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On Some Trace Elements of Zechstein Younger Salts in Poland

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ABSTRACT

Underground galleries in the Klodawa salt mine were subjected to systematic sampling of the Zechstein younger salts exposures. The potash-bearing series of Klodawa, over 120 m thick, usually contains pure rock salt with kieserite and carnallite. In addition to the potash-bearing series, the underlying and overlying rock salt beds have been sampled and examined. Chemical analyses were made to determine the content of Br, I, B, Rb, Cs, Sr, Fe, Mn, Cr, Co, Cu, Ni. Altogether over 250 analyses were made and are presented in a table and figures. Distribution of these elements in the profiles of evaporites is significant for stratigraphical purposes, and may help to recognize the concentration zones of some useful trace elements.

INTRODUCTION

For several years extensive geochemical investigations have been carried out into Zechstein evaporites in Poland. Besides routine chemical analyses of samples from salt mines and drill cores, some trace elements within the Zechstein profile have been determined. In Klodawa salt mine, it was possible to sample almost the complete profile of younger salts, fully exposed along the underground galleries and chambers.

The Zechstein younger salts in Klodawa reveal a quite different petrologic development compared with other profiles in Middle Poland, particularly younger potash salt (K3) together with overlying younger upper rock salt (Na3b) form the so-called 'potash-bearing series', over 120 m thick.

Moreover, in numerous stratigraphic horizons of PZ3, such epigenetic potash salts as: polyhalite, sylvite, carnallite, and kieserite occur.

REGIONAL POSITION OF THE KLODAWA SALT DEPOSIT

An oblong salt structure, Izbica Kujawska–Klodawa–Leczyca, is situated in Kujawy region, Central Poland (Fig. 1). The diapiric structure of Klodawa itself was discovered by gravimetric survey in 1937; the discovery was proved, however, by the first bore-hole made in 1947. As a result of successful prospecting, a salt mine was founded in Klodawa in 1951–1954. To date three shafts have been sunk to a depth below 750 m, opening access to mine levels operating at depths of between 450 m and 750 m.

The geological structure and general tectonics of the Klodawa salt deposit, as well as trace element content, have been discussed by Werner et al. (1960), Poborski (1970), Charysz (1973), Garlicki and Szybist (1986, 1991), Garlicki (1991), and others.

The Klodawa salt deposit is only part of an elongated anticline over 60 km long and several kilometres wide. The central part of the structure forms a salt dome, which is about 25 km long, up to

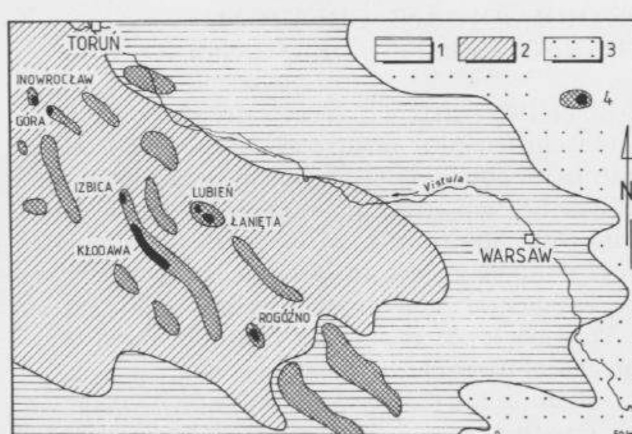

Fig. 1. Location map of the Klodawa salt structure. 1, Chloride facies; 2, chloride facies with potash salts; 3, carbonate–sulphate facies; 4, anticlinal structure with salt dome.

2 km wide, and about 3 km high. Diapiric stock of the deposit with a width of about 2 km has pierced the overlying Mesozoic rocks. Towards the south-west, the deposit borders on the Jurassic; the north-eastern wall borders on the Triassic. The cap of the dome as well as the surrounding Mesozoic strata are overlaid by Tertiary deposits, and the latter are overlaid by Pleistocene sediments.

