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Hydrogeochemistry of brines on the example of selected water phenomena in the Kłodawa Salt Mine (central Poland)

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Abstract: Chemical and isotopic studies of brines in salt mines are a key element in identifying their origins. This, in turn, is applied in determining the degree of water hazard. Studies of the chemical and isotopic composition of eight brine samples in two measurement series were carried out at the Kłodawa Inc. Salt Mine in 2022 for pH, electrolytical conductivity of water (EC), mineral alkalinity, total alkalinity, total hardness, carbonate hardness, non-carbonate hardness, HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+, K^+, Ba^{2+}, Li^+, Sr^{2+}, NH_4^+, Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, Br^-, F^-, I^-, CO_3^{2-} ions as well as $\delta^{18}O$ and δ^2H in H_2O. Analysed water phenomena were selected based on archival data which indicated their various chemical compositions. Using analyses based on hydrochemical indices and isotopic composition, it was found that the studied brines represented the isotopic composition of O and H in H_2O typical of Zechstein brines, Paleo-infiltration waters, pre-Pleistocene infiltration waters and waters of mixed origin. Their salinity was mainly primary (inherent) in nature. The dominant processes affecting chemical transformations were ion exchange, precipitation and dissolution of sulphate minerals and halite, redox processes and, to a lesser extent, mixing of waters. The possible influence of inclusions on water chemistry was also found. Additionally, the analysis showed limitations in the applicability of selected hydrochemical indices.

Keywords: brine hydrogeochemistry, Kłodawa salt dome, hydrochemical indices, brine isotopic composition, salt mine, hydrogeochemical processes

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INTRODUCTION

Brines of various chemical composition accompany bitumen deposits and different types of salt deposits: rock, potassium, magnesium or potassium-magnesium. In the case of bitumen deposits, brines are characterized by the relative dominance of Cl^- Na^+ and Ca^{2+} ions and a significant amount of other elements (e.g., Li^+, Mg^{2+}) with mining potential (Macioszczyk 1987, Spencer 1987, Dowgiałło et al. red. 2002). Zechstein rock salt deposits, which are often accompanied by potassium and magnesium salts, are characterized by much greater variability in brine chemistry depending on the origins of the groundwater. The primeval brines of the sedimentary basins are mainly water of different types trapped in the form of inclusion in the rocks, depending on the evaporite cyclothem and the type of rock. Cl-Ca type brines formed under hydrodynamic stagnation conditions have also been found (e.g., García-Veigas et al. 2011). However, as shown by

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Winid (2003) and Duliński and Brudnik (2017), the chemical and isotopic composition of brines in Miocene rock salt deposits (e.g., the Wieliczka Salt Mine) shows a virtually one hundred percent share of the Cl-Na water type with an infiltration origin.

Studying the origins of brines is an important issue due to the highest degree of water hazards present in salt mines (Górski & Rasała 2008, Staszczak & Krokos 2017). In order to indirectly establish the origin of brines, hydrochemical indicators determined by the relationship between elements are used, among other things. Depending on the type of salt deposit and its origin, location and the degree of anthropogenic influence (mainly mining), the values of hydrochemical indices may vary and change over time. Some of the most important hydrochemical indices for determining the origins of salinity are the weighted Cl^-/Br^- index, also known as the Vinogradov index, and the equivalent rNa^+/Cl^- index (Macioszczyk 1987, Davisson & Criss 1996). When testing brines, weighted indices are also used, among others: Ca^{2+}/Sr^{2+}, Cl^-/I^- and Br^-/I^-. They determine the genetic relationship between the studied brines and seawater (Macioszczyk 1987).

Examples of the use of the above indices in recognizing the origins of brines can be found in studies of salt deposits in Louisiana, USA (Knauth & Kumar 1983), the Gorleben dome in Germany (Berner 2002, Schramm et al. 2009) or brines from the oil fields of the Paris Basin (Matray & Fontes 1990). In Poland, on the basis of chemical indices, the genetic interpretation of the formation waters of the Main Zechstein dolomite in the Polish Lowlands was presented by Zubrzycki (2003), thanks to which their primeval origin was established, indicating the waters of the Zechstein sea and the two-track evolution leading to the transformation of the chemical composition.

In 1996, Davisson and Criss published the results of a study of waters from various sedimentary basins using the relationship between Na-Ca-Cl ions. They made it possible to develop and apply equations to determine the ratio of excess calcium ion (Ca_{excess}) in solution to the deficit of sodium ion ($Na_{deficit}$), and thus identify the processes leading to changes in chemistry (including dolomitization, ion exchange and halite dissolution) (Davisson & Criss 1996).

Studies of the chemical composition of brines are usually accompanied by analyses of the isotopic composition of O and H in H_2O, which are commonly performed to complete knowledge about origin of waters. These studies have been widely used in salt mines in Poland, including Wieliczka, Bochnia, Wapno and Inowrocław (e.g., Duliński et al. 2000), which are underground mines with different methods of mining such as: borehole or underground method, where mines mentioned above used both or even more method of mining during the mining operations, except salt mine in Inowrocław, where only one method was used (borehole method).

The aim of the presented research was to analyse hydrogeochemical indices in order to determine the origins of brines from selected water phenomena in the Kłodawa Salt Mine (Fig. 1A), which exploits Zechstein salts with underground (room and pillar) method. The analyses performed allowed to characterize the hydrogeochemical processes occurring within the formation waters and with the support of isotopic analyses, it allowed to make a preliminary assessment of the origins of the waters present in the salt dome under study. To date, water phenomena in the Kłodawa Salt Mine have not received such extensive analysis, despite several items of literature addressing the above issues (Duliński et al. 2000, Staszczak & Krokos 2017). This article contains a multi-threaded and insightful analysis of chemical data, taking into account hydrochemical indicators. Article also presents a new perspective on the usability of tools commonly used in hydrogeology, especially mining hydrogeology.

STUDY AREA

Geological setting

At the Kłodawa Salt Mine Inc., established in 1956 in the central part of the Kłodawa salt dome, the deposit's resources were documented to a depth of 1000 m b.s.l. (Poborska-Młynarska 2013). The Kłodawa salt dome is part of the larger Izbica Kujawska – Kłodawa – Łęczyca salt structure with a length of 60 km and a NW–SE alignment (Fig. 1B, C).

