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Trace Elements and Mineralogy of Upper Permian (Zechstein) Potash Deposits in Poland

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Abstract: Mineral composition and content analysis of selected trace elements (Ag, As, Ba, Be, Br, Cd, Ce, Co, Cr, Cs, Cu, Ga, I, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, Tl, U, V, and Zn; 308 rock samples) were studied in the Upper Permian (Zechstein) potash-bearing deposits in Poland. They represented K–Mg chlorides of PZ2 and PZ3 cyclothems from four salt domes and stratiform K–Mg sulphates of PZ1 cyclothem. The dominant mineral components of K–Mg sulphates (polyhalite) are anhydrite and polyhalite. The most common minerals of the K–Mg salts of PZ2 cyclothem are halite, sylvite, kieserite, and anhydrite, and the most common of PZ3 cyclothem are halite, carnallite, kieserite, and anhydrite. Most analysed trace elements in the Zechstein potash-bearing deposits show a low content (up to 26 mg/kg) that eliminates them as potential profitable source rocks of such required elements as Ce, Cs, La, Li, or Rb. Common elements, such as Br, Fe, and Sr, are more easily exploited from natural brines, sulphate, and ore deposits.

Keywords: trace elements; minerals; potash-bearing deposits; Upper Permian (Zechstein); Poland

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1. Introduction

New technologies intensively use several trace elements, e.g., lithium (Li), strontium (Sr), rubidium (Rb), boron (B), caesium (Cs), or gallium (Ga), which are considered in the world as strategic and critical ore materials [1–6]. These elements are incorporated within many minerals, some of which occur in evaporitic deposits, such as rock and potash salts and sulphates. These sediments, and the recent and past environments of their accumulation, are in the interest of many modern countries e.g., China, the USA, and the European Union (e.g., [7–18]).

Nowadays, a large lithium volume is obtained due to the processing of brines and salts from intracontinental saline lakes in two giant salars of Bolivia [19–21]: Salar de Uyuni and Salar de Coipasa, with lithium reserves estimated at 21 mln tonnes (23.6% of the world reserves in 2021 [22]). Brines of the Salar de Atacama in Chile, which is two times smaller, contain 1000–7000 mg/L [23] or 1000–5000 mg/L of lithium (average—1400 mg/should be "L" - the symbol of "litre"), and in in 2017 they represent 27% of the world reserves [6,24,25]. Brines of salars in Altiplano have from 57 to 570 mg/L up to 8.9 g/L of lithium and 10.8 g/L of boron [26–29]. Brines of Quarham saline lake (Quaidam Basin, western China) contain 51.6–138.4 mg/L of boron [30].

Poland has large documented and predicted salt reserves, mainly of the Upper Permian (Zechstein) age [31]; therefore, it is a real necessity to estimate their efficacy as an economic source of the required trace elements. So far, geochemical studies of salt deposits are limited to determining the content of the main elements and components (e.g., [32–38]) e.g., sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), chlorine (Cl), bromine (Br), and iodine (I), which are significant in rock classification for human consumption, road salt, or fertiliser. First analyses of selected trace elements (Br, B, I, Li, Cs, Co, Cr, Fe, Mn, Ni, Rb, Sr, V, and Cu) content in various evaporitic rocks of the Permian and Neogene age from Poland were done from the late 1980s [39–46] to the early 2000's [47,48]. Over the last twenty years, such geochemical studies were conducted on some Upper Permian salts from salt domes (e.g., [49–53]).

This paper presents an archive and published data on the content of selected trace elements in the Upper Permian (Zechstein) potash-bearing deposits in Poland, as well as reports new data. The geochemical characteristics of the analysed evaporites were supplemented with the description of the main minerals detected, some of them being responsible for a higher content of several elements in the rocks.

2. Geological Setting

The Upper Permian (Zechstein) has evaporites up to 1.8 km thick [54], occupying over 60% of the Poland area (Figure 1B) and infilling the eastern part (Polish Permian Basin) of the giant epicontinental Southern Permian Basin (Figure 1A). Evaporites compose ca 75% of all the Zechstein deposits, with an estimated thickness at over 2.3 km [54,55].

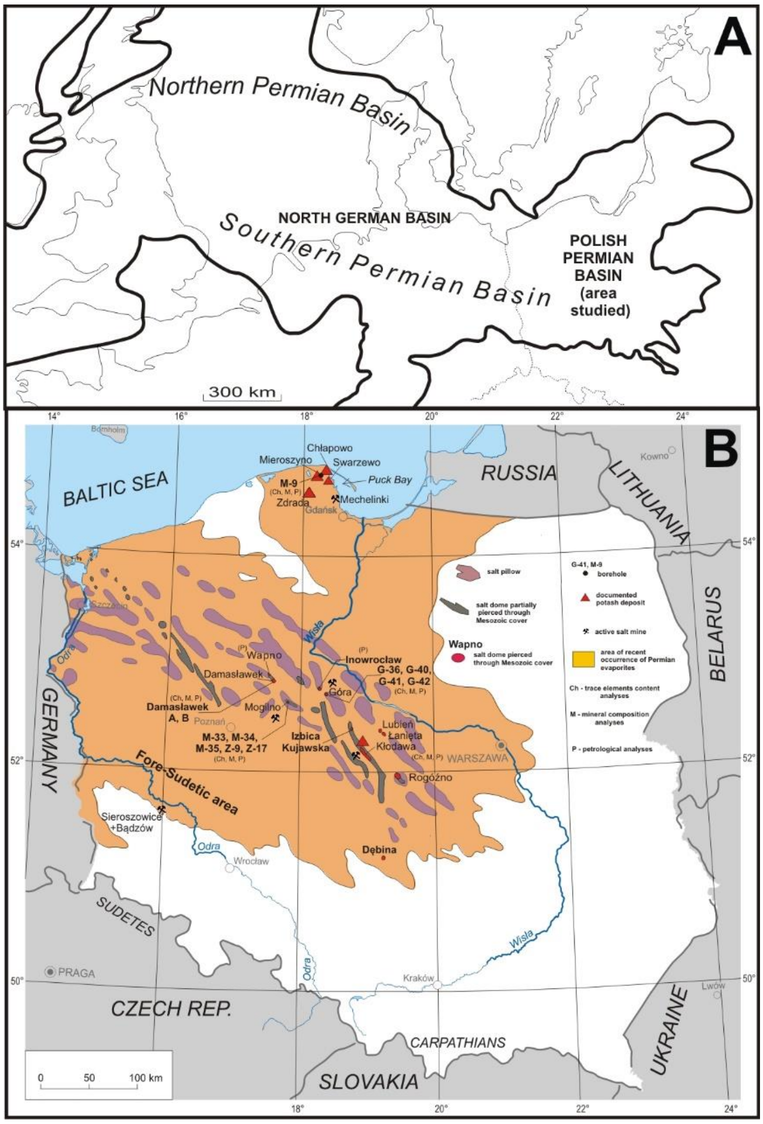

Figure 1. Studied Zechstein potash-bearing deposits in Poland. (**A**) Extent of the European Permian Basin with the area studied (after [56]). (**B**) Sites of analysed potash-bearing deposits.

The dominant evaporite rocks (salts and sulphates) together with subordinate clastics and carbonates formed distinct lithostratigraphic units, grouped into four cyclothem successions (Table 1) equivalent with ones defined in the German portion of the basin (e.g., [55,57–65]).

Table 1. Stratigraphy of commented evaporite Zechstein succession in Poland with studied potash-bearing deposits.

Global Stratigraphic Units [62,66]		European Regional Stratigraphic Units [61]		Evaporite Zechstein Lithostratigraphic Units in Poland [55] (modified)	
Epoch	**Age**	**Stage**	**Group**	**Name and Symbol of Unit**	**Cyclothems**
Lopingian	**Wuchiapingian**	**Thuringian**	**Zechstein**	Brown Zuber (Na3t) upper Younger Halite (Na3b) Younger Potash (K3) Transitional beds Na3+K3 lower Younger Halite (Na3a) Main Anhydrite (A3)	PZ3
				Screening Anhydrite (Na2r) Screening Halite (Na2r) Older Potash (K2) Transitional beds Na2+K2 Older Halite (Na2) Basal Anhydrite (A2)	PZ2
				Upper Anhydrite (A1g) Oldest Halite (Na1) Lower Anhydrite (A1d) (with polyhalite)	PZ1

Discussed potash-bearing deposits occur in the successions of the first three Zechstein cyclothems: Werra (PZ1; Z1 in Germany), Stassfurt (PZ2; Z2), and Leine (PZ3; Z3). Indicator "P" (polish) in the cyclothem standard symbol was based on some differences in evolution of the Upper Permian basin in the Poland area compared with the German portion [55,63–65].

A stratigraphy of the selected evaporite Zechstein rocks with studied potash-bearing deposits is presented in Table 1.

The potash-bearing rocks belong to all the Zechstein K–Mg evaporites, including both chloride salts (main minerals: bischofite, carnallite, sylvitee, and tachydrite) and sulphate salts (main minerals: polyhalite, kainite, kieserite, langbeinite, and hexahydrate).

The best recognised and analysed potash-bearing deposits—due to sampling accessibility in the underground mines and borehole cores located in the salt domes in central Poland (Figure 1)—represent two rock complexes occurring within the PZ2 and PZ3 cyclothems in Poland. These complexes include the following lithostratigraphic units:

(a) In PZ2 cyclothem: the Transitional beds Na2+K2, composed of rock and K–Mg salt interbeds and the Older Potash (K2) unit with dominant K–Mg salts.

(b) In PZ3 cyclothem: the Transitional beds Na3+K3 and the Younger Potash (K3) unit of the same composition for older deposits.

Sulphate K–Mg deposits (polyhalites), occurring within sulphates of the Lower Anhydrite (A1d) unit in northern Poland, westward from the Puck Bay, compose there (Figure 1) the four potash deposits with registered resources (e.g., [67–70]).

