and the relatively

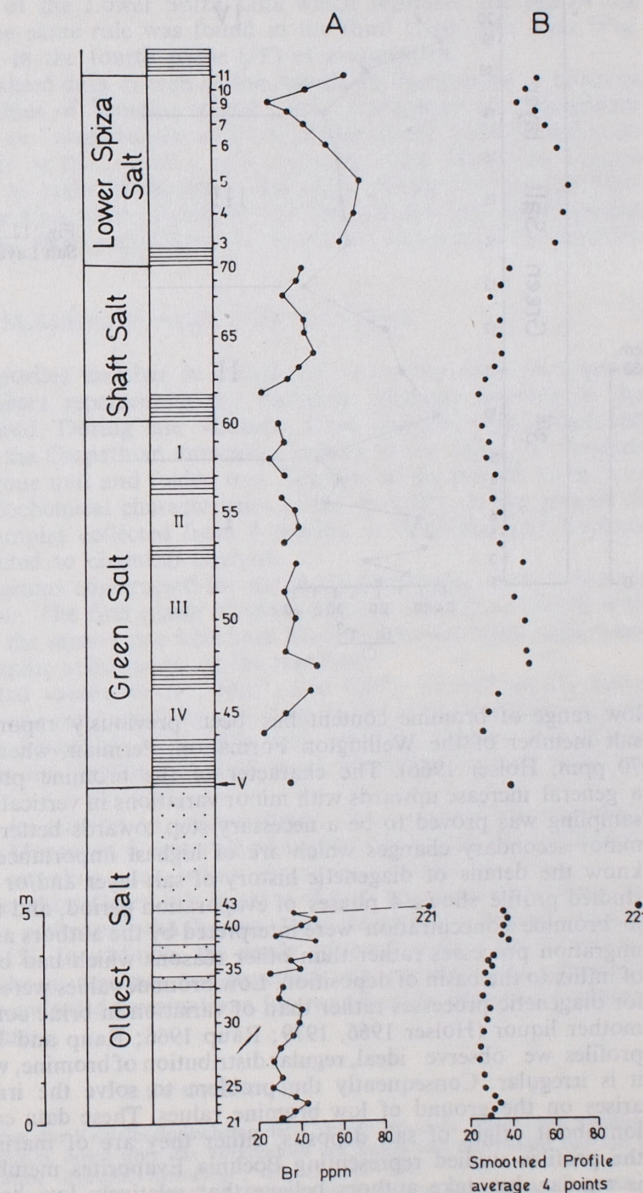


Fig. 11. Bromine profile of Bochnia Evaporites Member

IVth level „Wieliczka”