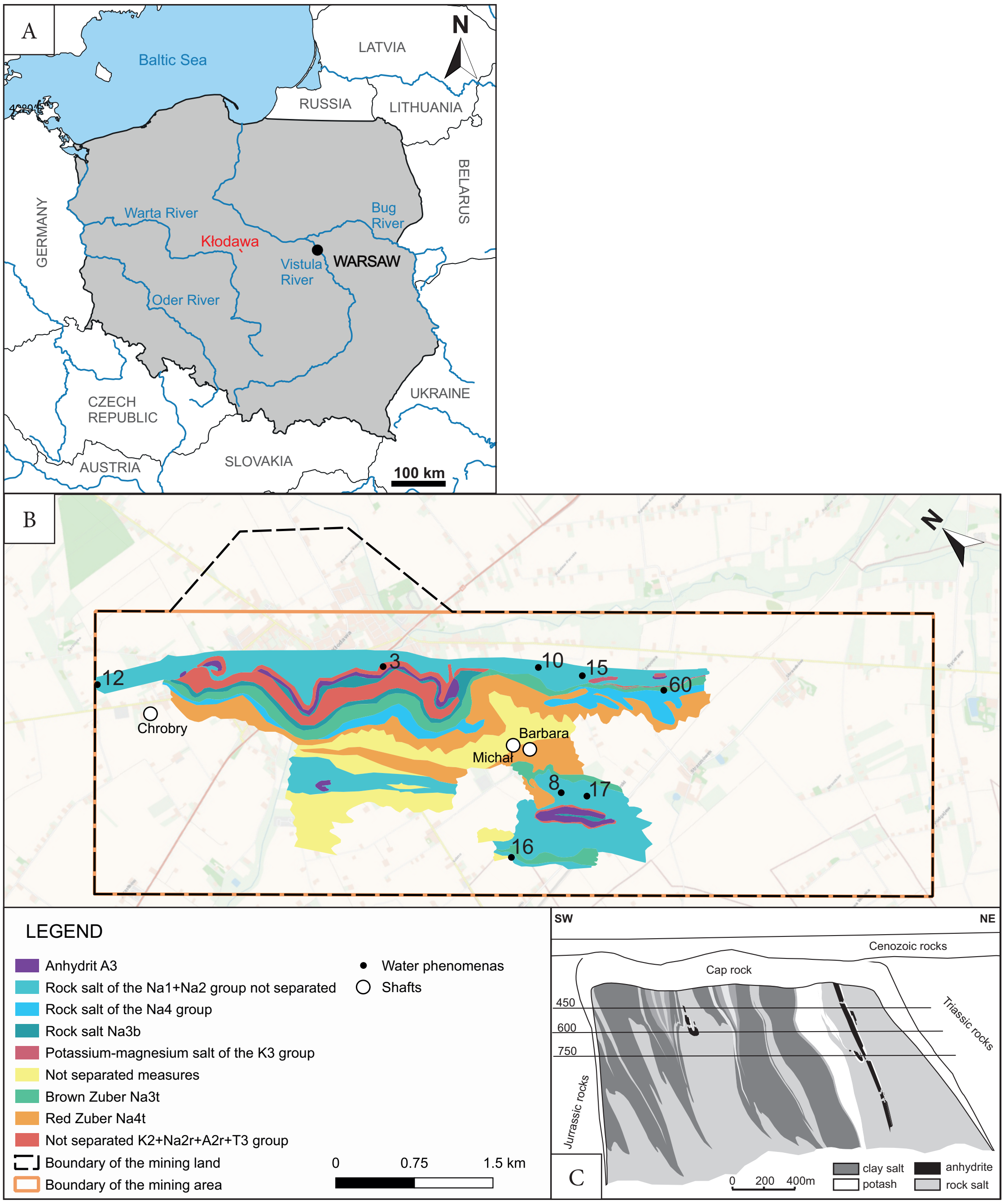

Fig. 1. *Location of the research area (A); location of the water phenomena included in the analyses against the background of mining level 600 (after Burliga & Staszczak 2016 – changed) and base map (BDOO 2024) (B); geological cross-section of the Kłodawa salt dome (after Burliga 2014) (C)*

It has the shape of an irregular trunk surrounded on the sides by Triassic and Jurassic rocks (Fig. 1C). The rock layers that build up the dome are bedded chronologically, deposited in the form of four salt cyclothems. The oldest cyclotheme, PZ1, is the least recognized salt cell, as its occurrence has only been recorded in a few places in the deposit. The thickness of the older rock salt lying at the NE boundary of the dome and in its southern part is about 250 m (Wachowiak 2010). The cyclotem of younger rock salt, i.e. PZ2, with a thickness of about 300 m, contains admixtures of anhydrite and older potassium salt. The PZ3 cyclothem is the lower and upper rock salt cells, interbedded with a layer of younger potassium salt reaching 60 m in thickness. The cyclothem also contains veins of carnallite and sylvinite, as well as a 40-meter thick layer of anhydrite and a 150-meter thick layer of brown zuber. The youngest cyclotite PZ4 of the Kłodawa salt dome is built up by rock salts of various colours and of the highest purity (NaCl up to 98%) and a layer of red zuber. The cap of the salt dome is built up by clays, anhydrites and gypsum, all covered by Neogene and Quaternary formations (Poborska-Młynarska 2013, Burliga 2014).

Hydrogeology

In the study area, Quaternary, Neogene, Cretaceous and Jurassic aquifers were found in the formations surrounding the dome (Trzeciakowska & Owczarczak 2002). The Quaternary multiaquifer formation is the first unconfined aquifer and the interclay aquifer with a thickness of 10–20 m. It is characterized by a confined water table and local hydraulic connection with the waters of the Miocene aquifer in the salt mine area. The Miocene horizon, on the other hand, occurs beneath the brown-coal complex at a depth of 60–70 m and is recharged by a flow in hydrogeological windows. Despite a number of boreholes having been drilled during the exploration of the deposit, hydrogeological recognition of the Mesozoic formations located in the vicinity of the dome is poor (Mazurek et al. 2016).

Water hazard

The water hazard at the Kłodawa mine (d'Obyrn et al. 2018) is described as the highest, due to the high solubility of the deposit and the presence of aquifers around the dome, so various manifestations of water inflows, from outflows to dampness, have been recorded since the beginning of mining. As of March 31, 2021, 575 water phenomena were recorded at the Kłodawa mine, 323 of which were active (mine archives – unpublished). They are in general all types of manifestations of water inflow in mine from moisturizations and drip leaks to larger leakages. The water phenomena described in this article, examined at the mine, are manifestations of outflows, which are permanent in nature.

METHODOLOGY

The research was carried out in 2022, taking brine samples from 8 water phenomena each time during two measurement series (April and October), for chemical and isotopic analyses (Fig. 1B). The measurement points were located at mining levels 450, 525, 600, 619, and were selected on the basis of the mine's archival data, where both the different chemical composition of the brines and the continuing water hazard associated with them were found. Preliminary (field) preparation included taking brine samples into sterile containers, acidifying a 200-milliliter sample with 5% sulfuric acid p.a. for determination of ammonium ion concentration, and filtration of 2-milliliter samples with a disposable 0.45 μm nylon syringe filter into glass vials for analysis of isotopic ratios of O and H in H_2O. Analyses of the chemical composition in terms of: pH, electrolytical conductivity of water (EC), mineral alkalinity, total alkalinity, total hardness, carbonate hardness, non-carbonate hardness, HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+, K^+, Ba^{2+}, Li^+, Sr^{2+}, NH_4^+, Cl^-, SO_4^{2-}, NO_3^-, NO_2^-, Br^-, F^-, I^-, CO_3^{2-} ions were performed at the Laboratory of Environmental Analyses (Department of Environmental Monitoring SC at the Central Mining Institute in Katowice) using the following methods: potentiometric, conductometric, potentiometric titration, spectrophotometric, ion chromatography, plasma emission spectrometry and flow injection analysis. The uncertainties of the chemical lab tests performed are summarized in Table 1.

Analyses of isotopic ratios of O and H in H_2O were performed at the Department of Applied Geology, Geochemistry and Environmental Management of the Institute of Geological Sciences of the University of Wrocław using an L2140-i spectrometer. The accuracy of measurements for the analysis of oxygen in water was SD (σ) $\delta^{18}O$ ±0,1‰, and for hydrogen in water SD (σ) $\delta^{2}H$ ±0,1‰.