3. Previous Geochemical Studies of Zechstein Potash-Bearing Deposits in Poland

3.1. Sulphate (Polyhalites) and Chloride K–Mg Salts of PZ1 (Werra) Cyclothem from Northern Poland

The documenting of rock salt and polyhalite deposits in northern Poland in the 1970s supplied Br content data (370–2175 mg/kg) on chloride salt (carnallite) interbeds, several being a dozen or so m thick [35,71]. Boron (B) content in polyhalites was 1–110 mg/kg, and strontium (Sr)—0.9–2.3%, but in carnallitic interbeds, the boron content was 240 mg/kg, and bromine—370–2175 mg/kg [72]. The mean Br content in the rock salt seam, overlying and surrounding these potash salts, was determined to be 80–166 mg/kg [71]. Subsequent analyses of polyhalite interbeds [73–75] within anhydrites of the Lower Anhydrite (A1d) lithostratigraphic unit (Table 1) evidenced a measured concentration of strontium (600–900 mg/kg) and boron (10 to >500 mg/kg).

3.2. K–Mg Salts of PZ2 (Stassfurt) and PZ3 (Leine) Cyclothems from SALT Domes in Central Poland

The potash-bearing deposits of PZ2 and PZ3 cyclothems (Table 1) formed the stock parts of many salt domes in the central Poland area (Figure 1).

Early studies of the Zechstein salts in the Kłodawa salt dome (Figure 1) determined boron and bromine content of 0.01–0.092% and 0.2%, respectively [76], in the potash-bearing deposits.

Subsequent studies of salt reserves for this dome showed varied content values of such trace elements as Br, B, Mn, Cs, Li, and Sr in the K–Mg salts of PZ2 cyclothem [33,34,77]. In the potash-bearing complex of PZ3 cyclothem, Br content was reported from 160–1050 mg/kg [34] to 1232 mg/kg [77], B—75.6–438 mg/kg, lithium (Li)—5.6 mg/kg, rubidium (Rb)—8.1 mg/kg, and strontium—16.1 mg/kg [77]. Analyses of potash-bearing deposits of PZ2 cyclothem in 2005–2007 documented a Br content of 77–1840 mg/kg and in the analogous complex of PZ3 cyclothem of 273–376 mg/kg (see: [50,78]). Selected geochemical analyses of the Younger Potash (K3) deposits showed Br content of 110–4500 ppm and of Rb—0.9–5915 ppm [39,40].

Bromine analyses of both potash-bearing complexes in the Góra salt dome (Figure 1) documented its content of 59–651 mg/kg for Transitional beds Na2+K2 of PZ2 cyclothem and 234–649 mg/kg for PZ3 cyclothem [79].

Both potash-bearing deposits in the Mogilno dome (Figure 1) were analysed for content of Br [52,53,80] and Al, Fe, Zn, Ni, As, Li, I, and Cd [53]. Bromine content in core samples from the M-24 borehole [80] showed in the Transitional beds Na2+K2 at 70–232 mg/kg (average: 139 mg/kg), in the Older Potash (K2)—at 69–238 mg/kg (average: 164 mg/kg), and in the Younger Potash (K3)—at 146–308 mg/kg (average: 226 mg/kg). Other bromine data from the Older Potash (K2) unit in the M-29 borehole were 69.4–148.7 mg/kg [52].

The Younger Potash (K3) rocks in the Łanięta dome (Figure 1) contained the following elements: Rb—17–33.7 ppm, Br—181–210 ppm, I, Li and vanadium (V); 0.1–1.2 mg/kg, manganese (Mn), chromium (Cr) and copper (Cu); 2.5–7.2 mg/kg, B, Sr, caesium (Cs), cobalt (Co) and nickel (Ni); and 25–60 mg/kg and iron (Fe): >100 mg/kg [39,40].

3.3. K–Mg Salts of PZ2 (Stassfurt) and PZ3 (Leine) Cyclothems from the Fore-Sudetic Area (SW Poland)

The main elements and bromine content were detected in the potash-bearing deposits of PZ2 and PZ3 cyclothems, drilled in the sixties and seventies of the past century in the Fore-Sudetic area (Figure 1), were defined to calculate a bromine/chlorine index. Its value for the Older Potash (K2) was 0.22–0.46 and for the Younger Potash (K3)—0.19–1.2 (see: [81]).

4. Materials and Methods

4.1. Rock Material

Sulphate K–Mg deposits (polyhalites), drilled within sulphates of the Lower Anhydrite (A1d) unit in PZ1 cyclothem, were analysed in nine available core samples from the single Mieroszyno M-9 borehole located in the northern Poland (Figure 1).

The potash-bearing complex of PZ2 cyclothem represented 91 samples, taken from: the Kłodawa salt dome—73, the Góra dome—1, the Damasławek dome—10, and the Mogilno dome—7.

A total of 207 samples represent the potash-bearing complex of PZ3 cyclothem. They were taken from: the Kłodawa salt dome—193, the Góra dome—4, the Damasławek dome—4, and the Mogilno dome—6.

The number and location of all (308) rock samples and analyse types are listed in Table 2.

Table 2. Location and number of analysed (trace elements content) samples from Zechstein potash-bearing deposits in Poland.

Zechstein Lithostratigraphic Units	Number of Samples					Number of Samples
	Puck Bay Surroundings	Góra Salt Dome	Damasławek Salt Dome	Mogilno Salt Dome	Kłodawa Salt Dome	
Polyhalites within A1d	9	-	-	-	-	9
Na2+K2, K2	-	1	11	7	73	92
Na3+K3, K3	-	4	4	6	193	207
Number of samples	9	5	15	13	266	308

4.2. Geochemical Analyses

The following trace elements were analysed in the 308 rock samples: silver (Ag), arsenic (As), barium (Ba), beryllium (Be), Br, cerium (Ce), cadmium (Cd), Co, Cr, Cs, Cu, iodine (I), Fe, gallium (Ga), lanthanum (La), Li, Mn, molybdenum (Mo), nickel (Ni), lead (Pb), Rb, antimony (Sb), selenium (Se), tin (Sn), Sr, titanium (Ti), thallium (Tl), uranium (U), vanadium (V), and zinc (Zn). For several samples, a content of insoluble (in water) residuum was identified.

282 samples were analysed in the certificated Central Chemical Laboratory of Polish Geological Institute—National Research Institute in Warsaw.

A powdered rock sample (fraction < 1 mm) was dried and dissolved in HCl solution (1 g of sample to 50 g of solution). For Br and I detection the powdered sample was dissolved in heat water.

The following analytical methods were applied for detecting:

- Ba, Cr, Cu, Fe, Mn, Sr, Ti, V, and Zn—emission atomic spectrometry with activation in inductively coupled plasma (ICP-OES);
- Ag, As, Be, Ce, Cd, Co, Cs, Ga, La, Li, Mo, Ni, Pb, Rb, Sb, Se, Sn, Tl, and U—mass spectrometry with ionization in inductively coupled plasma (ICP-MS);
- Br and I—ion chromatography (IC).

24 samples were analysed by the Hydrogeochemical Laboratory at the Hydrogeology and Engineering Geology Department of the AGH University of Science and Technology in Cracow.

A powdered rock sample (fraction 0.1–1 mm) of ca. 0.3 g was dissolved in a mixed solution of HCl and HNO_3 (proportion 1:3) at 230 °C and pressure 35 atm. Chloride and bromide content was detected in a solution of dissolved sample (ca. 5 g sample and 100 mL H_2O). Chlorides were detected with the argentometric method, and bromine, as well as other trace elements were detected with mass spectrometry, using the Spectrometer ICP MS "Elan 6100" (produced by Perkin-Elmer) with inductively activated plasma.

4.3. Mineral Composition Study

Mineral composition analyses of the selected 55 rock samples (1–10 g) were completed by the Laboratory of XRD and XRF Analyses at the Hydrogeology and Engineering Geology Department of the AGH University of Science and Technology in Cracow.

The sample was powdered to a 5–10 µm fraction and analysed with the Rietveld method. XRD data were collected by the Panalytical X'Pert Pro MD PW 2030 powder diffractometer (produced by Panalytical, previously Philips) using K1 radiation from Cu anode. The configuration was a standard Bragg–Brentano setup with a Ge (111) monochromator at the incident beam. All measurements were performed at room temperature with the 0.016° step size at a 5°–90° scanning range. Phase analysis was based on the PDF4+ (ICDD) crystallographic database. The full pattern fitting procedure for quantitative analysis and determining structural parameters was performed using Panalytical HighScore Plus 3.0 software.

4.4. Petrographic Studies

Rock structure and mineral composition were studied in 26 thin sections (35 µm thick) from chloride K–Mg salts, using the optic microscope Olimpus BX-12 (produced by Nikon) with transmitted light—one polar, crossed polars (X), and magnification up to 200× were applied.

Thin sections (9) from the sulphate K–Mg salts were studied with an optic microscope Eclipse E600 Pol (produced by Nikon) and the electron microscope CAMECA SX 100 with microprobe (4 analyses of sulphate phases).

Number and location of analyses types are listed in Table 3.

Table 3. Types, number, and location of analyses of sampled Zechstein potash-bearing deposits in Poland.

Location	Zechstein Lithostratigraphic Units	Type of Analyse		
		Chemical (Elements Content)	XRD (Mineral Composition)	Petrographic (Mineral Composition)
Puck Bay surroundings	A1d	9	2	8
Góra salt dome	Na2+K2, K2	1	1	6
	Na3+K3, K3	4	4	4
Damasławek salt dome	Na2+K2, K2	11	4	1
	Na3+K3, K3	4	3	1
Mogilno salt dome	Na2+K2, K2	7	3	5
	Na3+K3, K3	6	4	4
Kłodawa salt dome	Na2+K2, K2	73	20	2
	Na3+K3, K3	193	14	6
Total number of analyses		308	55	37

5. Geology and Sampling of Potash-Bearing Deposits

5.1. Sulphate K–Mg Salts

In the sixties and seventies of the past century, four deposits of sulphate K–Mg salts (polyhalite)—Chłapowo, Mieroszyno, Swarzewo, and Zdrada (Figure 1)—were documented at the Puck Bay in northern Poland (see: [36–38,68,70]). Polyhalites are concentrated in three layers 1.9–7.0 m thick [68,82,83] located in the upper part of Lower Anhydrite (A1d) 19.5–173.6 m thick [84,85].

Nine samples of polyhalite came from the new Mieroszyno M-9 borehole (Figure 1), in which profile (Figure 2) two polyhalite anhydrite beds were drilled at depths of 767.7–782.8 m and 809.0–811.4 m. They occur within the A1d seam and are developed as grey micro to fine crystalline anhydrite with yellow-olive concentrations, strings, and interbeds of polyhalite and carbonates.