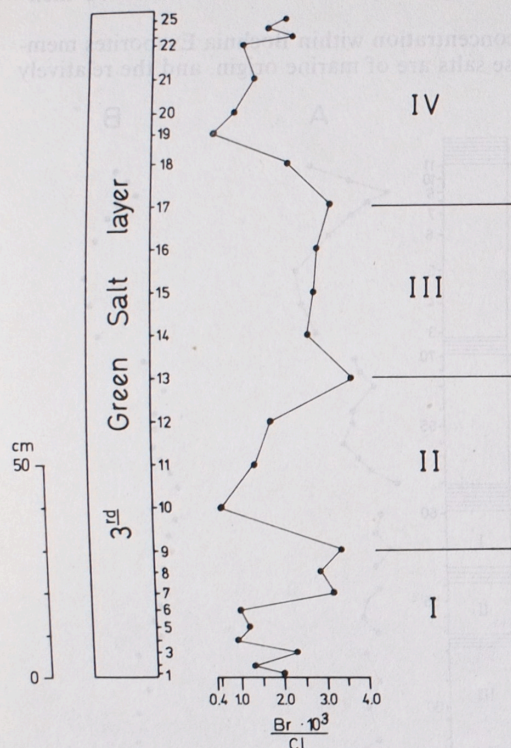


Fig. 12. Br:Cl relation, 3rd Green Salt Layer, VIIth level, Wieliczka mine

low range of bromine content has been previously reported (e.g. Hutchinson salt member of the Wellington Formation, Permian, where the range was 10–70 ppm, Holser 1966). The character of the bromine profile (Fig. 11) shows a general increase upwards with minor variations in vertical profile. Narrow space sampling was proved to be a necessary step towards better understanding of the minor secondary changes which are of highest importance if we would like to know the details of diagenetic history of salt layer and/or layers. In Fig. 12 the studied profile shows 4 phases of evaporation period, and the recorded decreases in bromine concentration were interpreted by the authors as a result of diagenetic migration processes rather than other reasons which had been stated as a result of influx to the basin of deposition. Low bromine values were suggestive indications for diagenetic processes rather than of variation in brine concentration within the mother liquor (Holser 1966, 1979; Raup 1966; Raup and Hite 1978). In several profiles we observe ideal, regular distribution of bromine, whereas in the majority it is irregular. Consequently the problem to solve the irregularity in question arises on the ground of low bromine values. These data cause apparent confusion about origin of salt deposits, either they are of marine or non-marine. In the profiles studied representing Bochnia Evaporites member, the general trend is regular, but take authors believe that relatively low bromine values are the

result of diagenetic processes. Raup (1966), in his analysis of the Pennsylvanian Paradox no 2 salt considers the initial high value of bromine content in the profile as to the result of a carryover of bromide-rich brine from the preceding cycle. The same result was achieved by Küfn (1968), in support of this idea. Such initially high and rapidly decreasing bromine concentrations are not found in the earliest salts in a given basin, but only in later sequences (Holser 1979), as in the case of the Lower Spiza salts which represent the top of the member (Fig. 11). The same rule was found in the third Green salt layer (Fig. 12), as could be seen in the fourth phase (IV) of evaporation.

Following the obtained data as well as the criteria of fluctuations in bromine content, some low values of bromine content may correspond to "descendent salts" of Kühn (1968) or "second-cycle salts" of Holser (1966). Such second-cycle salts occur more likely at the top of a salt sequence, and they also require some tectonic factor, in order to facilitate re-solution (Holser 1979). The Miocene evaporites of the Carpathian Foreland had been folded and thrust during several tectonic phases, what could result in secondary changes of the bromine concentration.

SUMMARY AND CONCLUSIONS

The Bochnia Evaporites member is considered to be the most widespread one among five members representing the Badenian Miocene deposits in the southern part of Poland. During late Miocene, these deposits were folded and thrust northwards by the Carpathian movement leading to the origin of two units known as autochthonous unit and folded one. The aim of the present work is to throw the light on geochemical characteristics of the member, on the ground of examination of 58 samples collected from 4 profiles in Wieliczka and Bochnia salt mines and subjected to chemical analyses.

Petrochemical diagrams constructed for the analysed samples show 2 distinct types of sedimentation. The first phase of sedimentation can be correlated with Green salt layers and the second one with both Shaft and Lower Spiza salts, what supports the stratigraphic subdivision of the member.

From the calculated values for K^+ , Mg^{2+} , and Ca^{2+} , as well as the ratios of $Mg:Cl$ and $K:Cl$, one may conclude that close to top of the member a strong indications for future formation of $K-Mg$ salts could be foreseen. In addition within the same layer the duplication phenomena (multirepetition of beds) are observed, too.

Bromine analysis in relation to palaeosalinity, does confirm the previously achieved conclusions. Moreover, a new method applied emphasizes the significance of small distance of sampling sites, within the range between 2–10 cm.

The present profile (third Green salt layer) is of high importance and gives the results which may be compared with the same layer shown in the detailed bromine profile (Figs 11 and 12). In addition, the newly adopted method for Br and Cl determinations is a cheap, accurate and practical one, providing the advantage of carrying out the required determinations for considerable amount of samples in relatively short time.

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GEOCHEMICZNA CHARAKTERYSTYKA OGNIWA EWAPORATÓW Z BOCHNI ORAZ NOWE ASPEKTY OKREŚLENIA STOSUNKU Br DO Cl

Streszczenie

Ogniwo ewaporatów z Bochni odpowiadające trzeciemu cyklotemowi osadów chemicznych, jest zespołem warstw o największej miąższości pośród wszystkich pięciu cyklotemów reprezentujących badeńskie ewaporaty miocenu w południowej

Polsce. Osady trzeciego cyklotemu można podzielić na 2 podcykle, A i B, powstałe w odmiennych warunkach sedymentacji.