LITHOSTRATIGRAPHIC PROFILE OF THE ZECHSTEIN SEDIMENTS

Many years of underground mining at the Klodawa mine has enabled the study of both the stratigraphy and tectonics of this salt deposit. The lithostratigraphic column studied in the mine (Fig. 2) presents an almost complete profile of Zechstein strata, approximately 1420 m thick. Within these sediments, the series of younger salts (stage PZ3) is about 330 m thick.

The stratigraphic profile of younger salts in the Middle Poland region was divided into three sub-stages: lower, middle, and upper (Charysz, 1973). The lower sub-stage represents a consistent salt subcyclothem, formed in the marine megafacies, and consists of: grey salty clay (T3), basal dolomite (Ca3), main anhydrite (A3), younger lower rock salt (Na3a), and younger potash salt (K3).

The middle sub-stage is composed of several microcycles, reflecting frequent changes of depositional conditions. This sub-stage represents the younger upper rock salt (Na3b) with thin beds of potash salts.

The upper sub-stage represents the recessive subcyclothem, developed in typical lagoonal–terrestrial megafacies. It comprises exclusively brown clayey salts and brown salty clays (typical "zubers").

PETROLOGIC AND CHEMICAL CHARACTERISTICS OF YOUNGER SALTS

Stage PZ3 starts with grey salty clay (T3), laminated and dolomitic, about 5 m thick. This is overlaid with basal dolomite (Ca3), fine-grained, clayey and anhydritic, and about 0.5 m thick. The main anhydrite (A3), 30–40 m thick, is commonly laminated with dark clay. Within massive anhydritic rock, thick epigenetic veins of potash salts occur in places.

Younger lower rock salt (Na3a), 40–60 m thick, consists of three characteristic layers:

– basal salt, a pale brown-orange rock salt, 1–2 m thick, with numerous intercalations and laminae of anhydrite. The NaCl content is about 70%;

– lined salt, over 40 m thick, composed of white, light brown or light orange rock salt with thin layers and laminae of anhydrite (yearly rhythms). Approaching the top of lined salt, thin layers of anhydrite are replaced by thin layers of carnallite and kieserite. The average content of NaCl is 97.5%;

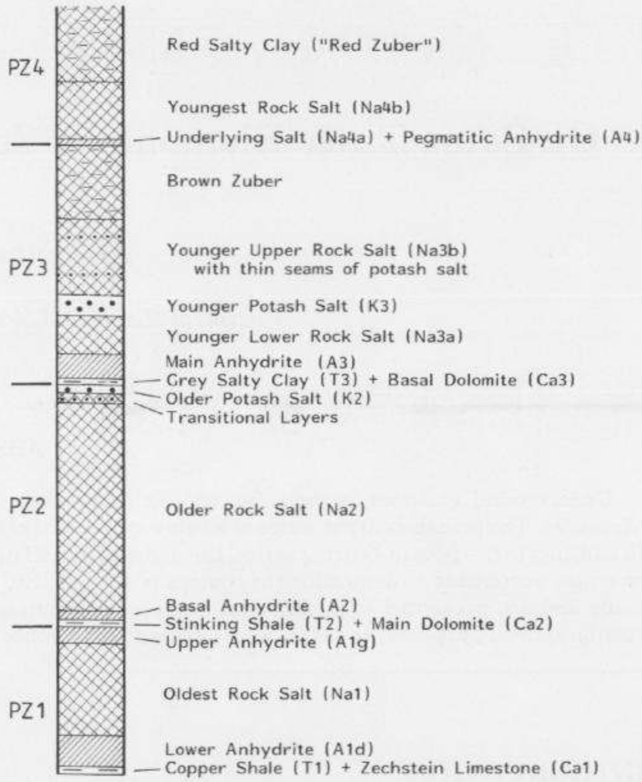

Fig. 2. Generalized lithostratigraphic column of the Klodawa salt deposit.

– accompanying salt, 2–3 m thick, fine-grained, white, interbedded with anhydrite, carnallite and kieserite. The chemical composition of this component is: NaCl, 78%; K_2O, 2.8%; MgO, 2.5%.

Within the tectonically disturbed strata of younger lower rock salt, epigenetic intergrowths and veins occur. Very typical in underground exposures of 600 m level is a 2 m thick sylvinite vein, composed of white sylvite and blue halite crystals.