5.2. Potash-Bearing Deposits of PZ2 Cyclothem

The potash-bearing deposits of PZ2 cyclothem represent two lithostratigraphic units: the Transitional beds Na+K2 and the Older Potash (K2). They are underlain by the chlorides of Older Halite (Na2) units and overlain by rock salts of the Screening Halite (Na2r) or by the Screening Anhydrite (A2r) units. These potash rocks were sampled in the four salt domes: Damasławek, Góra, Kłodawa, and Mogilno.

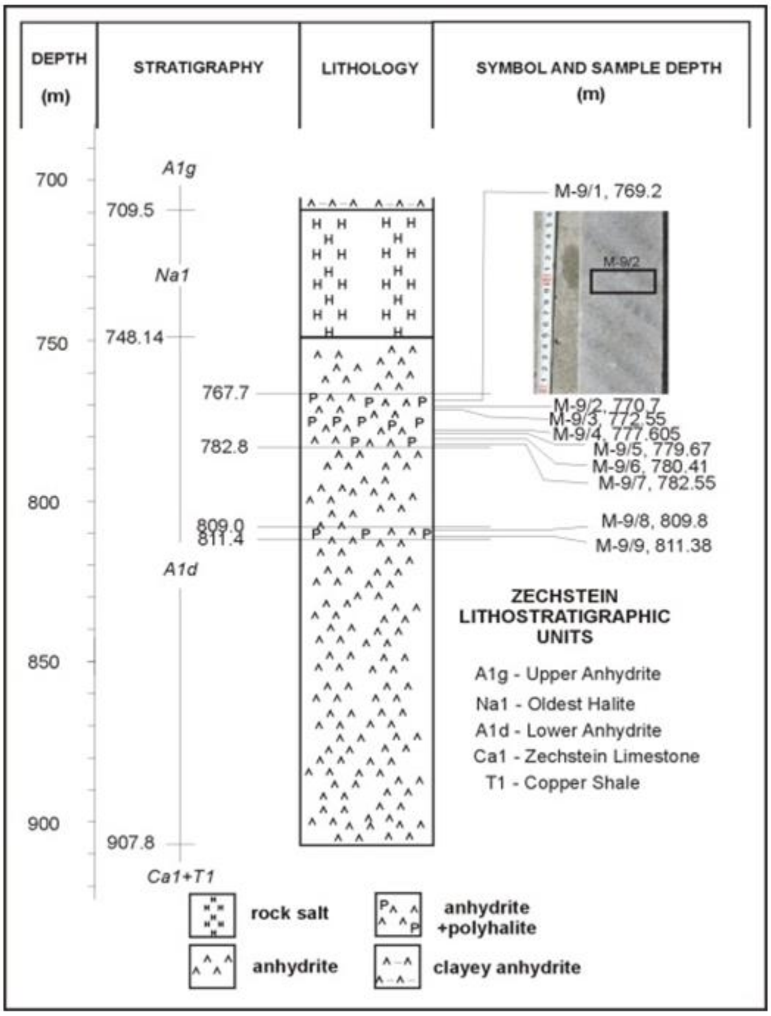

Figure 2. Sampled profile of Mieroszyno M-9 borehole with polyhalite interbeds within the Lower Anhydrite (A1d) unit. M-9/1, 769.2—sample number and depth in metres, in frame—thin section (sample M-9/2) on Figure 11.

The Older Potash seam in the Fore-Sudetic area, several to 24 m thick, is composed of repetitive yellow to red layers of rock salt, salt with sylvite and anhydrite-polyhalite-halite beds [85–91]. The main minerals are halite, sylvite, polyhalite, anhydrite, with minor addition of clay matter, and iron oxides, less frequent are quartz and boracite aggregates.

The potash-bearing complex in the Kłodawa salt dome is 11–17 m thick including the Transitional beds Na2+K2 of ca. 5 m [92]. These beds are composed of white-grey coarse crystalline rock salt (Figure 3) with a clay admixture and anhydrite laminae, as well as more or less regular concentrations and interfingers of K–Mg salts, dominated by kieserite, polyhalite, carnallite, and sylvite [93]. The overlain Older Potash (K2) unit is composed of anhydrite-sylvite-polyhalite rock (Figure 4) admixed with carnallite and kainite in the lower part [93].

This complex was sampled (70) in three galleries located at mine levels 600 m and 750 m of the underground salt mine KŁODAWA S.A. [30,49]: Z2/1 profile (29 samples; Figure 3), Z2/2 profile (19 samples) and Z2/3 profile (22 samples). They are supplemented by geochemical data of three samples taken from other three galleries at mine level 750 m [52].

The potash-bearing complex in the Damasławek salt dome is composed of a repetitive (Figure 5) series of Transitional beds Na2+K2 and Older Potash (K2), ca 1.5 m thick [31]. They are built by white-grey-red polymorphic halite kieserite salts with laminae and aggregates of kainite, anhydrite, and clay matter. Ten samples were taken from the cores of Damasławek A (seven samples) and Damasławek B (three samples) boreholes (Figure 6).

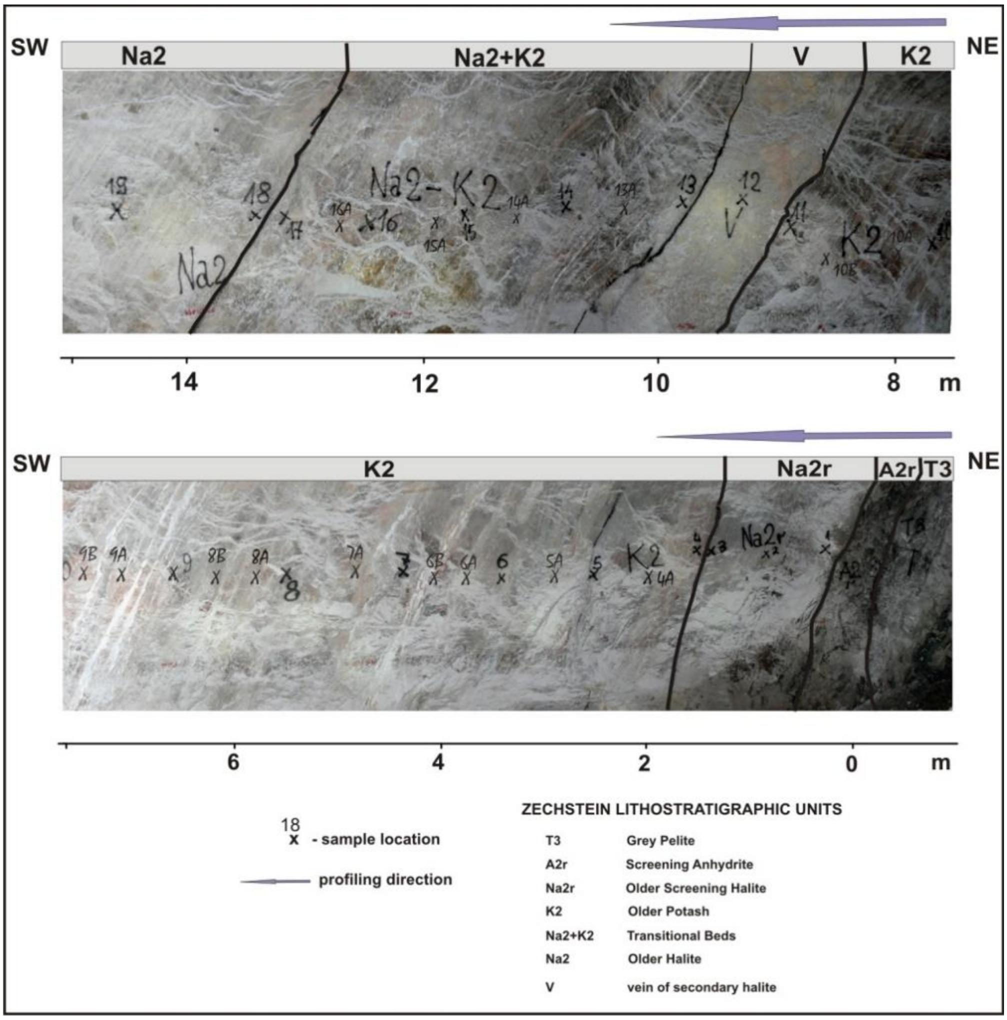

Figure 3. Sampled profile Z-2/1 of Na2+K2 and K2 lithostratigraphic units in the gallery of salt mine KŁODAWA S.A., mine level 600 m, Kłodawa salt dome.

Figure 4. Sample of kieseritic salt from the Older Potash (K2) unit. The Z-2/1 section in the gallery of salt mine KŁODAWA S.A., Kłodawa salt dome.

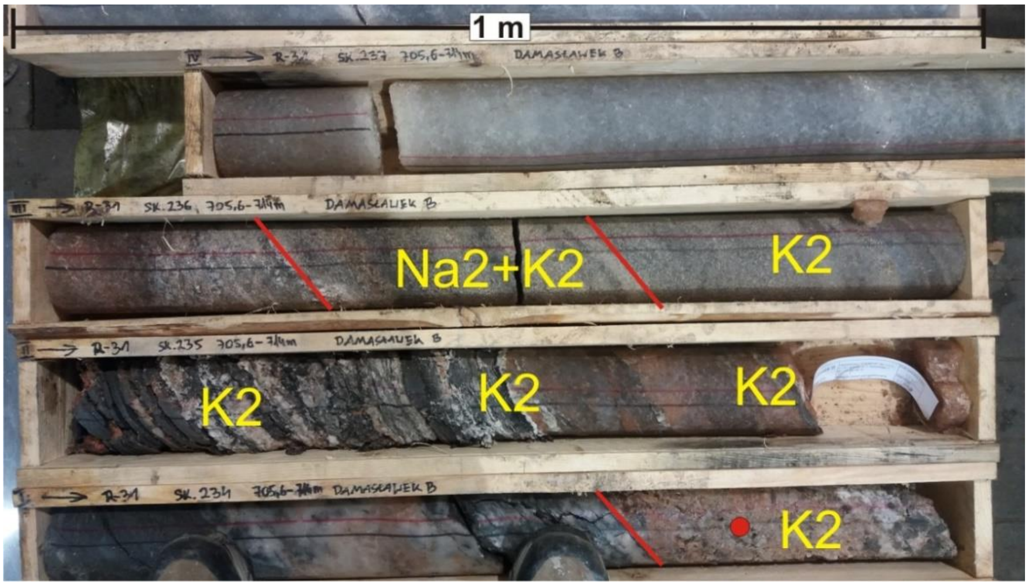

Figure 5. Core of Older Potash (K2) and Transitional beds Na2+K2 units in the profile of Damasławek B well, depth interval 705.6–709.6 m. Red point—sample.