Brine types were determined using Piper diagram with ternary-diamond plots. The following hydrochemical indices were calculated: Cl^-/Br^-, rNa^+/Cl^-, $rSO_4^{2-} \cdot 100/Cl^-$, Ca^{2+}/Sr^{2+}, Cl^-/I^-, Br^-/I^-, and Br^-/Li^+. Their interpretation was used to evaluate the processes forming the chemical composition of brines (Macioszczyk 1987) (Table 2).

Table 1
Range of chemical analyses performed in brine samples in 2022 along with the measurement uncertainty of each analytical method

Parameter	Unit	Method	Method application range	Measurement uncertainty
pH	–	potentiometric	2.0–13.0	0.2 for <2.0–13.0>
Electrolytic conductivity	μS/cm	conductometric	10–250,000	5% for entire range
Mineral alkalinity	mmol/L	potentiometric titration	0.10–200	15% for <0.40 10% for ≥0.40
General alkalinity	mmol/L	potentiometric titration	0.10–200	15% for <0.40 10% for ≥0.40
Carbonates	mg/L	from calculations	–	–
Bicarbonates HCO_3^-	mg/L	from calculations	–	–
Total hardness	mmol/L	from calculations based on determination of Ca^{2+}, Mg^{2+}, alkalinity	–	–
Permanent hardness	mmol/L	as above	–	–
Carbonate hardness	mmol/L	as above	–	–
Calcium Ca^{2+}	mg/L	inductively coupled plasma-optical emission spectrometry (ICP-OES)	0.02–2000	25% for ≤2.00 20% for 2.00–5.00 10% for >5.00
Magnesium Mg^{2+}	mg/L	inductively coupled plasma-optical emission spectrometry (ICP-OES)	0.012–12,200	25% for ≤1.20 20% for 1.20–3.00 10% for >3.00
Sodium Na^+	mg/L	inductively coupled plasma-optical emission spectrometry (ICP-OES)	0.023–115,000	25% for ≤2.30 20% for 2.30–5.75 10% for >5.75
Potassium K^+	mg/L	inductively coupled plasma-optical emission spectrometry (ICP-OES)	0.039–39,100	25% for ≤3.91 20% for 3.91–9.77 10% for >9.77
Barium Ba^{2+}	mg/L	inductively coupled plasma-optical emission spectrometry (ICP-OES)	0.0002–2000	25% for ≤0.10 20% for 0.10–0.50 10% for >0.50
Lithium Li^+	mg/L	inductively coupled plasma-optical emission spectrometry (ICP-OES)	0.0010–1000	25% for ≤0.20 20% for 0.20–1.00 10% for >1.00
Strontium Sr^{2+}	mg/L	inductively coupled plasma-optical emission spectrometry (ICP-OES)	0.0002–1000	25% for ≤0.10 20% for 0.10–0.50 10% for >0.50
Ammonium NH_4^+	mg/L	flow injection analysis (FIA) with spectrophotometric detection	0.020–1000	20% for <0.010–0.050> 10% for >0.050
Chloride Cl^-	mg/L	ion chromatography (IC)	0.28–177,300	20% for <0.28–0.71> 15% for (0.71–2.8> 10% for 2.8–177,300
Sulfur SO_4^{2-}	mg/L	ion chromatography (IC)	0.10–10,000	20% for <0.10–0.80> 10% for >0.80
Nitrate NO_3^-	mg/L	ion chromatography (IC)	0.0045–249	20% for <0.020–0.10> 10% for >0.10
Bromide Br^-	mg/L	ion chromatography (IC)	0.020–500	20% for <0.020–0.10> 10% for >0.10
Fluoride F^-	mg/L	ion chromatography (IC)	0.010–500	20% for <0.010–0.050> 10% for >0.050
Nitrite NO_2^-	mg/L	spectrophotometric	0.0018–30.4	10% for entire range
Iodide I^-	mg/L	titration	0.40–250	25% for ≤1.0 15% for >1.0

Table 2
Hydrochemical indices used for analyses and their meaning (see the text for a more detailed explanation)

Index	Meaning	Threshold value/ Interpretation	Source
Cl^-/Br^-	salinity origin	<400 → primary water salinity	e.g., Matray & Fontes (1990); Winid & Witczak (2004)
rNa^+/Cl^-	seawater infiltration/salinity origin	≈0.86 → primary water salinity	e.g., Davisson & Criss (1996)
$r(SO_4^{2-} \cdot 100)/Cl^-$	redox conditions	<0.5 → reducing; >1 → oxidizing conditions	e.g., Macioszczyk (1987)
Ca^{2+}/Sr^{2+}	marine water influence	<33 → significant marine water input	e.g., Macioszczyk (1987)
Cl^-/I^-; Br^-/I^-	fossil vs. marine or hydrocarbon-related influence	high → marine; low → fossil or hydrocarbon-related origin	e.g., Macioszczyk (1987)
Br^-/Li^+	secondary inflow diagnostics	low values → presence of old, Li^+ ion rich brines	from this study
$Na_{deficit}$ and Ca_{excess}	chemical transformations processes e.g., ion exchange or water mixing processes	directional change → identifies active transformation processes	Davisson & Criss (1996)

Values of the weight index Cl^-/Br^- and the equivalent rNa^+/Cl^- index below 400 and 0.86, respectively, indicate the primeval origin of water salinity (Macioszczyk 1987, Davisson & Criss 1996). The index $(rSO_4^{2-} \cdot 100)/rCl^-$, determining the redox conditions present in the aquifer environment, reaches values below 0.5 for reducing conditions and above 1 for oxidizing conditions. Ca^{2+}/Sr^{2+} index values below 33 indicate the influence of seawater on the chemical composition of brines (Macioszczyk 1987). The value of the Cl^-/I^- weight index for seawater is $3.8 \cdot 10^5$ and is significantly lower for fossil waters or those associated with bitumen deposits. On the other hand, the value of the Br^-/I^- weight index for seawater is 1300, and for waters associated with bitumen deposits it decreases significantly (Macioszczyk 1987). A $Na_{deficit} - Ca_{excess}$ diagram, made from calculated values from the following equations (Davisson & Criss 1996), was used to interpret processes based on the Na-Ca-Cl relationship:

$$Ca_{excess} = [Ca_{meas} - (Ca/Cl)_{sw}Cl_{meas}]\ 2/40.08,$$

$$Na_{deficit} = [(Na/Cl)_{sw}Cl_{meas} - Na_{meas}]\ 1/22.99,$$

where: Ca_{meas} – Ca^{2+} – ion concentration in tested sample [mg/L], Na_{meas} – Na^+ – ion concentration in tested sample [mg/L], Cl_{meas} – Cl^- – ion concentration in tested sample [mg/L], $(Ca/Cl)_{sw}$ – weight ratio of Ca^{2+} and Cl^- ion content in seawater equals 0.0212, $(Na/Cl)_{sw}$ – weight ratio of Na^+ and Cl^- ion content in seawater equals 0.556.