Younger potash salt (K3) is a 20–35 m thick set of rock salt strata, with 3 seams of kieseritic carnallite, reaching the following thicknesses from bottom to top respectively: seam I, 2 m; seam II, 3 m; seam III, 15–22 m. The average K_2O content amounts to 8.5% and MgO is 8.1%.

Younger upper rock salt (Na3b) comprises a more than 100 m thick set of rock salt strata, composed of 3 distinguished members, as shown in Figs. 3 and 4:

– white-grey salt intercalated with kieserite, 15–25 m thick, with a single layer of kieseritic carnallite 3–6 m thick. The NaCl content does not exceed 72.5%;

– banded white-grey rock salt, 17–27 m thick, with intercalations of dark clay and grey anhydrite;

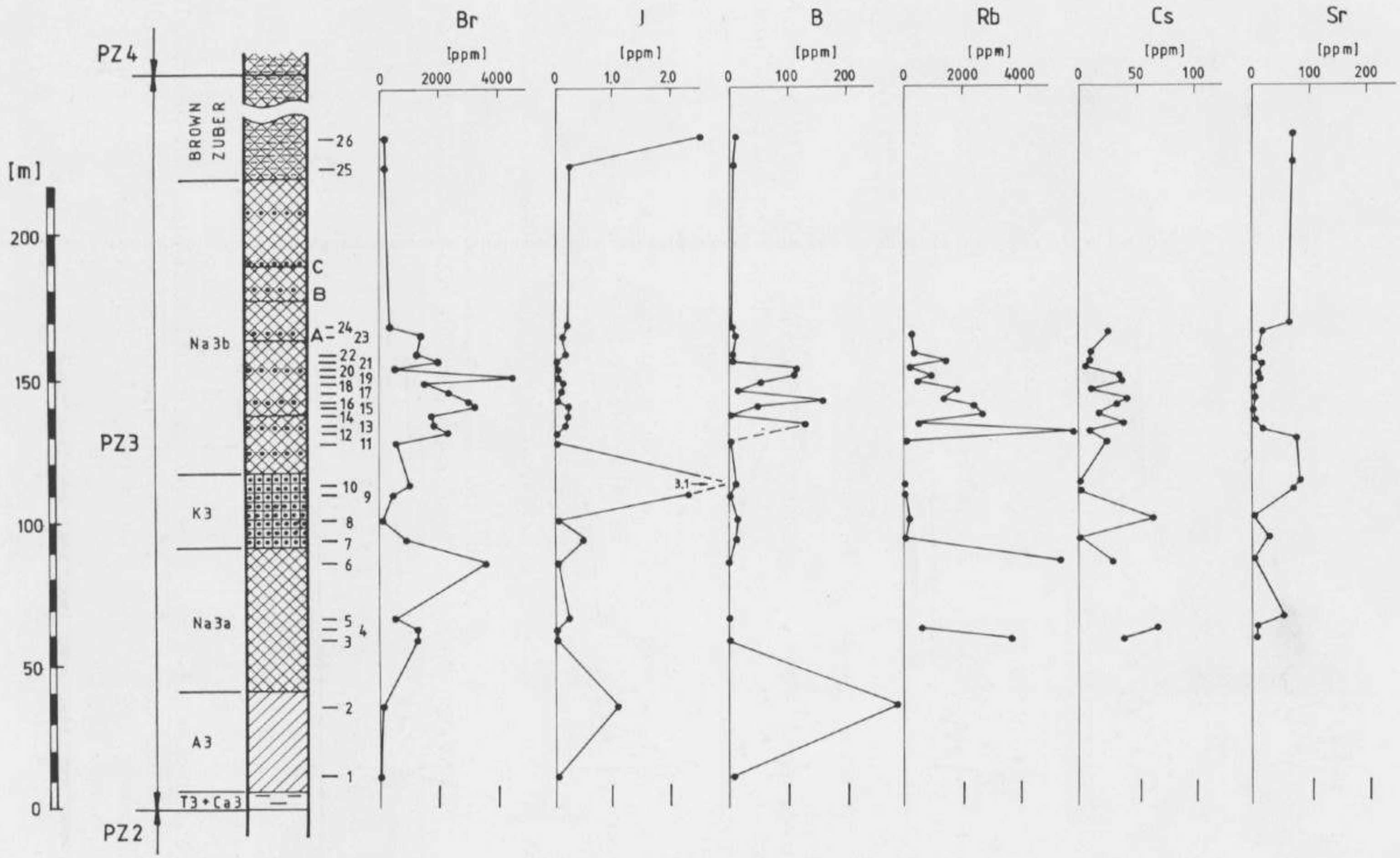

Fig. 3. Lithological column of younger salts in Klodawa mine and contents of some trace elements (Br, I, B, Rb, Cs, Sr).