In the Góra salt dome, the Older Potash (K2) unit is developed as repetitive beds impressed within the huge profile of Older Halite (Na2). It is comprised of thin laminae and layers, several to a dozen or so cm thick, of medium to coarse crystalline K–Mg salts, highly tectonised and reduced. Only a single sample was taken from the core of the G-41 borehole (Figure 7).

The Older Potash (K2) deposits in the Mogilno salt dome are up a dozen or so cm thick [53]. They consist of white-grey-red, medium to coarse crystalline salts, frequently stratified with repetitive kieserite-halite (white-grey in colour) and sylvite-halite (red) beds. They were sampled in the M-33 (four samples) and M-35 (three samples) boreholes (Figure 8).

5.3. Potash-Bearing Deposits of PZ3 Cyclothem

The studied potash-bearing complex of PZ3 cyclothem is composed of two lithostratigraphic units: the Transitional beds Na3+K3 and the Younger Potash (K3). The latter complex overlies the lower Younger Halite (Na3a) deposits and is covered by the upper Younger Halite (Na3b) unit (a case of the Kłodawa salt dome) or by the Brown Zuber (Na3t) unit.

The Younger Potash seam in the Fore-Sudetic area is 3–41 m thick and includes two rock salt beds with concentrations of polyhalite, sylvine, and anhydrite, separated by a single halite bed [86,94].

The complex was accessible for sampling (207 samples taken from underground galleries and borehole cores) only in the four salt domes: Kłodawa, Damasławek, Góra, and Mogilno.

The Transitional beds Na3+K3 in the Kłodawa dome, ca 14.7 m thick, are built by grey fine crystalline rock salt, rhythmically stratified with fine and several thicker (0.3–5.3 m) beds of kieseritic carnallite. The Younger Potash (K3) unit, 20–120 m thick, is composed of interbeds of: (a) fine to medium crystalline rock salt, stratified with clay matter + anhydrite laminae and with laminae and nests of kieseritic carnallite, as well as (b) kieseritic carnallite layers with nests of coarse crystalline and transparent giant halite [93]. This potash unit is highly folded (Figure 9) in the central profile part (Figure 10).

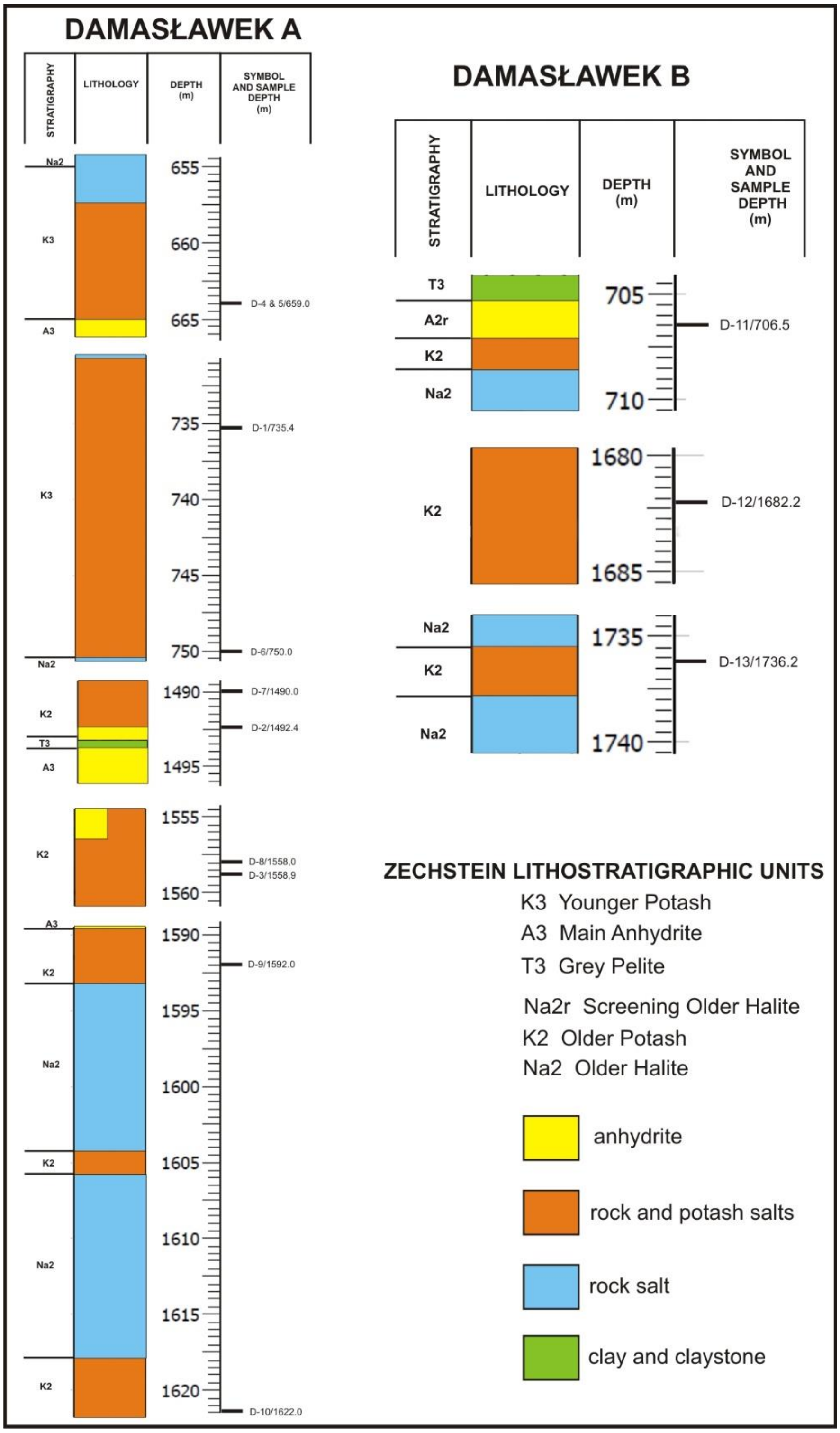

Figure 6. Sampled parts of the Damasławek A and B boreholes profiles with Na2+K2, K2, and K3 lithostratigraphic units, Damasławek salt dome.

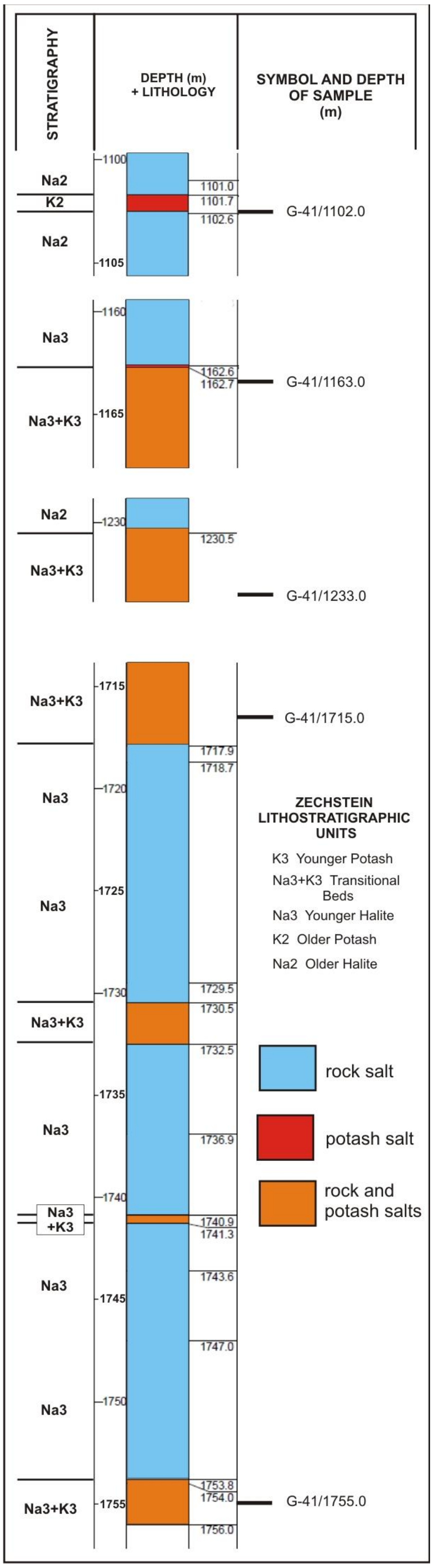

Figure 7. Sampled parts of the G-41 borehole profile with K2 and Na3+K3 lithostratigraphic units, Góra salt dome.