RESULTS

The results of chemical analyses performed for the brine samples indicate a great variation in the content of both main and secondary components, and trace elements. The water reaction ranged from 4.20 for the 60/600 water phenomenon to 7.70 in the 16/600 water phenomenon (Table 3 on the interleaf). In addition to the high concentrations of selected main components (maximum values: Cl^- = 482,000 mg/L, SO_4^{2-} = 24,600 mg/L, Na^+ = 127,000 mg/L, Mg^{2+} = 121,000 mg/L, Ca^{2+} = 89,100 mg/L), NH_4^+, NO_3^-, Li^+, Br^- and Sr^{2+} ions were also present in high concentrations in most of selected water phenomena, e.g., Sr^{2+} = 1.810 mg/L (brine 12/525) (Table 3). The contents of most of the determined components, were also subject to high variability depending on the measurement series. For the concentrations of Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-} and Br^- ions these changes were evident in each of the water phenomena, but due to the high concentrations of these ions, reaching up to several hundred grams per liter, as in the case of the Cl^- ion, their variability can be considered small.

Table 3

Results of chemical and isotopic analyzes performed in 2022 in water samples taken from water phenomena

Measurement point	$\delta^{18}O$ (H_2O)	δ^2H (H_2O)	pH	EC	General alkalinity	Mineral alkalinity	Total hardness	Carbonate hardness	Permanent hardness	CO_3^{2-}	HCO_3^-	Na^+	K^+	Mg^{2+}	Ca^{2+}	NH_4^+	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	Ba^{2+}	Li^+	Br^-	F^-	I^-	Sr^{2+}	Analytical error
	[‰]		[–]	[mS/cm]	[mmol/L]					[mg/L]																	[%]
APRIL 2022 – FIRST MEASUREMENT SERIES																											
3/619	8.41	−0.80	5.90	208	18.7	<0.1	1980	18.7	1960	3	1140	67,500	39,600	23,500	928	240	206,000	4.5	9.1	7020	0.12	207	2800	3.2	0.4	17.7	0.31
16/600	−4.71	−57.90	7.20	219	1.82	<0.1	296	1.82	294	3	111	117,000	3570	3220	618	18	184,000	0.26	10	10,700	0.066	1.3	330	0.2	1.4	24.7	0.54
10/600	0.00	−43.50	5.90	190	1.34	<0.1	3340	1.34	3340	3	81.8	51,300	19,800	30,000	17,400	1340	216,000	0.19	890	528	2.15	2.75	1900	2.6	0.62	468	0.17
8/450	−6.54	−81.60	4.40	86.3	<0.1	<0.1	9310	0	9310	3	6.1	2770	1970	74,600	63,600	54	329,000	0.006	680	104	6.13	106	4000	36	2.5	1070	0.90
60/600	−6.13	−71.70	4.20	60.8	<0.1	<0.1	9960	0	9960	3	6.1	1940	949	121,000	14.5	11	334,000	0.15	87	23,500	0.054	79.8	6600	14	2.5	0.53	0.42
15/600	3.76	−31.30	5.60	162	1.67	<0.1	1,0200	1.67	1,0200	3	102	47,200	60,800	117,000	11,400	1500	482,000	0.18	2600	1520	0.21	14.7	5500	6.5	3.6	353	0.60
17/450	−6.60	−35.10	4.40	108	<0.1	<0.1	8150	0	8150	3	6.1	5220	7070	68,200	50,800	24	299,000	0.006	3.1	177	3.75	80.3	3400	33	2.4	796	0.56
12/525	3.17	−15.40	4.40	157	<0.1	<0.1	6210	0	6210	3	6.1	16,800	5300	24,900	83,300	440	249,000	4.5	5.1	120	1.79	83	3300	13	0.7	1810	0.45
OCTOBER 2022 – SECOND MEASUREMENT SERIES																											
3/619	4.25	−14.90	6.00	211	16.5	<0.1	1780	16.5	1760	<3.0	1010	81,400	38,500	21,000	947	220	216,000	0.006	8	6730	0.073	180	2500	2.2	0.4	16.5	0.47
16/600	−4.95	−58.50	7.70	218	3.02	<0.1	253	3.02	253	<3.0	184	127,000	2790	2700	619	9.1	196,000	3.1	8.6	10,200	0.059	0.93	340	0.2	1.5	25.2	0.87
10/600	−2.41	−45.50	5.90	191	1.71	<0.1	3440	1.71	3440	<3.0	104	54,800	20,400	31,600	16,800	1060	222,000	0.26	960	416	2.2	2.98	2000	2.2	0.61	501	0.81
8/450	−5.00	−75.40	4.60	97.5	<0.1	<0.1	8730	0	8730	<3.0	6.1	3830	2380	72,200	55,900	140	321,000	0.51	670	154	6.04	100	3800	28	1.3	1060	0.68
60/600	−5.14	−68.20	4.20	61.2	<0.1	<0.1	9900	0	9900	<3.0	6.1	2130	884	120,000	16.9	15	338,000	0.12	67	24,600	0.01	90.3	6700	12	2.4	0.62	0.63
15/600	0.86	−38.00	5.60	165	2.32	<0.1	5130	2.32	5130	<3.0	142	25,600	32,900	58,900	5620	1280	247,000	0.18	1400	906	0.15	6.45	2600	1.6	3.3	199	0.86
17/450	−8.47	−43.40	5.10	117	16	<0.1	7300	16.0	7280	<3.0	976	6980	11,400	65,000	38,900	70	282,000	0.75	5.6	100	5.48	55	2800	23	1.6	711	0.65
12/525	2.57	−14.40	6.00	211	<0.1	<0.1	6600	0	6600	<3.0	6.1	17,000	5220	26,200	89,100	390	268,000	0.006	5.2	93	1.76	81.2	3400	16	0.52	1660	0.50

Explanations: EC – electrolytic conductivity; 3/619 – leak number /mining level.

Table 4

Water types and values of hydrochemical indices determined for individual brines sampled in 2022

Measurement point	Water type	Cl^-/Br^-	rNa^+/Cl^-	$(rSO_4^{2-} \cdot 100)/rCl^-$	Ca^{2+}/Sr^{2+}	Cl^-/I^-	Br^-/I^-	Br^-/Li^+	$Na_{deficit}$	Ca_{excess}
APRIL 2022 – FIRST MEASUREMENT SERIES										
3/619	Cl-Na-K	73.57	0.50	2.51	52.42	515,000	7000	13.52	2045.93	−171.61
16/600	Cl-Na-K	557.57	0.98	4.29	25.02	131,428	235	253.84	−639.23	−163.81
10/600	Cl-mixed	113.68	0.36	0.18	37.17	348,387	3064	690.90	2992.43	639.76
8/450	Cl-Mg	82.25	0.01	0.02	59.43	131,600	1600	37.73	7836.18	2825.60
60/600	Cl-Mg	50.60	0.008	5.19	27.35	133,600	2640	82.70	7993.21	−352.60
15/600	Cl-Mg	87.63	0.15	0.23	32.29	133,888	1527	374.14	9603.82	58.96
17/450	Cl-Mg	87.94	0.02	0.04	63.81	124,583	1416	42.34	7004.08	2218.62
12/525	Cl-Ca	75.45	0.10	0.03	46.02	355,714	4714	39.75	5291.17	3893.27
OCTOBER 2022 – SECOND MEASUREMENT SERIES										
3/619	Cl-Na-K	86.40	0.58	2.30	57.39	540,000	6250	13.88	1683.17	−181.25
16/600	Cl-Na-K	576.47	1.00	3.84	24.56	130,666	226	365.59	−783.99	−176.46
10/600	Cl-mixed	111.00	0.38	0.14	33.53	363,934	3278	671.14	2985.30	603.47
8/450	Cl-Mg	84.47	0.02	0.04	52.74	246,923	2923	38	7596.61	2449.84
60/600	Cl-Mg	50.45	0.01	5.38	27.26	140,833	2791	74.19	8081.69	−356.72
15/600	Cl-Mg	95.00	0.16	0.27	28.24	74,848	787	403.10	4860.03	19.14
17/450	Cl-Mg	100.71	0.04	0.03	54.71	176,250	1750	50.90	6516.40	1642.79
12/525	Cl-Ca	78.82	0.10	0.03	53.67	515,384	6538	41.87	5741.97	4162.59

Explainations: 3/619–leak number /mining level; Cl^-/Br^-–weight ratio; rNa^+/Cl^-–miliequivalent ratio.