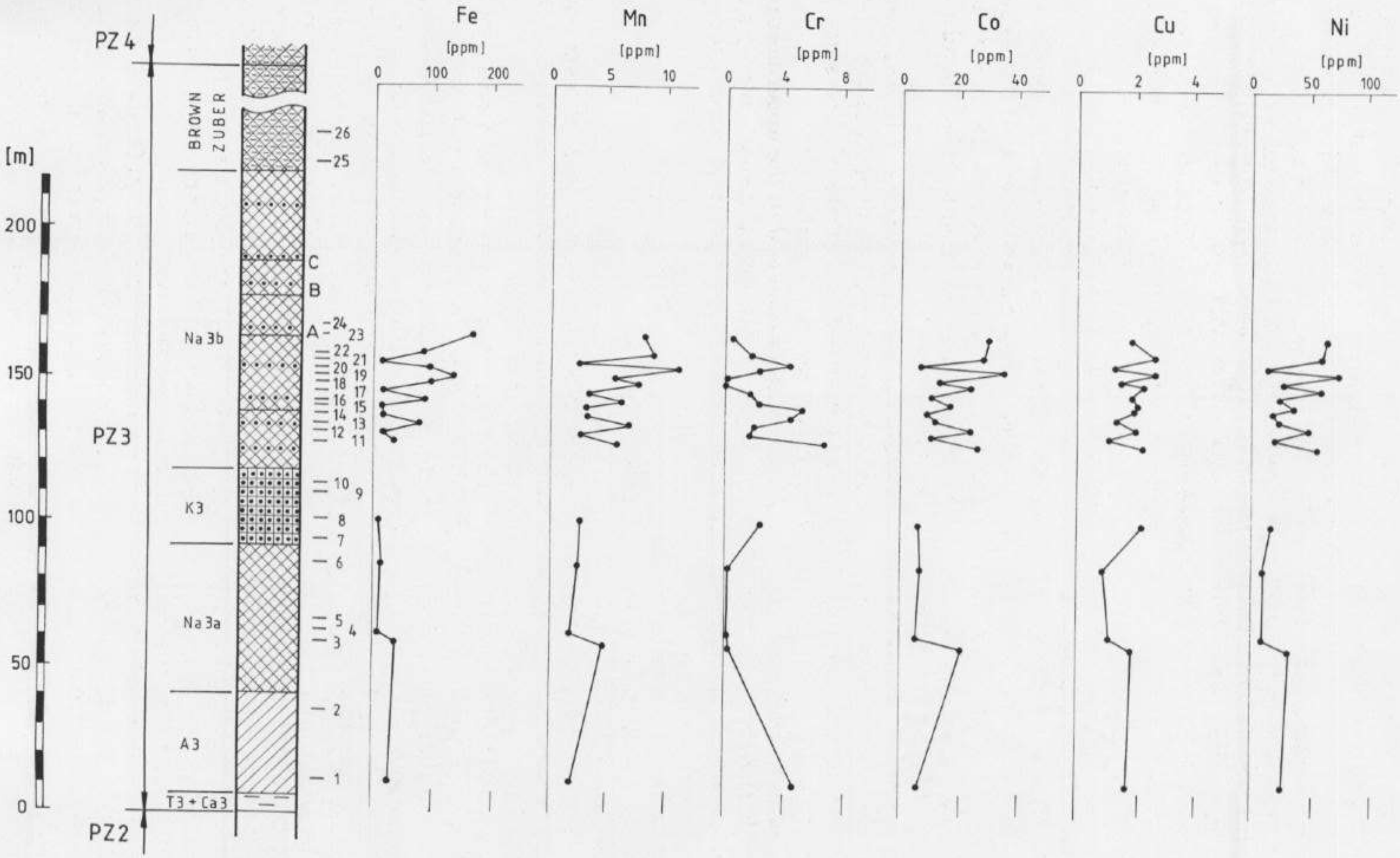

Fig. 4. Lithological column of younger salts in Klodawa mine and contents of some trace elements (Fe, Mn,Cr, Co, Cu, Ni).

salt contains intergrowths and several layers of carnallite, each 0.25–3 m thick; the NaCl content is about 95%;

– flamy salt, 50–70 m thick, with 3 marker beds of anhydrite A, B, C. The salt layers: light-orange, yellow-brown, smoky are pure salts or clayey ones, with an NaCl content of 97.2–93.0%.

Over anhydrite C in the uppermost section of Na3b profile, clayey salt occurs with a marker bed of carnallite 1–3 m thick.

The end of the PZ3 profile forms brown salty clay, 80–140 m thick ("brown zuber"). The lowest part consists of bedded rock salt, with an NaCl content of 86.3%.

METHODS OF SAMPLING AND LABORATORY TECHNIQUES

Apart from the samples of Zechstein rocks available from drill cores, the most reliable sampling was provided from underground galleries in Klodawa salt mine. Along main and auxiliary levels, at the depth between 690 m and 750 m, it was possible to perform systematic sample collection comprising full profiles of Zechstein younger lower rock salt (Na3a), younger potash salt (K3), and younger upper rock salt (Na3b) with numerous thin layers, intercalations and intergrowths of potash salts.

In some chambers and galleries it was possible to obtain continuous samples representing one section 2–5 m long (channel samples or systematic chip samples collected along designated lines). In many cases, single geological samples have been taken at random. The most uniform sampling took place within the strata overlying younger potash salt (Figs. 3 and 4). A total of 26 samples were taken for laboratory analysis.