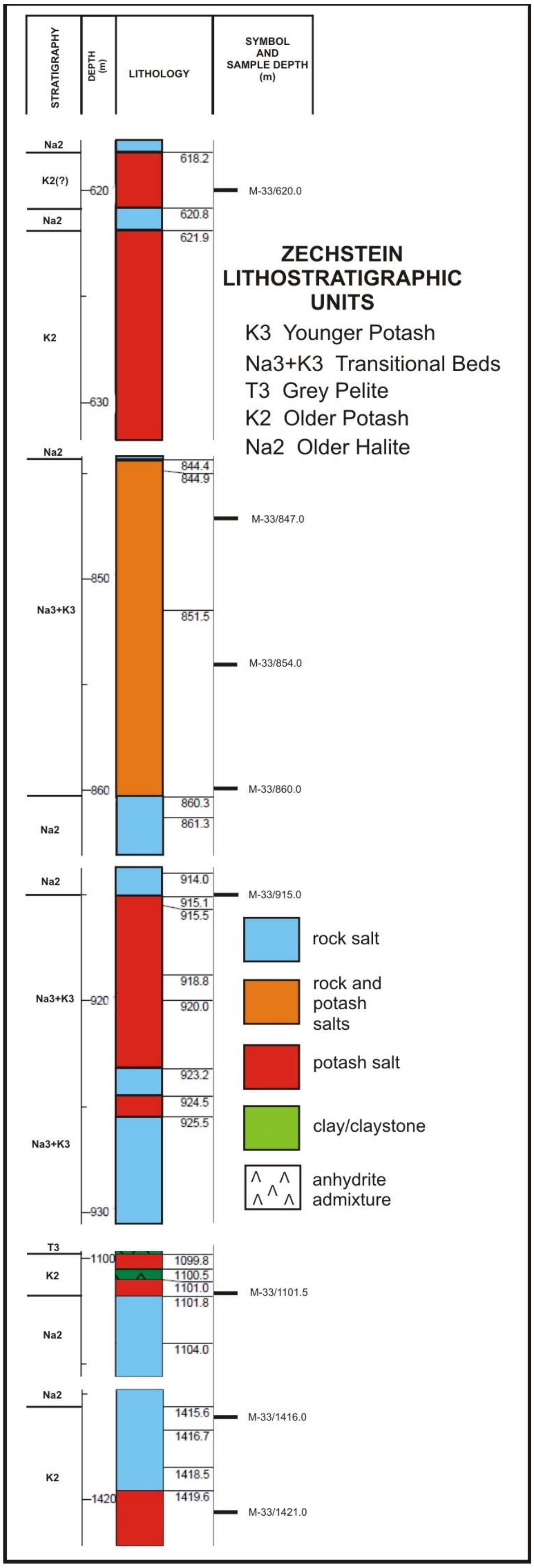

Figure 8. Sampled parts of the M-33 borehole profile with K2 and Na3+K3 lithostratigraphic units, Mogilno salt dome.

Figure 9. Folded beds of rock salt (dark) and carnallite-kieserite (red and pink). The Younger Potash (K3) unit, Z-3/2 profile in the gallery of salt mine KŁODAWA S.A., mine level 600 m, Kłodawa salt dome.

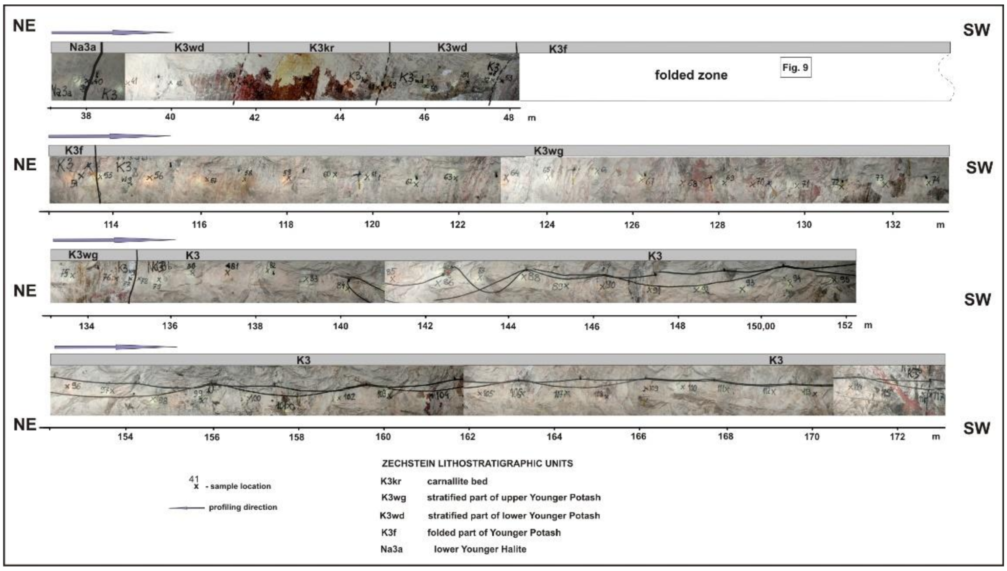

Figure 10. Sampled profile Z-3/2 of K3 in a gallery of salt mine KŁODAWA S.A., mine level 600 m, Kłodawa salt dome.Location of Figure 9 was indicated in profile.

This potash-bearing complex was sampled (187) in two galleries located at mine levels 600 m and 750 m of the underground salt mine KŁODAWA S.A. [31,50]: Z3/1 profile (109 samples) and Z3/2 profile (78 samples; Figure 10). They are supplemented by geochemical data of six samples taken from two other galleries there [51].

The potash-bearing series of PZ3 cyclothem in the Damasławek dome is represented by the Younger Potash (K3) deposits ca. 8.5–10 m thick, twice repeated in the Damasławek A borehole profile (four samples; Figure 6). They are tectonically squeezed in rock salts of the Older Halite (Na2) and sulphates of the Main Anhydrite (A3). This series is dominated by grey-red medium crystalline rock salt with sylvite, either textureless or with anhydrite–clay matter flames. Some kieserite nests are covered with a white epsomite powder. Additionally, fine kainite admixture is observed.

Repetition of beds of the Younger Potash unit was registered in many borehole profiles from the Góra dome. These beds are composed of rock salt and K–Mg salt layers, several cm to over 5 m thick. The sampled (four samples) core intervals of G-41 borehole (Figure 7) represent a medium to fine crystalline "hard" kieseritic langbeinite salt, built of repetitive thin layers of grey K–Mg salt and grey-orange rock salt. The main minerals are halite, kieserite, sylvite, langbeinite, and anhydrite, as well as a bitumen admixture.

The sampled cores of two boreholes, M-33 (four samples; Figure 8) and M-35 (2 samples), represented the potash-bearing complex of PZ3 cyclothem from the Mogilno dome. In the M-33 profile is defined the Transitional beds Na3+K3, over 16 m thick and four times folded together with rock salts of the Older Halite (Na2) unit. In the M-35 borehole, these Na3+K3 beds are repeated five times, and the single bed of Younger Potash (K3), ca. 3 m thick, was recorded [53].

Sampled core intervals represent a "hard" kieseritic salt, composed of orange to brown, medium crystalline rock salt layers with anhydrite aggregates and a clay matter admixture. Salt is stratified with repeated fine beds of white-grey kieserite and of grey-orange halite-sylvite.

6. Results

6.1. Mineral Composition of Potash-Bearing Deposits

The mineral composition of the studied potash-bearing Zechstein deposits was defined using data of XRD analyses (55 rock samples) and the results of petrographic thin section studies (37 new rock samples and data from archive six thin sections) supplemented with SEM microprobe analyses of sulphates in selected samples (four analyses [31]).

Thirty distinguished individual minerals and three mineral groups (chlorites, carbonates, and clay minerals) and their occurrence frequency (number/percent of detections of each mineral in the whole number of studied petrographic, XRD, and SEM analyses) are listed in Table 4.

Table 4. Frequency of detected main minerals in the Upper Permian (Zechstein) potash-bearing deposits of Poland (PZ1, PZ2 and PZ3 cyclothems).

Mineral Chemical Formula	Number (Percent) of Analyses with Detected Mineral			Sum (Percent) of Analyses with Detected Mineral
	Cyclothem and Lithostratigraphic Unit			
	PZ1, Polyhalites within A1d	PZ2, Na2+K2 and K2	PZ3, Na3+K3 and K3	
** anhydrite $CaSO_4$	9 (42.85)	28 (10.85)	38 (14.96)	75 (14.07)
+ berlinite $AlPO_4$	-	-	1 (0.39)	1 (0.18)
** bischofite $MgCl_2 \cdot 6H_2O$	-	3 (1.16)	3 (1.18)	6 (1.12)
** bloedite $Na_2SO_4 \cdot MgSO_4 \cdot 5H_2O$	-	3 (1.16)	-	3 (0.56)
** calcite $CaCO_3$	-	2 (0.77)	4 (1.57)	6 (1.12)
** carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$	-	7 (2.71)	26 (10.23)	33 (6.19)
+ cronstedtite $Fe^{2+}{}_2Fe^{3+}((Si,Fe^{3+})_2O_5)(OH)_4$	-	5 (1.93)	-	5 (0.93)
** gypsum $CaSO_4 \cdot 2H_2O$	1 (4.76)	3 (1.16)	-	4 (0.75)
** halite NaCl	-	47 (18.21)	49 (19.29)	96 (18.01)
** hexahydrite (sakiite) $MgSO_4 \cdot 6H_2O$	-	-	1 (0.39)	1 (0.18)

Table 4. *Cont.*

Mineral Chemical Formula	Number (Percent) of Analyses with Detected Mineral			Sum (Percent) of Analyses with Detected Mineral
	Cyclothem and Lithostratigraphic Unit			
	PZ1, Polyhalites within A1d	PZ2, Na2+K2 and K2	PZ3, Na3+K3 and K3	
+ hexahydroborite $Ca[B(OH)_4]_2 \cdot 2H_2O$ or $CaB_2O_4 \cdot 6H_2O$	-	-	1 (0.39)	1 (0.18)
** kainite $4KCl \cdot 4MgSO_4 \cdot 11H_2O$	-	21 (8.13)	25 (9.84)	46 (8.63)
** kieserite $MgSO_4 \cdot H_2O$	-	32 (12.4)	44 (17.32)	76 (14.25)
** langbeinite $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$	-	2 (0.77)	4 (1.57)	6 (1.12)
** leonite $K_2SO_4 \cdot 2MgSO_4$	-	2 (0.77)	1 (0.39)	3 (0.56)
** loewite $6Na_2SO_4 \cdot MgSO_4 \cdot 15H_2O$	-	2 (0.77)	-	2 (0.37)
* magnesite $MgCO_3$	2 (9.52)	6 (2.32)	4 (1.57)	12 (2.25)
+ nantokite CuCl	-	1 (0.38)	1 (0.39)	2 (0.37)
** picromerite $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$	-	1 (0.38)	-	1 (0.18)
** polyhalite $K_2SO_4 \cdot 2CaSO_4 \cdot MgSO_4 \cdot 2H_2O$	9 (42.85)	20 (7.75)	6 (2.36)	35 (6.56)
+ spodumene $LiAlSi_2O_6$	-	2 (0.77)	1 (0.39)	3 (0.56)
** starkeyite (leonhardite) $MgSO_4 \cdot 4H_2O$	-	1 (0.38)	3 (1.18)	4 (0.75)
** sylvite KCl	-	34 (13.17)	24 (9.44)	58 (10.88)
+ trevorite $Ni^{2+}Fe^{3+}{}_2O_4$	-	-	1 (0.39)	1 (0.18)
* quartz SiO_4	-	16 (6.20)	2 (0.78)	18 (3.37)
+ talc $Mg_3Si_4O_{10}(OH)_2$	-	6 (2.32)	2 (0.78)	8 (1.50)
chlorite group	-	4 (1.55)	2 (0.78)	6 (1.12)
* pyrite FeS_2	-	5 (1.93)	2 (0.78)	7 (1.31)
+ boracite $Mg_2B_7O_{13} \cdot Cl$	-	3 (1.16)	1 (0.39)	4 (0.75)
+ hydrotalcite $Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$	-	1 (0.38)	-	1 (0.18)
+ goethite α-$Fe^{3+}O(OH)$	-	1 (0.38)	-	1 (0.18)
* celestite $SrSO_4$	-	1 (0.38)	-	1 (0.18)
carbonates	-	-	2 (0.78)	2 (0.37)