Studium geochemiczne opisywanych osadów zostało przeprowadzone na podstawie licznych próbek pobranych w sposób systematyczny w wyrobiskach podziemnych kopalni soli w Wieliczce i Bochni. Badaniami chemicznymi objęto 58 próbek, w których oznaczono zawartości (w % wag.) : Cl, SO₄ i części nierozpuszczalne. Ponadto spektrofotometrycznie oznaczono zawartości (w % wag.): Na, K, Mg, Fe, Zn, Cu, Mn, Pb, Ni, Co, Sr, Cd, a spektrochemicznie B/bor.

Przeprowadzono także oznaczenia bromu, których większość została wykonana metodą kolorymetryczną, ale dla wybranego i szczegółowo opróbowanego odcinka trzeciego pokładu soli zielonej (próbki pobierane w odstępach 2–10 cm) zastosowano ilościowe oznaczenia mikrosondą elektronową. Wyniki badań przedstawiono na tablicach 1–7 i figurach 3–12.

Diagramy petrochemiczne wykreślone dla analizowanych próbek wykazują istnienie 2 wyraźnych typów sedymentacji. Pierwsza faza sedymentacji może odpowiadać osadzeniu się zielonych soli pokładowych, a w drugiej fazie powstały: sól szybkowa i sole spizowe dolne.

Zestawione graficznie zawartości K, Mg i Ca, jak i wartości współczynników Mg:Cl i K:Cl (fig. 7–10) wskazują, że w stropowej części ogniwa panowały już warunki bliskie tworzeniu się soli potasowo-magnezowych. Zjawisko to znajduje również potwierdzenie w przedstawionych profilach bromowych (fig. 11 i 12).

Nowa zastosowana metoda określania zawartości Br pozwala na pobranie licznych próbek w odstępach od 2 do 10 cm, a tym samym na zbadanie szczególnych zmian zawartości bromu w profilu pionowym warstwy soli.

OBJAŚNIENIA FIGUR

- Fig. 1. Mapa występowania badeńskich ewaporatów na obszarze zapadliska przedkarpackiego w Polsce
1 – wychodnie utworów starszych od miocenu, 2 – pole facji węglanowo-litoralnej, 3 – pole facji siarczanowej, 4 – pole facji chlorkowej, 5 – złoża soli w jednostce sfałdowanej i nasuniętej, 6 – obszary bez ewaporatów, 7 – brzeg nasunięcia Karpat fliszowych
- Fig. 2. Podział stratygraficzny ogniwa ewaporatów z Bochni
- Fig. 3. Diagram petrochemiczny, poziom VI, 320 m na SE od szybu Kinga, kopalnia Wieliczka
- Fig. 4. Diagram petrochemiczny, poziom VIII, 1100 m na E od szybu Kinga, kopalnia Wieliczka
- Fig. 5. Diagram petrochemiczny, poziom V, chodnik Pachman, kopalnia Bochnia
- Fig. 6. Diagram petrochemiczny, poziom IX, chodnik prostopadły do chodnika Grubenthal, kopalnia Bochnia
- Fig. 7. Zawartość K, Mg, Ca, w wyrobiskach poziom VI, 320 m na SE od szybu Kinga, kopalnia Wieliczka
- Fig. 8. Zawartość K, Mg, Ca, w wyrobiskach poziom IX, chodnik Grubenthal, kopalnia Bochnia
- Fig. 9. Stosunki K:Cl i Mg:Cl w wyrobiskach poziom VI, 320 m na SE od szybu Kinga, kopalnia Wieliczka
- Fig. 10. Stosunki K:Cl i Mg:Cl w wyrobiskach poziom IX, chodnik prostopadły do chodnika Grubenthal, kopalnia Bochnia
- Fig. 11. Profil bromowy ogniwa ewaporatów z Bochni
- Fig. 12. Stosunek Br:Cl w trzecim pokładzie soli zielonej, poziom VI, kopalnia Wieliczka