Samples prepared for chemical analyses were dissolved in hot redistilled water. Insoluble residue was dissolved in a mixture of hot concentrated hydrofluoric acid, nitric acid, and perchloric acid (in volume ratio 4:2:1).

Contents of Fe, Ni, Co, Cu, Mn, Cr, Rb and Cs were determined by the AAS method (using a Philips PU-9100 x spectrophotometer). Concentration of B and Sr was analyzed by spectrophotometer ICP (in Ar plasm). Contents of Br and I were determined by colorimetric methods (an absorbency measured with a SPEKOL-10 spectrophotometer).

Some control analyses have shown that the relative error of all measurements did not exceed 5%. All chemical analyses were carried out at the Laboratory of Mineralogy and Geochemistry, Institute of Geology and Mineral Deposits, Academy of Mining and Metallurgy, Cracow.

RESULTS

Chemical analyses were usually made to determine the contents of the following elements: Br, I, B, Rb, Cs, Sr, Fe, Mn, Cr, Co, Cu, Ni.

Altogether, over 250 analyses were made and are presented in Table 1 and Figs. 3 and 4.

The content of small trace elements within the examined profile vary widely, namely: Br, 22–4500 ppm; B, 0.2–290 ppm; Rb, 9–5915 ppm; Cs, 0.5–70 ppm; Fe, 7–164 ppm; Sr, 1–188 ppm.

The highest concentrations of Br and Rb were found within layers underlying and overlying the younger potash salt (K3). Particularly higher concentrations of Rb are typical for veins and other epigenetic occurrences of halite, sylvite, carnallite and polyhalite. The highest concentration of Cs occurs also in epigenetic sylvinite.

Elements such as Fe, Mn, Cr, Co, Cu, Ni are mainly present in clayey, terrestrial constituents of evaporites. Their concentrations do not show any regularity, but their determination is very important for solution mining and underground storage operations.