Table 4. *Cont.*

Mineral Chemical Formula	Number (Percent) of Analyses with Detected Mineral			Sum (Percent) of Analyses with Detected Mineral
	Cyclothem and Lithostratigraphic Unit			
	PZ1, Polyhalites within A1d	PZ2, Na2+K2 and K2	PZ3, Na3+K3 and K3	
* hematite Fe_2O_3	-	-	4 (1.57)	4 (0.75)
clay minerals	-	-	2 (0.78)	2 (0.37)
Sum of mineral detections	21	258	254	533 (100%)

Mineral formula after: * [95], ** [96], + [97].

As far as the frequency is concerned, five groups of minerals are proposed: very rare (<1%), rare (1 to <5%), frequent (5 to <10%), common (10 to <20%), and dominant (≥20%) minerals.

The analysed potash-bearing sulphates of PZ1 cyclothem (two XRD analyses and eight petrographic studies; Table 2) are composed by dominated anhydrite and polyhalite (>42%, Figure 11). Gypsum as a secondary (after hydration of anhydrite) mineral is rare (4.8%) compared to magnesite (9.5%).

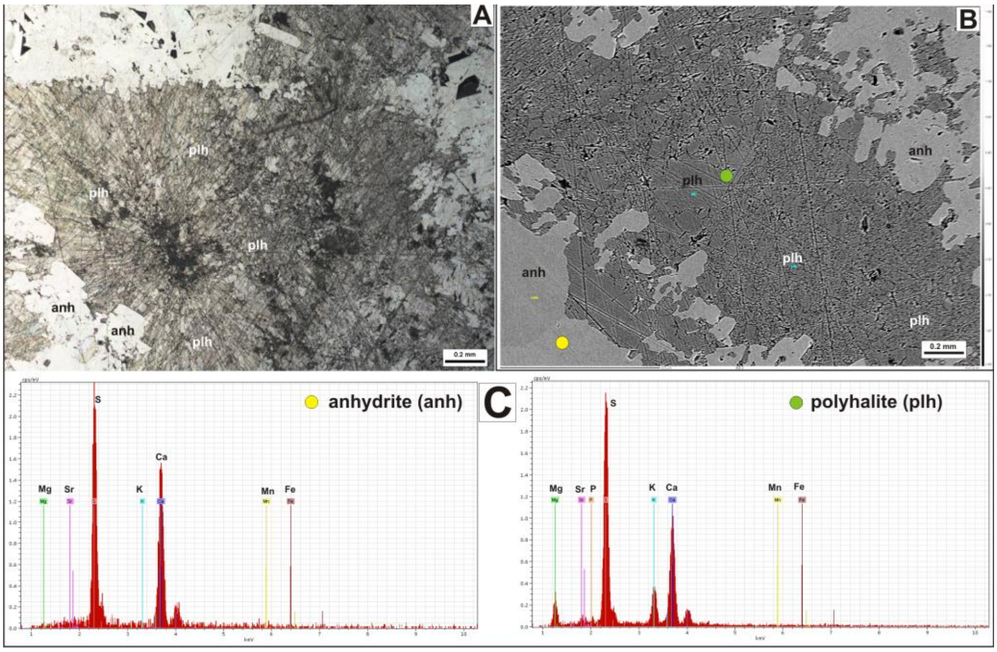

Figure 11. Thin section study, Mieroszyno M-9 borehole, sample M-9/2, depth 770.72 m. Sample location on Figure 2. (**A**) Radial and tabular crystals of polyhalite (plh, grey) and anhydrite plates (anh, white), microscope image (II polars). (**B**) SEM image of analysed anhydrite and polyhalite crystals with microprobe results; (**C**) colour dots—analytic points.

The analysed potash-bearing deposits of PZ2 cyclothem (28 XRD analyses and 14 petrographic studies supplemented with archive data of four thin sections) contain (Table 4) common minerals (frequency 10–18%), such as: halite (Figure 12A,C), sylvite (Figure 12F), kieserite (Figure 12C,D), and anhydrite (Figure 12E). The frequent (6–8%) ones are: kainite, polyhalite (Figure 12E), and quartz. The rare (1–3%) minerals that were detected: bischofite (Figure 12F), bloedite, carnallite (Figure 12A), cronstedtite, gypsum, magnesite, talc, pyrite, boracite, and minerals of chlorite group (Table 4). Calcite, leonite, loewite, langbeinite, nantokite, picromerite, spodumene, starkeyite, hydrotalcite, goethite, and celestite were sporadically identified. Secondary minerals after kieserite, such as hexahydrite (Figure 12D) and epsomite were, also noticed.

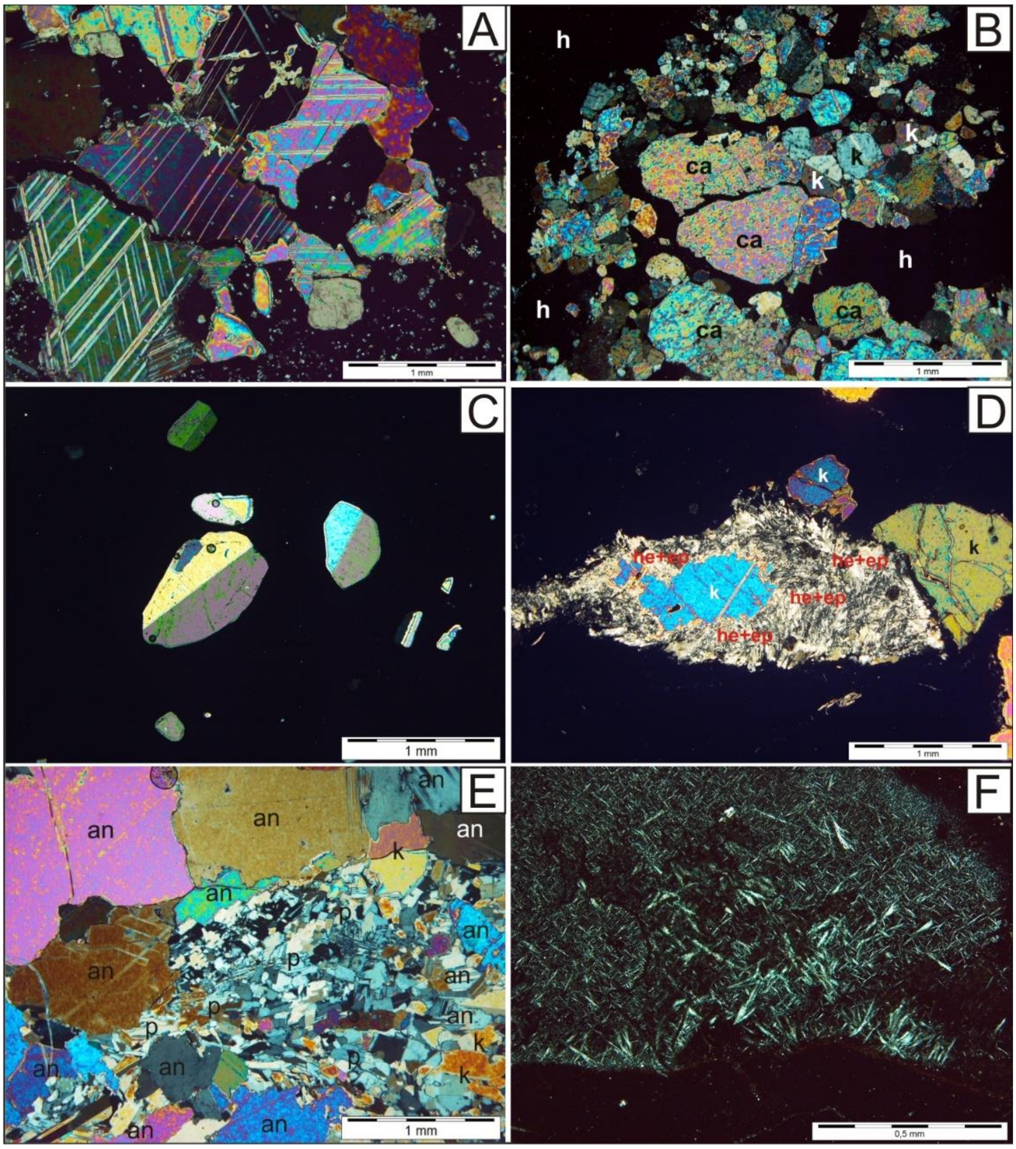

Figure 12. Main minerals of Zechstein potash-bearing deposits (thin sections, X polars). (**A**) Twinned carnallite crystals within halite-sylvite mass (black). Older Potash (K2) unit, Inowrocław salt dome. (**B**) Large carnallite (ca) and fine twinned kieserite (k) crystals within halite (h). Younger Potash (K3) unit, salt mine KŁODAWA S.A., NE-SW gallery, mine level 600 m. (**C**) Twinned kieserite crystals within halite-sylvite mass (black). Older Potash (K2) unit, Damasławek B well, depth 706.5 m. (**D**) Kieserite crystals (k) transformed into hexahydrite and epsomite (he + ep), halite-sylvite background (black). Older Potash (K2) unit, G-42 well, depth 1720 m. (**E**) Fine polyhalite crystals (p) framed by large anhydrite (an) and smaller kieserite (K) ones. Older Potash (K2) unit, M-34 well depth 487 m. (**F**) Needle crystals of bischofite, halite-sylvite background (black). Older Potash (K2) unit, Inowrocław salt dome.