ХИМИЧЕСКАЯ ХАРАКТЕРИСТИКА ЭВАПОРИТОВ БОХНИ И НОВЫЕ АСПЕКТЫ ОПРЕДЕЛЕНИЯ ОТНОШЕНИЯ БРОМА К ХЛОРУ

Резюме

Эвапоритовые образования Бохни, эквивалентные третьей циклотеме химических отложений, представляют свиту слоев, обладающую самой крупной мощностью среди всех пяти циклотем баденских эвапоритов в миоцене Южной Польши. Отложения третьей циклотемы подразделяются на два подцикла А и В, отличающиеся разными условиями их осадконакопления.

Геохимическое исследование рассматриваемых отложений проводилось на большом числе образцов, взятых в итоге систематического опробования подземных выработок соляной копи в Бохне и Величке. В 58 образцах проведены химические анализы на содержание (в % вес.) Cl, SO₄ и нерастворимого остатка. Кроме того, спектрофотометрически определялись содержания (в % вес.) Na, K, Mg, Fe, Zn, Cu, Mn, Pb, Ni, Co, Sr, Cd и спектрохимически содержание бора.

Определено также содержание брома, в большинстве колориметрическим методом, а в отношении избранного и детально опробованного интервала третьего пласта зеленой соли (опробование через 2—10 см) было применено количественное определение электронным микрозондом. Данные анализов приведены в таблицах 1—7 и на фигурах 3—12.

Составленные петрохимические диаграммы исследованных образцов показывают наличие двух разных типов седиментации. Первая фаза седиментации характеризовалась образованием зеленых пластовых солей, вторая же накоплением шибиковой соли и нижних спизовых солей.

Из графического изображения содержаний K, Mg и Ca, а также показателей Mg:Cl и K:Cl (Фиг. 7—10) видно, что в кровельном интервале данной свиты господствовали уже условия, благоприятствующие образованию калий-магневых солей. Это явление подтверждается также и на приведенных бромовых профилях (фиг. 11 и 12).

Примененный новый способ определения содержания брома позволяет проводить частое опробование в интервалах от 2 до 10 см и, таким образом, детально исследовать колебания в распределении брома в вертикальном разрезе солей.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Карта распространения баденских эвапоритов Предкарпатского прогиба на территории Польши
1 — выходы пород домиоценового возраста, 2 — поле карбонатно-литеральной фации, 3 — поле сульфатной фации, 4 — поле хлоридной фации, 5 — соляные залежи в смятой и надвинутой единицах, 6 — области, лишенные эвапоритов, 7 — край надвига флишевых Карпат
- Фиг. 2. Стратиграфическое расчленение эвапоритовой свиты Бохни
- Фиг. 3. Петрохимическая диаграмма, горизонт VI, 320 м к ЮВ от шахты Кинга, соляная копь Величка
- Фиг. 4. Петрохимическая диаграмма, горизонт VIII, 1100 м к В от шахты Кинга, соляная копь Величка
- Фиг. 5. Петрохимическая диаграмма, горизонт V, штрек Пахман, соляная копь Бохня

- Фиг. 6. Петрохимическая диаграмма, горизонт IX, штрек перпендикулярный к штреку Грубенталь, соляная копь Бохня
- Фиг. 7. Содержание K, Mg, Ca в выработках горизонта VI, 320 м к ЮВ от шахты Кинга, соляная копь Величка
- Фиг. 8. Содержание K, Mg, Ca в выработках горизонта IX, штрек Грубенталь, соляная копь Бохня
- Фиг. 9. Отношения K:Cl и Mg:Cl в выработках горизонта VI, 320 м к ЮВ от шахты Кинга, соляная копь Величка
- Фиг. 10. Отношения K:Cl и Mg:Cl в выработках горизонта IX, штрек перпендикулярный к штреку Грубенталь, соляная копь Бохня
- Фиг. 11. Бромовый профиль эвапоритового интервала месторождения Бохня
- Фиг. 12. Отношение Br:Cl в третьем пласте зеленой соли, горизонт VI, соляная копь Величка