Difference between measurement series was mainly marked in the concentrations of subordinate and trace components (such as Li^+, Ba^{2+}, Sr^{2+} or I^- ions). Large differences in ion concentrations during two measurement series were marked in the case of HCO_3^- ion, as well as nitrogen compounds (Table 3). Of the mineral nitrogen compounds, the NO_3^- ion dominated in water phenomena, alternating with the NH_4^+ ion, whereas the NO_2^- ion, as a transitional form in the transformation of nitrogen, was characterized by low concentrations (brines 3/619 and 12/525) (Table 3). In the 15/600 water phenomenon, both forms: NH_4^+ and NO_3^- showed high concentrations (more than 1000 mg/L) in both measurement series (Table 3).

The values of $\delta^{18}O$ (H_2O) and δ^2H (H_2O) in the water phenomena ranged from −8.47‰ to +8.41‰ and from −81.40‰ to −0.80‰, respectively, and were characterized in each brine by varying degrees of variability, depending on the measurement series (Table 3). Water phenomena 15/600, 10/600 and 3/619 were marked by the largest delta differences, while 17/450 and 8/450 water phenomena were of slightly smaller differences (Table 3). In addition, for the previously mentioned 15/600, 10/600 and 3/619 water phenomena, the isotopic composition of oxygen was heavier during the first measurement series. Analysing the brines in terms of their main ion relative ratio, four types of water can be distinguished: Cl-Na-K (brines 3/610 and 16/600), Cl-Ca (brine 12/525), Cl-Mg (brine 17/450, 8/450, 15/600, 60/600) and a mixed chloride type with no dominant cation in the composition (water phenomenon 10/600) (Fig. 2A, Table 4 on the interleaf).

DISCUSSION

Chemical composition of brines

Comparing the types of water obtained from the results of chemical analyses (Table 4, Fig. 2A) with other results, e.g., in Vinograd and Porowski (2020), for groundwater taken from Devonian formations in Russia, they obtained types which were similar to Kłodawa brines (both Cl-Mg and Cl-Na). Also, similar types were obtained in the work of Taj and Aref (2015) for brines in the alluvial brine basin off the Red Sea coast. The type of water itself, however, as shown in the cited works, does not make it possible to unequivocally determine the origin of the groundwater, especially in the case of strong processes of mixing of different types of water, ion exchange, precipitation or dissolution of halite and gypsum, or dolomitization, commonly occurring in salt domes.

The concentrations of subordinate elements e.g., I^-, Sr^{2+}, Li^+, which are diagnostic elements in brine studies due to their common occurrence in evaporites, may also vary considerably. This depends mainly on the type of brines, such as brines associated with hydrocarbon deposits, brines of salt formations of different ages, or brines of salt lakes (e.g., Spencer 1987, Matray & Fontes 1990, Berner 2002). Moreover, the chemical composition of brines may differ between mines exploiting a deposit of the same age or even within a single mine (e.g., Winid 2003, d'Obryn et al. 2018). Frequently therefore, it is only the interrelationships between ions, expressed as hydrochemical indices, that allow a more detailed analysis and interpretation of the processes that transform the chemical composition of brines and make their origin difficult to determine. On the other hand, variations in the concentrations of nitrogen compounds, depending on their form of occurrence in water, may indicate various types of transformations (e.g., pH, solubility or redox potential changes), mainly influenced by bacteria (Macioszczyk 1987). They may also be an indicator of various types of pollution (mainly anthropogenic, related to mining). Their amount also depends on the presence of nitrogen in the salts and the amount of dissolved minerals of the salt bed (Winid 2003). However, taking into account the exploitation of rock salt in the Kłodawa Salt Mine, using explosives containing nitrogen compounds, their very high concentration in brines is probably a resultant of all the factors mentioned above. Sulfate reduction processes occurring under the influence of bacteria may have been responsible for the increase in HCO_3^- ion concentrations during the second series of measurements in water phenomena 17/450 and 12/525 (Macioszczyk 1987).

Isotopic composition of O and H in H_2O

The obtained $\delta^{18}O$ and δ^2H values group the analysed brines into three main genetic types: Zechstein brines, pre-Pleistocene infiltration waters, and Paleo-infiltration and mixed waters (Grabczak & Zuber 1983, Winid 2003).