Studied potash-bearing deposits of PZ3 cyclothem (55 XRD analyses and 15 petrographic studies supplemented with archive data of two thin sections) evidenced (Table 4) that common minerals (frequency 10–19%) are halite, carnallite, kieserite, and anhydrite (Figure 12B). The frequent (>9%) minerals are kainite and sylvite, and the rare (1–2%) ones are bischofite, calcite, langbeinite, magnesite, polyhalite, and hematite. Sporadically, the following were registered: berlinite, hexahydrite, hexahydroborite, leonite, nantokite, spodumene, trevorite, quartz, talc, pyrite, boracite, carbonates, and minerals of the chlorite group (Table 4).

The common minerals (frequency 10 to <20%) registered in the studied Zechstein potash-bearing deposits are halite, kieserite, sylvite, and anhydrite. The frequent (5 to <10%) ones are carnallite, kainite, and sylvite, but the rare (1 to <5%) minerals are as follows: bischofite, calcite, langbeinite, magnesite, quartz, talc, pyrite, and minerals of the chlorite group (Table 4). Other listed minerals sporadically occurred are as follows: berlinite, bloedite, cronstedtite, gypsum, hexahydrite, hexahydroborite, leonite, loewite, nantokite, picromerite, spodumene, starkeyite, trevorite, boracite, hydrotalcite, goethite, celestite, hematite, carbonates, and clay minerals (Table 4). Only few of the minerals are the primary ones of evaporitic deposits: halite, carnallite, sylvite, and celestine, and others, including anhydrite, boracite, bloedite, hexahydrite, bischofite, kainite, langbeinite, loewite, and maganese could be precipitated from brines as well as transformed from the primary minerals due to diagenetic and metamorphic processes. Typical secondary minerals of the primary evaporitic ones are epsomite, hexahydroborite, kieserite, leonite, picromerite, and starkeyite [95,96,98]. Some detected minerals, such as berlinite, cronstedite, nantokite, trevorite, spodumene, talc, hydrotalcite, pyrite, hematite, and goethite are primary or secondary mineral components of magmatic, metamorphic, and hydrothermal rocks, and they are an accessory in studied evaporites together with clay minerals.

Some of most required trace elements are attributed to defined minerals: boron (B) to boracite, hexahydroborite to chlorites and clay minerals, strontium (Sr) to celestine and gypsum or anhydrite (replacing Ca), lithium (Li) to spodumene, clay minerals, and chlorites, nickel (Ni) to trevorite, and iron (Fe) mainly to pyrite, goethite, and hematite (Table 4). Because such minerals are rare or occasional in studied deposits, the content of these elements is very low.

6.2. Trace Elements Study

Content data of selected trace elements in the potash-bearing deposits of PZ1, PZ2, and PZ3 cyclothems in Poland were presented in the archival reports [30,49,50] and the paper of J. Wachowiak [51,52]. The commented below analytical results refer only to the rock samples with a precise location, other published data of samples with a less defined position in the deposit section were omitted from the statistic calculations.

Content characteristics of trace elements in the Zechstein potash-bearing deposits were based on the analytical data of 308 samples and expressed by five statistic parameters: maximum and minimum values, arithmetic mean, median, and standard deviation. The content values below the detection limit of each element were not regarded in statistic calculations and the number of such results is also indicated (Tables 5–7).

6.2.1. Sulphate K–Mg Salts (Polyhalite)

Calculated statistic parameters of trace element content in nine point samples, taken from the polyhalite interbeds within the core of Lower Anhydrite from M-9 borehole, are listed in Table 5.

Content included such elements as: Ag, As, Be, Cd, Co, Cs, Ga, Sb, Se, Sn, La, and Tl at the value of their detection limits (<0.05 to <2 mg/kg; Table 5).

Low content (mean and median: 0.07–2.0 mg/kg) characterises Ni, Rb, Mo, Ce, Pb, V, and U. Higher values (3–13 mg/kg) were noticed for Ba, Cu, Mn, Ti, and Zn.

Lithium content is relatively high (mean and median are 20–26 mg/kg)—higher was the iron content (29–33 mg/kg)—but the most abundant element is strontium (723–1075 mg/kg) due to a sample mineral composition dominated by sulphates (polyhalite, anhydrite and gypsum; Table 4). Low content variability (standard deviation 0.03–4 mg/kg) characterises Ba, Cu, Ce, Mn, Mo, Ni, Pb, Rb, Ti, and Zn, a higher variability (13–14 mg/kg) is represented by Fe and Li but the most varied data belongs to strontium (691 mg/kg).

The valuation of studied deposits as an economic source of required trace elements, e.g., Li, Cs, Sr, or Se is difficult because of few accessible samples taken from one borehole.

Such a conclusion needs more data for its support, actual geochemical results indicate that the content of most analysed elements is low (up to 13 mg/kg), only lithium, iron, and strontium occur in higher amounts.

Table 5. Statistic parameters of trace element content in the sulphate potash-bearing deposits (polyhalites) of PZ1 cyclothem in Poland.

Trace Elements		Statistic Parameters					
		n	Min.	Max.	Arithmetic Mean	Geometric Mean	Median
Li		9	15.1	59.6	26.3	23.7	20.6
Be		9 (9)	<0.3	<0.3	<0.3	<0.3	<0.3
Co		9 (9)	<0.05	<0.05	<0.05	<0.05	<0.05
Ni		9	1.1	3.5	1.9	1.8	1.6
Ga		9 (9)	<0.1	<0.1	<0.1	<0.1	<0.1
As		9 (9)	<1	<1	<1	<1	<1
Se		9 (9)	<2	<2	<2	<2	<2
Rb		9 (1)	<0.5	2.1	1.4	1.4	1.6
Mo		9	0.07	1.62	0.43	0.28	0.29
Ag		9 (9)	<0.1	<0.1	<0.1	<0.1	<0.1
Cd		9 (9)	<0.05	<0.05	<0.05	<0.05	<0.05
Sn		9 (9)	<0.5	<0.5	<0.5	<0.5	<0.5
Sb		9 (9)	<0.05	<0.05	<0.05	<0.05	<0.05
Cs	content in mg/kg	9 (9)	<0.1	<0.1	<0.1	<0.1	<0.1
La		9 (9)	<0.05	<0.05	<0.05	<0.05	<0.05
Ce		9 (4)	<0.05	0.13	0.07	0.07	0.07
Tl		9 (9)	<0.1	<0.1	<0.1	<0.1	<0.1
Pb		9 (2)	<0.1	1.3	0.3	0.2	0.2
U		9	0.1	1.0	0.3	0.25	0.2
Ba		9	1	10	5	4	4
Cu		9	4	17	12	11	13
Fe		9	12	51	33	30	29
Mn		9	2	14	5	4	3
Sr		9	454	2378	1075	888	723
Ti		9	6	10	7	7	7
V		9 (8)	<1	2	2	2	2
Zn		9	3	13	9	9	10

n—number of analysed samples; (. . .)—number of samples with element content lower than detection limit.

6.2.2. Potash-Bearing Deposits of PZ2 Cyclothem

Statistic parameters of trace element content in the potash-bearing deposits of PZ2 cyclothem were calculated for analytical results of 92 samples taken from salt domes Damasławek, Góra, Kłodawa, and Mogilno (Table 6). They include data from 86 new samples (analysis of all trace elements) and are supplemented with archival results of selected trace elements: three samples (Ag, Br, Cd, Co, Cu, Fe, I, Mn, Ni, Pb, Se, and Zn detected [51]) and three samples (only Br [53]).

These include the content of such elements as Ag, Be, Se and Sn at the value of their detection limits (<0.01 to <0.5 mg/kg; Table 6).

Very low and low content (mean and median: 0.09–0.47 mg/kg) characterises the following elements: Cd, Ce, Co, Cs, Ga, I, La, Mo, Pb, Sb, Tl, and U.

Eight elements, including As, Ba, Cr, Cu, Li, Mn, Ni, and V, have a higher content (mean and median: 1–6 mg/kg); the other three, including Rb, Ti, and Zn, are more common (3–24 mg/kg). The most abundant are bromine (Br): 119–259 mg/kg—such a high content is common in potash salts with sylvite, kainite and carnallite minerals—(e.g., [18,19,96]); iron (Fe): 100–146 mg/kg; and strontium (Sr): 76–218 mg/kg. The last two elements are mainly connected with the insolubles (0.78–1.71%), composed of gypsum, anhydrite, chlorites, and pyrite.

Low content variability (standard deviation 0.03–4 mg/kg) characterises Cd, Co, Cr, Cu, Cs, Ga, I, La, Li, Mn, Mo, Ni, Pb, Sb, Tl, U, and V, a higher variability (9–25 mg/kg) is represented by Rb, Ti, and Zn, and more varied is iron (143.59 mg/kg), but the largest differences were registered for bromine and strontium (351–358 mg/kg).

It should be noticed there that these geochemical characteristics reflected mostly the features of PZ2 potash-bearing deposits that occurred in the Kłodawa salt dome (73 samples) and analogous deposits in other three domes (Damasławek, Góra, and Mogilno) were represented by only 19 samples (11 samples from Damasławek, 1 from Góra, and 7 samples from Mogilno domes; Table 2).

These data show that the studied PZ2 potash-bearing deposits are unprofitable as economic sources of such trace elements as Ga, La, Li, Cs, or Se because their content there is undetected (Se case) or they occur in an almost minimal amount (0.3–3 mg/kg). Only strontium content is higher there, but it is connected with such sulphate minerals as gypsum, anhydrite, polyhalite, and celestite.

Table 6. Statistic parameters of trace element content in the potash-bearing deposits of PZ2 cyclothem in Poland.