Considerable concentrations of B have been distinguished within younger upper rock salt (Na3b) — below marker bed "anhydrite A". The same layers display very low Sr content.

High concentration of J in the uppermost part of younger potash salt (K3) is a result of only a single sample and needs more detailed examination.

CONCLUSIONS

The results obtained from trace element analyses contribute considerably to the geochemical characteristics of evaporites.

The distribution of these elements in the normal profile of Zechstein strata is significant for stratigraphical purposes, and may help to recognize the zones of useful trace element concentrations.

Rock salts with higher contents of some trace elements are used in the food industry. The higher content of Br, B, Rb, and Cs within potash salts is a subject of interest of pharmaceutical industry. Some types of sulphate–chloride potash salts (especially those with a low K and Mg content) have already been applied in agriculture for cultivation of meadows and pastures.

From the preliminary study of trace elements, the following practical conclusions might be deduced:

– for the next stage of research it is necessary to obtain more detail sampling of each Zechstein potash salt horizon and adjacent rock salt strata;

TABLE 1

Results of chemical analyses (ppm)

Sample no.	Br	J	B	Rb	Cs	Sr	Fe	Mn	Cr	Co	Cu	Ni
1	22	0.05	8.1	160.0	26.6	188.2	25.2	1.8	4.7	5.5	1.7	8.3
2	67	1.10	290.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	1250	0.05	0.4	3700.0	39.2	8.1	34.3	4.6	0.2	2.6	1.9	33.1
4	1240	0.05	0.2	655.8	70.5	11.6	7.1	1.6	0.1	5.1	1.1	11.1
5	544	0.22	1.3	n.a.	n.a.	56.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
6	3600	0.05	0.3	5400.0	31.6	2.2	12.2	2.3	0.1	6.6	0.9	11.6
7	840	0.53	12.6	27.0	0.5	30.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
8	110	0.05	15.9	186.0	64.2	1.2	8.4	2.5	2.4	5.9	2.2	15.5
9	388	2.30	0.9	13.0	0.5	70.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
10	1000	3.10	10.6	9.0	0.5	85.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
11	550	0.05	1.0	42.8	25.0	77.0	34.8	5.7	6.9	26.0	2.2	57.4
12	2300	0.05	0.0	5915.0	10.2	19.8	14.7	2.6	1.7	9.9	1.1	19.8
13	1880	0.17	131.1	528.4	39.3	6.8	77.3	6.6	2.1	24.2	2.0	48.8
14	1800	0.22	5.7	2700.0	16.8	1.4	16.7	3.2	4.7	11.4	1.4	24.1
15	3170	0.23	52.4	2450.0	33.8	2.4	13.1	3.1	5.4	9.1	2.0	18.9
16	3050	0.05	162.9	1395.0	42.6	6.6	88.3	6.1	2.4	16.9	2.1	36.2
17	2340	0.11	12.2	1845.0	13.8	1.2	15.5	3.2	1.8	10.3	1.9	24.4
18	1550	0.12	56.2	440.0	38.4	14.0	94.4	7.4	0.1	23.7	2.3	60.0
19	4500	0.05	113.0	984.0	34.2	9.4	136.6	5.6	0.2	12.9	1.5	26.4
20	545	0.05	117.8	198.1	5.0	17.6	96.9	11.0	2.3	35.4	2.7	75.3
21	1940	0.05	8.7	1470.0	9.8	3.6	13.9	2.2	4.5	6.2	1.3	14.2
22	1250	0.22	6.5	345.0	11.8	13.6	82.2	8.7	1.9	28.2	2.7	59.4
23	1360	0.12	11.3	272.0	25.8	17.8	164.5	8.1	0.5	30.2	1.9	67.8
24	310	0.18	0.9	n.a.	n.a.	63.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
25	122	0.24	4.8	n.a.	n.a.	70.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
26	135	2.50	9.6	n.a	n.a	70.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

– epigenetic potash salts (including Mg salts) due to their irregular occurrence should be sampled and examined separately;

– higher contents of Br, Rb and Cs are generally observed above and below the younger potash salt.

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