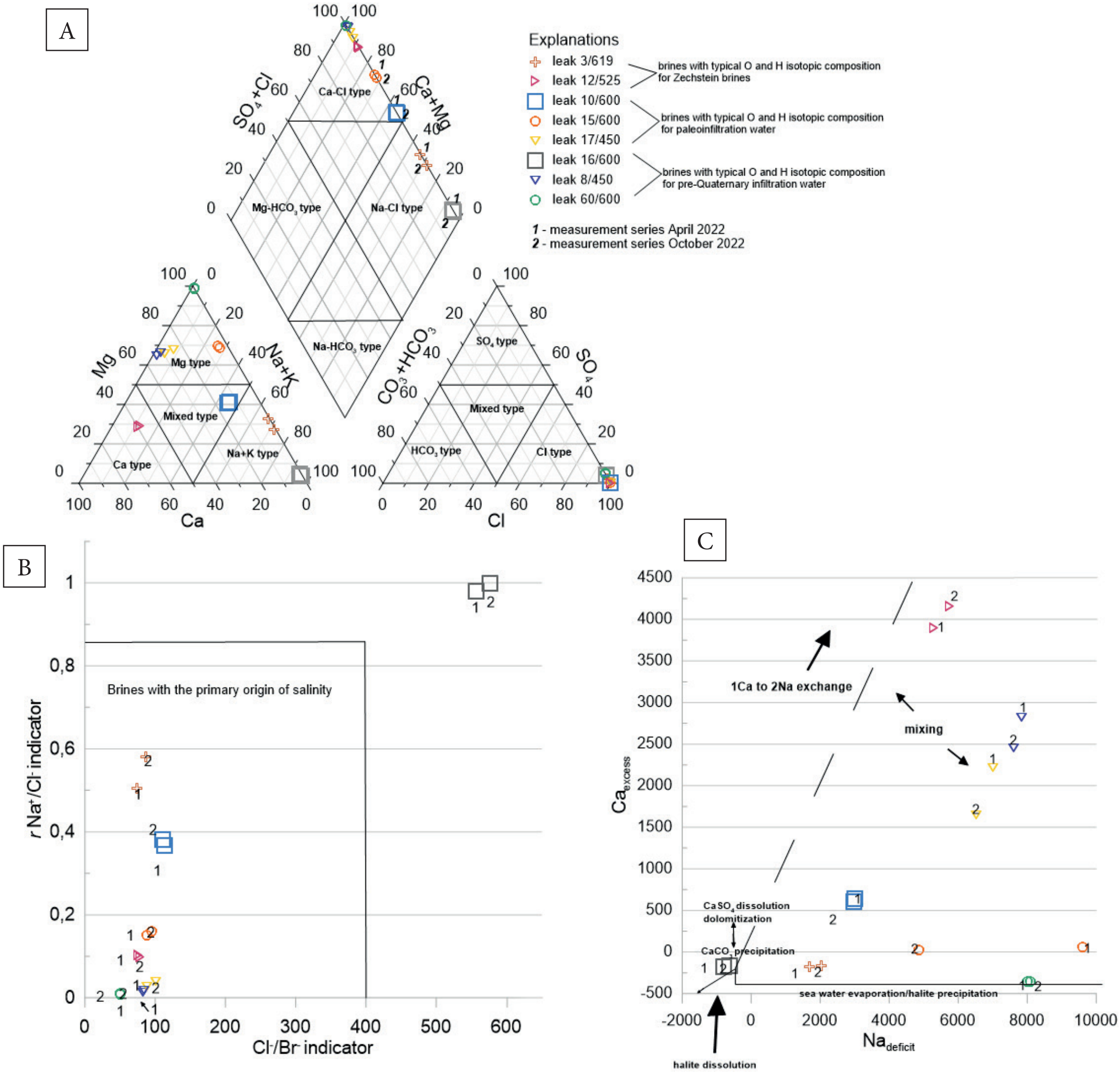

Fig. 2. Water types in the Piper diagram determined for brine samples from water phenomena 3/619, 16/600, 10/600, 8/450, 60/600, 15/600, 17/450 and 12/525 taken in 2022 (A); values of salinity origin indices Cl^-/Br^- and rNa^+/Cl^- calculated for brine samples from water phenomena 3/619, 16/600, 10/600, 8/450, 60/600, 15/600, 17/450 and 12/525 taken in 2022 (B); values of $Na_{deficit} - Ca_{excess}$ indices calculated for brine samples from water phenomena 3/619, 16/600, 10/600, 8/450, 60/600, 15/600, 17/450 and 12/525 taken in 2022 (based on Davisson & Criss 1996 – changed) (C)

Taking into account all the results of isotopic analyses of O and H in H_2O performed at the Kłodawa Salt Mine, brine 17/450 can be classified as Mesozoic water, while brines 10/600 and 15/600 are difficult to genetically classify mixed waters. Similar results were presented by Duliński et al. (2000). Brine 16/600 can be classified as pre-Quaternary infiltration water. In the Bochnia Salt Mine, in turn, a similar isotopic composition to the Kłodawa brine 17/450 was obtained for one of the water phenomena, interpreting it as Quaternary infiltration water (Duliński et al. 1998). Moldovanyi et al. (1993) obtained isotopic compositions similar to leakages 3/619 and 12/525 for waters of the Jurassic salt formation. Boschetti et al. (2020) obtained much heavier isotopic compositions for oilfield brines than in brine 12/525 (where bitumen was found – unpublished data). Additionally, based on isotopic studies of Permo-Triassic evaporite rocks of the eastern Alps and crystallization waters, Bojar et al. (2019) obtained values which were different from the Kłodawa brines. As shown in the above-mentioned studies, the O and H isotopic composition of brines undergoes large transformations, often under the influence of locally occurring processes (e.g., ultrafiltration, evaporation, H_2S exchange or different stages of rocks formation). That is why the interpretation of the results can be particularly difficult. The influence of the mine atmosphere on the degree of isotopic fractionation cannot be overlooked either. Horita (1989) also points out the methodological problems of performing oxygen and hydrogen analyses, mainly in brines rich in $MgCl_2$ and $CaCl_2$.

Hydrochemical indices

rNa^+/Cl^- and Cl^-/Br^- indices

All of the analysed water phenomena, with the exception of brine 16/600, were characterized by low values of both hydrochemical indices – *r*Na^+/Cl^- and Cl^-/Br^- (Table 4). This indicated the primeval origin of salinity (Table 2). They were also characterized by low difference between measurement series (Fig. 2B), with the highest in the case of brine 3/619. For the *r*Na^+/Cl^- index, the highest value was obtained in brine 16/600, but this is still equal to or close to 1, indicating a borderline value for the primeval nature of salinity (Macioszczyk 1987, Winid 2003). For all the brines studied, juxtaposing the two indices with each other, a trend of changing values along the Y axis (*r*Na^+/Cl^- index) is marked, i.e., an increase in the value of the *r*Na^+/Cl^- index, with little change in the Cl^-/Br^- index (Fig. 2B). This indicates rather processes associated with dissolution or precipitation of halite or other evaporite rocks. On the other hand, low values of the Cl^-/Br^- index suggest that the waters were subjected to evaporation and compaction, and acquired bromine from diagenesis of sedimentary organic sediments (Edmunds 1996). Studies done by other researchers indicate that the values of these two indices in Kłodawa brines are very similar to the results obtained for, among others, inclusions in halite from the Devonian Saskatchewan Formation in Canada (Horita et al. 1996), for inclusions in halite from Silurian formations in the Michigan Basin (Das et al. 1990) or for evaporites of the Paris Basin (Matray & Fontes 1990). Interestingly, the values presented in Kloppmann et al. (2001) obtained for brines of the Gorleben dome were much higher and similar to the values obtained for leakages in the Wieliczka Salt Mine (Winid 2003), which were characterized by secondary salinity associated with leaching of the deposit. The papers by Das et al. (1990), Horita et al. (1996) and Kovalevich et al. (1998), indicated the transformation of the chemical composition of brines of old sedimentary basins from SO_4^{2-} ion-rich with a small amount of Ca^{2+} ion, into Cl^- ion-rich with a large amount of Ca^{2+} ion, through the action of local factors related to water-rock interaction, sulphate reduction, dolomitization or hydrothermal processes, among others. In the case of the study of inclusions in Zechstein rocks, the occurrence of a high range of lithium concentrations was marked, which was also high in the Kłodawa brines 17/450, 3/619, 8/450, 12/525 and 60/600 (Table 3). Similar concentrations were observed in evaporite cyclothemic rocks in the Polish Lowlands, including those of the Kłodawa dome (Czapowski et al. 2022), as well as in salt lyes from the Gorleben dome (Schramm et al. 2009, Mertineit & Schramm 2019).

$Na_{deficit}$ and Ca_{excess} relationship

In their study, Davisson and Criss (1996) obtained the same $Na_{deficit}$ and Ca_{excess} values for inclusions in halite as the values calculated for the Kłodawa brines. Here, the 17/450, 8/450 and 12/525 brines differed from the rest of the analysed water phenomena and had different isotopic compositions (Table 3). They were characterized by changes in values along the Y axis (Ca_{excess}) and difference between series in these values, indicating mixing of different types of water or ion exchange processes (Fig. 2C). The 15/600 brine was characterized by the greatest values differences. However, it ran along the X axis ($Na_{deficit}$), indicating mixing of different types of water. This may indicate an inflow of water of different chemical composition, thus the existence of hydraulic connection with another extraction level cannot be excluded. A large change in the oxygen isotopic ratio of nearly 4‰ $\delta^{18}O$ (H_2O) is also marked in this water phenomenon (Table 3). Similar isotopic changes were marked in the 10/600 brine. In both brines, the dominant process was the mixing of different types of water. At the same time, the 10/600 water phenomenon was characterized by a lower degree of intensity of these processes than the 15/600 brine. In contrast, the 12/525 water phenomenon showed a variation in values. This was also the only leakage with a chemical type defined as Cl-Ca. Brine 16/600, on the other hand, was the only one to represent the NaCl dissolution process. Brines from 3/619 and 60/600 measurement points were dominated by seawater evaporation or halite precipitation processes in the formation of the chemical composition, where the inflow of another type of water cannot be excluded either (the values are very close to the mixing line) (Fig. 2C).