Trace Elements		Statistic Parameters					
		n	Min.	Max.	Arithmetic Mean	Geometric Mean	Median
Ag	content in mg/kg	89 (89)	<0.01	<0.1	<0.1	<0.1	<0.1
As		86 (71)	<1	19	4	3	3
Ba		86 (39)	<1	30	5	3	3
Be		86 (86)	<0.3	<0.3	<0.3	<0.3	<0.3
Br		92 (1)	25	2280	259	153	119
Cd		89 (79)	<0.05	0.59	0.14	0.11	0.09
Ce		86 (14)	<0.05	2.87	0.47	0.26	0.25
Co		89 (42)	<0.05	2.52	0.23	0.13	0.09
Cr		89 (55)	<1	4	2	1.4	1.6
Cs		86 (81)	<0.1	0.6	0.2	0.2	0.2
Cu		89 (15)	<0.01	10	3	2	2
Fe		89	13	750	146	98	100
Ga		86 ((48)	<0.1	0.7	0.3	0.2	0.2
I		87 (84)	<50	0.3	0.21	0.2	0.22
La		86 (32)	<0.05	1.63	0.26	0.16	0.13
Li		86 (23)	<0.5	12.8	2.7	2.0	1.8
Mn		88 (29)	<1	13	3	2	2
Mo		86 (12)	<0.05	0.43	0.13	0.11	0.11
Ni		89 (8)	<0.5	19.3	1.9	1.4	1.3
Pb		89 (2)	<0.1	3.0	0.4	0.3	0.3
Rb		86 (15)	<0.5	60.6	6.7	3.6	4.0
Sb		86 (6)	<0.05	0.89	0.15	0.13	0.13
Se		89 (89)	<0.01	<2	<2	<2	<2
Sn		84 (84)	<0.5	<0.5	<0.5	<0.5	<0.5
Sr		86	2	1925	218	83	76
Ti		86 (5)	<1	90	24	13	15
Tl		86 (81)	<0.1	0.5	0.2	0.2	0.2
U		86 (63)	<0.05	0.28	0.11	0.1	0.09
V		86 (69)	<1	3	1	1	1
Zn		89 (9)	<1	131	6	3	3
Insoluble residue	%	70	0.01	33.93	1.71	0.65	0.78

n—number of analysed samples; (. . .)—number of samples with element content lower than detection limit.

Table 7. Statistic parameters of trace element content in the potash-bearing deposits of the PZ3 cyclothem in Poland.

Trace Elements		Statistic Parameters					
		n	Min.	Max.	Arithmetic Mean	Geometric Mean	Median
Ag	content in mg/kg	195 (190)	<0.1	0.1	0.1	0.1	0.1
As		195 (184)	<1	10.00	3.91	3.12	3.00
Ba		195 (151)	<1	28.69	4.71	2.94	2.2
Be		195	<0.3	<0.3	<0.3	<0.3	<0.3
Br		189	<50	1850	308	195	151
Cd		201	<0.05	0.6	0.23	0.16	0.12
Ce		195	<0.05	2.23	0.38	0.2	0.16
Co		200	<0.05	2.5	0.28	0.15	0.1
Cr		195	<1	3.77	1.76	1.65	1.59
Cs		195	<0.1	1.4	0.45	0.31	0.25
Cu		195	<1	6.5	3.98	3.74	3.88
Fe		200	6.06	8455.00	230.55	52.15	31.4
Ga		195	<0.1	0.6	0.26	0.22	0.2
I		190	<50.0	<50.0	<50.0	<50.0	<50.0
La		195	<0.05	1.11	0.25	0.16	0.14
Li		195	<0.5	16.8	3.13	2.66	2.9
Mn		200	<1	180.00	13.57	5.88	3.64
Mo		195	<0.05	5.27	0.15	0.1	0.09
Ni		200	<0.5	10.8	1.5	1.14	1.0
Pb		195	<0.1	1.5	0.2	0.18	0.2
Rb		195	<0.5	98.6	10.93	4.6	4.2
Sb		195	<0.05	0.42	0.13	0.11	0.11
Se		195	<2	<2	<2	<2	<2
Sn		195	<0.5	<0.5	<0.5	<0.5	<0.5
Sr		195	1.00	972.5	102.03	40.34	40.43
Ti		195	<1	531.00	24.66	10.66	7.8
Tl		195	<0.1	<0.1	<0.1	<0.1	<0.1
U		195	<0.05	0.19	0.1	0.09	0.09
V		195	<1	5.00	2.02	1.81	1.62
Zn		200	<1	7.00	2.12	1.82	1.58

n—number of analysed samples; (. . .)—number of samples with element content lower than detection limit.

6.2.3. Potash-Bearing Deposits of PZ3 Cyclothem

Presented statistic parameters of trace element content in the potash-bearing deposits of the PZ3 cyclothem (Table 7) were calculated for the analytical results of 201 samples taken from salt domes Damasławek, Góra, Kłodawa, and Mogilno. The reported statistics of analytical data represent 193 new samples (all trace elements) supplemented with archival results of selected trace elements: six samples (Br, Cd, Co, Fe, I, Mn, Ni and Zn detected [51]) and two samples (only Br [52]).

Contents of such elements as Be, I, Se, Sn, and Tl are at the value of their detection limits (<0.1 to <50 mg/kg; Table 7).

Very low and low content (mean and median: 0.09–0.47 mg/kg) characteries the following elements: Ag, Cd, Ce, Co, Cs, Ga, La, Mo, Pb, Sb, and U.

Higher content (mean and median: 1–5 mg/kg) characterises eight elements: As, Ba, Cr, Cu, Li, Ni, V, and Zn; other three elements, Mn, Rb and Ti, are more abundant (3–25 mg/kg). The highest content is characteristic of bromine (Br: 151–308 mg/kg), iron (Fe: 31–231 mg/kg), and strontium (Sr: 40–102 mg/kg). The last two elements are mainly connected with the insolubles (1.58–2.12%), composed of anhydrite, chlorites, clay minerals, hematite, and pyrite.

Low content variability (standard deviation 0–4 mg/kg) characterises Ag, As, Cd, Ce, Co, Cr, Cu, Cs, Ga, La, Li, Mo, Ni, Pb, Sb, U, V, and Zn, a higher variability (5–23 mg/kg) is represented by Ba, Mn and Rb, and more varied is strontium (159.74 mg/kg), but the largest differences were registered for bromine (367 mg/kg) and iron (706.54 mg/kg).

As in the case of the earlier-discussed deposits of the PZ2 cyclothem, this geochemical characteristic presented mainly the features of PZ3 potash-bearing deposits sampled in the Kłodawa salt dome (193 samples), but from the corresponding deposits in other three domes (Damasławek, Góra and Mogilno), only 14 samples were taken (6 samples from Mogilno and per 4 samples from Damasławek and Góra domes; Table 2).

Studied PZ3 potash-bearing deposits are non-prospective as an economic source of such trace elements as Se and Tl because they are undetected. Other ones, such as Ga, La, Li, and Cs, occur in almost minimal amounts (up to 3 mg/kg). Higher content of strontium is connected with sulphate minerals, such as anhydrite and polyhalite.

7. Conclusions

Complex studies of the Upper Permian (Zechstein, PZ1, PZ2, and PZ3 cyclothems) potash-bearing deposits (K–Mg chlorides and sulphates) in Poland enabled the first complete examination of the characteristics of the trace element geochemistry and mineral composition of these rocks in the eastern part of the Southern Permian Basin. These studies included geochemical (content of selected trace elements) and mineral composition (XRD and petrographic optic and SEM) analyses of 308 rock samples, taken mainly from four salt domes in central Poland (299 samples, PZ2 and PZ3 cyclothems) and several (9 samples) from the stratiform evaporites of PZ1 cyclothem in northern Poland.

Mineral composition studies documented a varied frequency of 30 detected minerals and three mineral groups. The most frequent minerals (frequency 10–20%) are halite, kieserite, sylvite, and anhydrite; the less frequent (5–10%) are carnallite, kainite, and sylvite. Quite rarely (1–5%), bischofite, calcite, langbeinite, magnesite, quartz, talc, pyrite and minerals of the chlorite group are found. Other detected minerals, such as berlinite, bloedite, cronstedtite, gypsum, hexahydrite, hexahydroborite, leonite, loewite, nantokite, picromerite, spodumene, starkeyite, trevorite, boracite, hydrotalcite, goethite, celestite, hematite, carbonates, and clay minerals occur sporadically.

Dominant mineral components of the K–Mg sulphates (polyhalite) of PZ1 cyclothem are anhydrite and polyhalite. For K–Mg salts of PZ2 cyclothem, the most common are halite, sylvite, kieserite, and anhydrite, but for such deposits of PZ3 cyclothem, halite, carnallite, kieserite, and anhydrite are most common.

Content of selected trace elements (Ag, As, Ba, Be, Br, Ce, Cd, Co, Cr, Cs, Cu, I, Fe, Ga, La, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, Tl, U, V, and Zn) was defined in 308 rock samples. For some samples, content of insoluble (in water) residuum was also detected.

K–Mg sulphates (polyhalite) of PZ1 cyclothem contain (arithmetic mean and median) up to 13 mg/kg of Ba, Cu, Mn, Ni, Rb, Mo, Ce, Pb, Ti, V, U, and Zn; higher is the content of Li (20–26 mg/kg), Fe (29–33 mg/kg), and Sr (723–1075 mg/kg).

Chloride K–Mg salts of PZ2 cyclothem characterise a relatively low (up to 6 mg/kg) content of As, Ba, Cd, Ce, Co, Cr, Cs, Cu, Ga, I, La, Li, Mn, Mo, Ni, Pb, Sb, Tl, U, and V, and more common (3–24 mg/kg) are Rb, Ti and Zn, but the highest content are Br (119–259 mg/kg), Fe (100–146 mg/kg) and Sr (76–218 mg/kg).

For chloride K–Mg salts of PZ3 cyclothem, the low (up to 5 mg/kg) content is typical for Ag, As, Ba, Cd, Ce, Co, Cr, Cs, Cu, Ga, La, Li, Mo, Ni, Pb, Sb, U, V, and Zn, and more common (3–25 mg/kg) are Mn, Rb and Ti, but the highest content characterises Br (151–310 mg/kg), Fe (31–231 mg/kg), and Sr (40–102 mg/kg).

Relatively low content (up to 26 mg/kg) of most analysed trace elements in the studied Zechstein potash-bearing deposits in Poland—defined in accessible rock samples—eliminate them as potential source rocks for the economically profitable extraction of such required elements as Ce, Cs, La, Li, or Rb. Bromine, iron, and strontium are easily accessible from the natural brines, sulphate (gypsum and anhydrite), and ore deposits.

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