($rSO_4^{2-} \cdot 100$)/rCl^- index

Against almost all water phenomena in 2022, the ($rSO_4^{2-} \cdot 100$)/rCl^- index was characterized by little difference between measurement series (Fig. 3, Table 4). Reducing conditions were present in brines 10/600, 12/525, 17/450, 15/600 and 8/450. Brines from water phenomena 3/619, 16/600 and 60/600 demonstrated index values characteristic of oxidizing conditions. Juxtaposing it with the concentration of Cl^- ions marked their very high difference between series in water phenomenon 15/600 (Fig. 3). Brines of an oxidizing nature are located below or close to the mixing line in Figure 2C, and the large decrease in Cl^- ion concentration in the 15/600 water phenomenon, with no change in redox conditions, indicates precipitation of NaCl. Considering the previously determined indices and the isotopic composition of O and H in the brines, several sources or processes (e.g., precipitation or dissolution of sulphate minerals, redox processes) for supplying SO_4^{2-} ions to the brines should be considered.

Ca^{2+}/Sr^{2+}, Cl^-/I^-, Br^-/I^- and Br^-/Li^+ indices

The values of the Ca^{2+}/Sr^{2+} index were characterized by variability (Table 4). In brines from water phenomena 3/619, 17/450, 8/450 and 12/525, they exceeded 33. For the remaining brines, their value was below 33 (Fig. 4A), which may indicate a genetic link to seawater (Table 2). Considering the contribution of the Ca^{2+} ion in the delivery

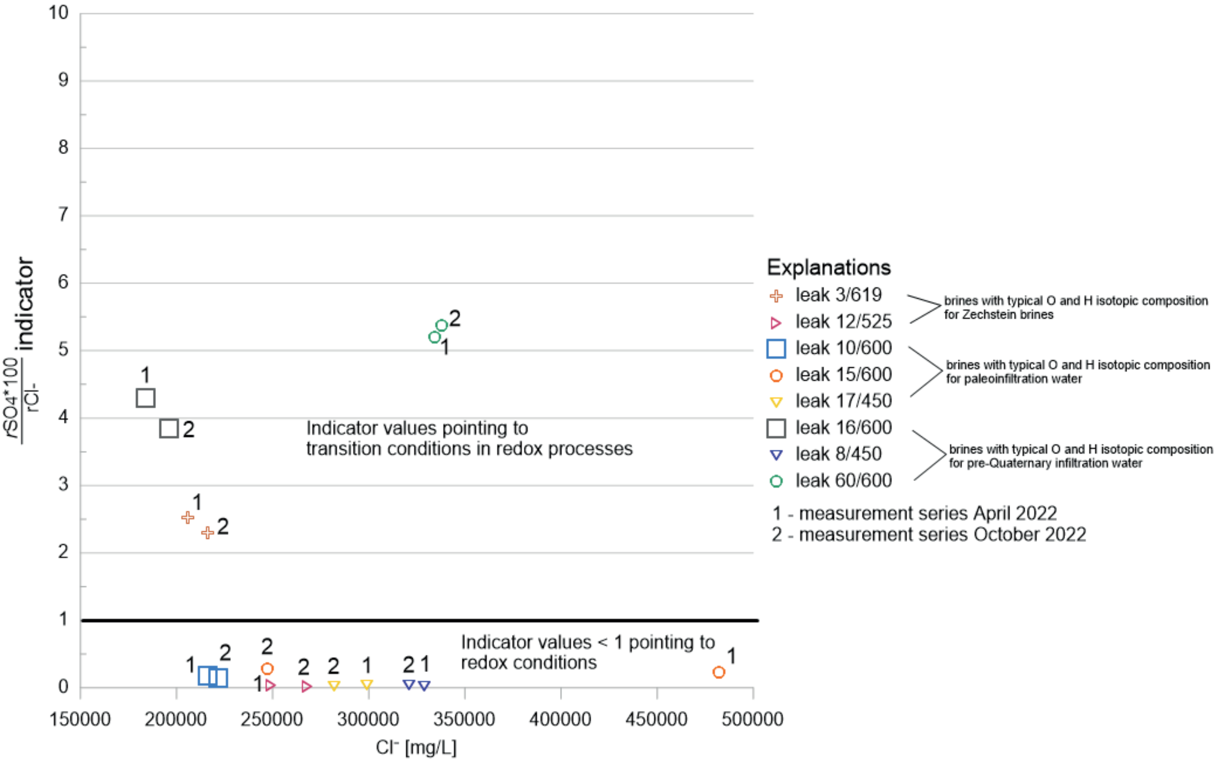

***Fig. 3.** Dependence of the sulphate index value on the concentration of Cl^- ion in brine samples from water phenomena 3/619, 16/600, 10/600, 8/450, 60/600, 15/600, 17/450 and 12/525 taken in 2022*

of Sr^{2+} ion to the waters, two groups of brines are marked: 12/525, 8/450 and 17/450, which were clearly enriched in Sr^{2+} and Ca^{2+} ions, and 16/600, 10/600, 60/600 and 15/600, which were depleted in both ions. The exception is brine 3/619, which deviates from the other points, but the concentrations of Ca^{2+} and Sr^{2+} ions were relatively low in its water (Table 3). The values obtained for brines 12/525, 17/450 and 8/450 in Figure 2C are similar, where the process of mixing of different types of water and dissolution of minerals may have a key influence on the high concentrations of Sr^{2+} ion in these waters.

In the Kłodawa brines, the I^- ion occurred in low concentrations, reaching up to 3.6 mg/L, making the Cl^-/I^- and Br^-/I indices take on very high values. Their highest values were recorded for brines 3/619, 12/525 and 10/600, with 12/525 marked by a large difference between series associated with an increase in Cl^- ion concentration (Fig. 4B, Table 3). Such high values rule out a fossil origin of these water phenomena and the presence of bitumen, contradicting previous conclusions about brines 12/525 and 3/619. In contrast, in the other water phenomena, the values were lower and indicate a fossil or mixed origin of these brines (Fig. 4B).

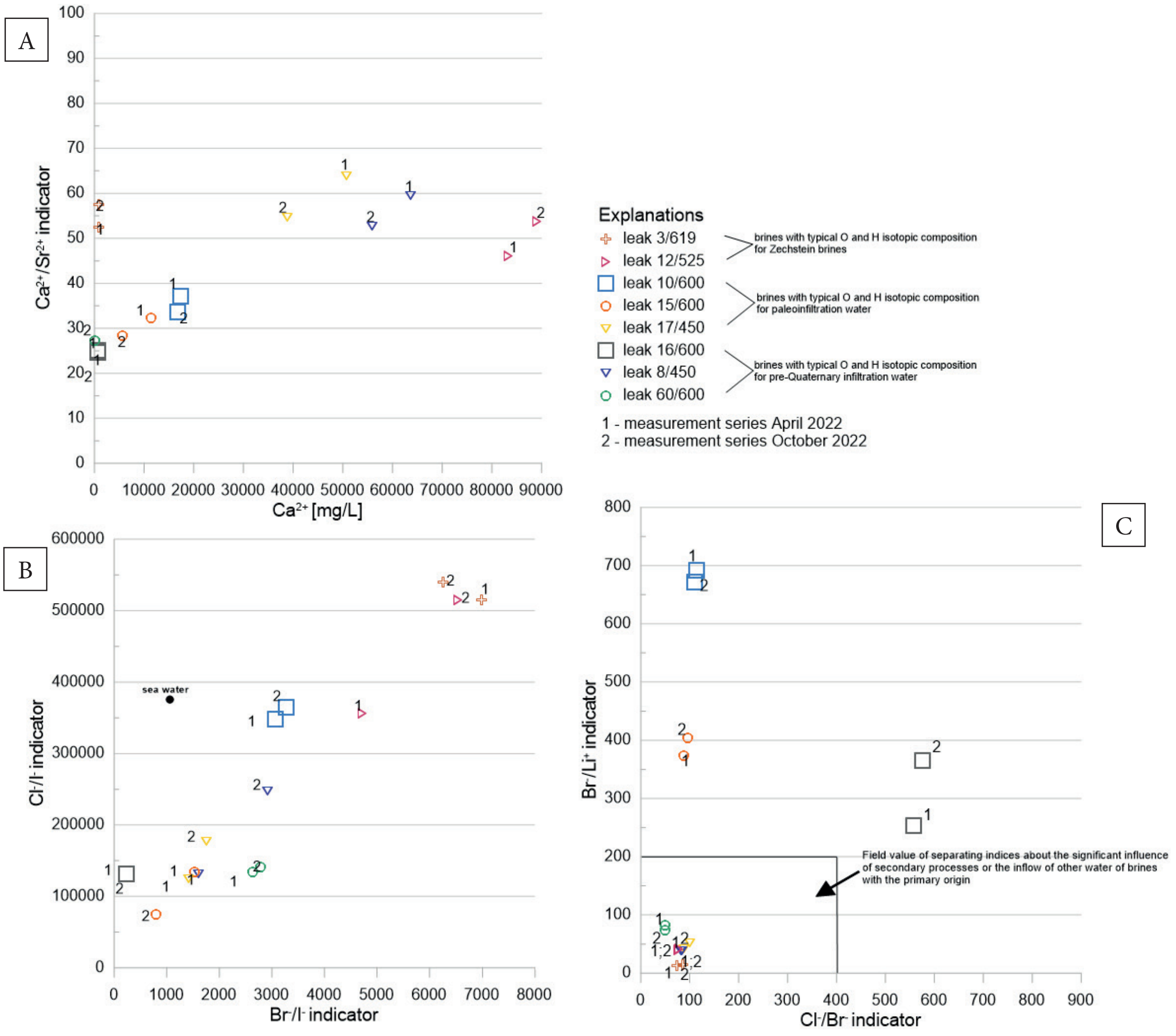

Fig. 4. *Dependence of Ca^{2+} ion content on Ca^{2+}/Sr^{2+} ratio values in brine samples from water phenomena 3/619, 16/600, 10/600, 8/450, 60/600, 15/600, 17/450 and 12/525 collected in 2022 (A); Cl^-/I^- and Br^-/I^- indices values calculated for brine samples from water phenomena 3/619, 16/600, 10/600, 8/450, 60/600, 15/600, 17/450 and 12/525 taken in 2022 (B); values of Cl^-/Br^- and Br^-/Li^+ indices calculated for brine samples from water phenomena 3/619, 16/600, 10/600, 8/450, 60/600, 15/600, 17/450 and 12/525 taken in 2022 (C)*

Considering previous conclusions and the isotopic composition of O and H in the brines, the values of these indices should give opposite results.

Lithium reaches its highest concentrations in fossil calcium brines and in the vicinity of oil deposits (Macioszczyk 1987). In the Kłodawa salt dome brines, its concentration varied. It reached the highest concentration (207 mg/L) in water phenomenon 3/619 and the lowest (0.93 mg/L) in 16/600 (Table 3), which may indirectly indicate the origin of these waters. The brines associated with the deposit, circulating in the bitumen environment, or circulating in the deposit for a long time and undergoing transformation (17/450, 8/450, 60/600, 12/525, 3/619), showed concentrations of Li^+ ion much higher than brines 16/600, 10/600, 15/600, which are probably younger waters, subject to processes of mixing of different types of waters, or inflowing from outside the dome. On the other hand, the relationship between the Br^- ion and the Li^+ ion (Fig. 4C) may be helpful in distinguishing the components of secondary inflows in leakages, which would confirm the secondary origin of brine 16/600 and the influence of younger waters in brines 10/600 and 15/600, or even in distinguishing salinity in shallow, less saline waters. In terms of abundance, this is not a significant tested relationship, but it may prove helpful in further studies or interpretations.

CONCLUSIONS

The study of hydrochemical indices made it possible to indicate the main processes forming the chemical composition of the analysed brines, and together with isotopic studies allowed for identification of their possible origin. Water phenomena 12/525 and 3/619 identified as Zechstein brines showed the primeval origin of salinity. They differed, however, in terms of the content of other chemical components and the values of hydrochemical indices. Water phenomena 17/450, 10/600 and 15/600 with isotopic compositions indicative of paleo- and mixed infiltration origin were characterized by primeval origins of salinity, reductive conditions and a dominant mixing process affecting their chemical composition. This process may have caused them to differ significantly in the values of other indicators, however. On the other hand, brines 8/450, 60/600 and 16/600, with isotopic compositions indicating a younger origin (pre-Pleistocene infiltration), were characterized by a primeval or mixed origins of salinity and showed high variability in other indicators.

Chemical and isotopic analyses conducted for brines indicated a broad variation of the results. Selected hydrochemical indices indicated the mainly primeval nature of salinity in the analysed waters. The dominant processes that influenced the chemical transformations were precipitation and dissolution of halite and sulphate minerals, redox processes and, to a lesser extent, water mixing or ion exchange. The chemistry of brines was also marked by the influence of rock inclusions.

Despite the wide range of chemical determinations, not all of them gave a clear picture of the origin of the brines in question and the hydrochemical processes that affect the obtained results of analyses. The hydrochemical indicators Br^-/I^-, Ca^{2+}/Sr^{2+}, Cl^-/I^- proved to be unhelpful in assessing the origin of the brines due to the varying values in each of the water phenomena, without being able to relate them to other conclusions drawn from other markers. This may be influenced by the degree of transformation of the chemistry of brines that circulate in the deposit and undergo secondary processes as well as mixing. It could also be influenced by some other process so far unidentified in the Kłodawa brines. In addition, the sulphate index indicated that there are several processes of supplying the SO_4^{2-} ion to brines. The obtained results indicate that detailed chemical studies enable the characterization of selected brines circulating in the deposit. Due to the use of universal analyses and interpretation tools, the conclusions drawn from the studies can also be used in other salt mines and beyond. They also show that in order to explore the obtained results and expand the state of knowledge about the processes affecting the chemistry of brines, it will be valuable to perform analyses of isotope ratios which can also improve the determination of water hazards.

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