The origin and chemical composition of Carpathians chloride CO_2-rich waters in the light of stable chlorine isotope studies (^{37}Cl and ^{35}Cl)

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Investigations into chloride CO_2-rich water occurring in the Polish and Slovakian Carpathians were carried out to gain a better understanding of the Cl$^-$ sources. The primary Cl$^-$ concentration in sea water, processes accompanying diagenesis, together with water-rock-gas interactions, have undoubtedly influenced the present content of chlorides. The Cl$^-$- concentrations in the waters analysed vary from 35.5 to 4148.3 mg/l, lower than in sea water, with a mean ~19000 mg/l. The measured δ^{37}Cl values range from –1.15 to –0.26‰, below the typical sea water value of 0‰. It might be concluded that the chemical and isotopic composition of these waters are the result of reactions during diagenesis (e.g., ion exchange or diffusion through low-permeability clay layers) as well as meteoric water influx.

Key words: Carpathians, chloride CO_2-rich water, chlorine isotopes, chemical composition, origin.

INTRODUCTION

The Carpathians CO_2-rich waters can be divided into two genetic groups: common CO_2-rich waters and chloride CO_2-rich waters. The common CO_2-rich waters are generally fresh groundwaters derived from relatively recent rainfall, while the chloride CO_2-rich waters are more highly mineralized because their residence time in bedrock is much longer (Świdziński, 1972). Our attention was drawn to the origin of chloride CO_2-rich waters that contain Cl$^-$ >20% meq and occur within the Outer Carpathians in the Magura Unit.

Carbon dioxide, both gaseous and dissolved, is one of the main components of CO_2-rich waters and significantly affects their properties. The carbon dioxide is generated in the subduction zone and then migrates upwards along deep-reaching faults (Rajchel, 2012) and mixes with diagenetically modified sea water (diagenetic waters). The waters saturated with CO_2 dissolve minerals from the rocks and as a consequence their salinity increases.

The important question in determining the chloride- and CO_2-rich waters' origin is ascertaining whether the currently increased content of many elements, including the chloride ion, was primary (derived from the primary sea water) or has been altered by secondary processes. That is a relatively difficult task, because the chemical composition of primary sea water has been transformed for many years as a result of chemical interactions between water and rock.

This article is especially devoted to the use of Cl isotopes as a tool for understanding the chloride ion origin in water. Importantly, measurements of the ^{37}Cl/^{35}Cl ratio have been applied for the first time to the Carpathians CO_2-rich waters. Stable chlorine isotope analyses, in conjunction with other geochemical parameters, are a useful tool for identifying the source of chlorine that can have surface origin or might be derived from the mantle.

GEOLOGICAL SETTING AND HYDROGEOLOGICAL CONDITIONS

The study area covers the Polish-Slovakian border zone. The Polish sector is located within the Małopolska province, in the southern part of the Nowy Sącz district and in the southwestern part of the Gorlice district. The area on the Slovak side belongs to the Bardejov province, Prešov district.

The research area is located within the Outer Carpathians that comprise a strongly deformed accretionary wedge composed of several nappes thrusted over the Miocene of the Carpathian Foredeep (Oszczypko, 1997). The water outflows

studied occur within the Magura Unit (Fig. 1) where four sub-units have been distinguished, namely (to the north): Krynica, Sącz, Gorlice and Siary. The first three subunits extend into Slovakia, where they are termed the Kochanovska (Udavska, Cerhovska or Białokarpatska), Bystrzyca and Rača subunits respectively. The Magura Unit consists of flysch strata, generally sandstone and shale successions of different thickness, covering the time span from the Late Jurassic to the Miocene. These rocks are locally accompanied by limestones, dolomites and marls as well as siliciclastic rocks (Oszczypko, 1992, 1999).

The research area is characterized by a complicated geological structure with complex hydrogeological conditions. The flysch strata are folded into synclines and anticlines and cut by deep faults e.g. Krynica Fault, Wysowa Fault, Malcov Fault. The faults enable endogenous carbon dioxide transport, which saturates the groundwaters, changing their physicochemical properties (Rajchel, 2012).

From the hydrogeological point of view, fissures play the most important role in the circulation of groundwater. In fine and medium-grained sandstones, the cracks are regular, and parallel or perpendicular to rock layers, while in thick-bedded sandstones fissures are irregular. The fissure coefficient is 1–2% for shales and 2–5% for sandstones. The flysch strata are characterized by low water-bearing capacity with low water permeability. The hydraulic conductivity values, calculated on the basis of pumping tests, are between 1×10^{-6} m/s and 1×10^{-5} m/s (Małecka et al., 2007). All mineral waters analysed are associated with the flysch aquifer. However, aquifers located in the Outer Carpathians are not clearly delimited, so the mineral waters from the flysch aquifer can mix with meteoric groundwaters from the Quaternary aquifer (Chowaniec, 1991).

Based on the regionalization of mineral and therapeutic waters by Paczyński and Płochniewski (1996), the waters investigated occur within the Carpathian province, the Outer Carpathian region and the Poprad subregion. However, according to the regionalization of Polish CO_2-rich waters (Rajchel, 2012), they are located within the Poprad Valley region (areas: Krynica, Zubrzyk and Żegiestów) and the Wysowa region.

METHODS

All the water samples used in this study were collected in July 2015. The samples were taken from 11 boreholes located in well-known spa villages such as Krynica (Zuber I and Zuber III), Wysowa (Słone, Aleksandra, Henryk, W-12), Zubrzyk (Z-3*), Żegiestów (Zofia II), Cigel'ka (CH-1) and Bardejovské Kupele (Alžbeta and Napoleon).

Unstable parameters such as temperature, pH, electrolytic conductivity and redox potential, as well as free CO_2 content, were measured in the field using a WTW™ pH 340/ION device. Alkalinity was determined by titration using a solution of 10% HCl and methyl orange as indicator. The physicochemical analyses were done at the hydrogeochemical laboratory of the Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology in Kraków. The measurements were carried out using a *Perkin Elmer ELAN 6100* inductively induced plasma mass spectrometer (ICP-MS) and Perkin Elmer Plasm 40 inductively coupled plasma spectrophotometer (ICP-OES). The hydrogeochemical types of water were specified in accordance with the Szczukariew-Prikłoński classification, which takes into account ions with a concentration >20% meq as well as specific components occur-
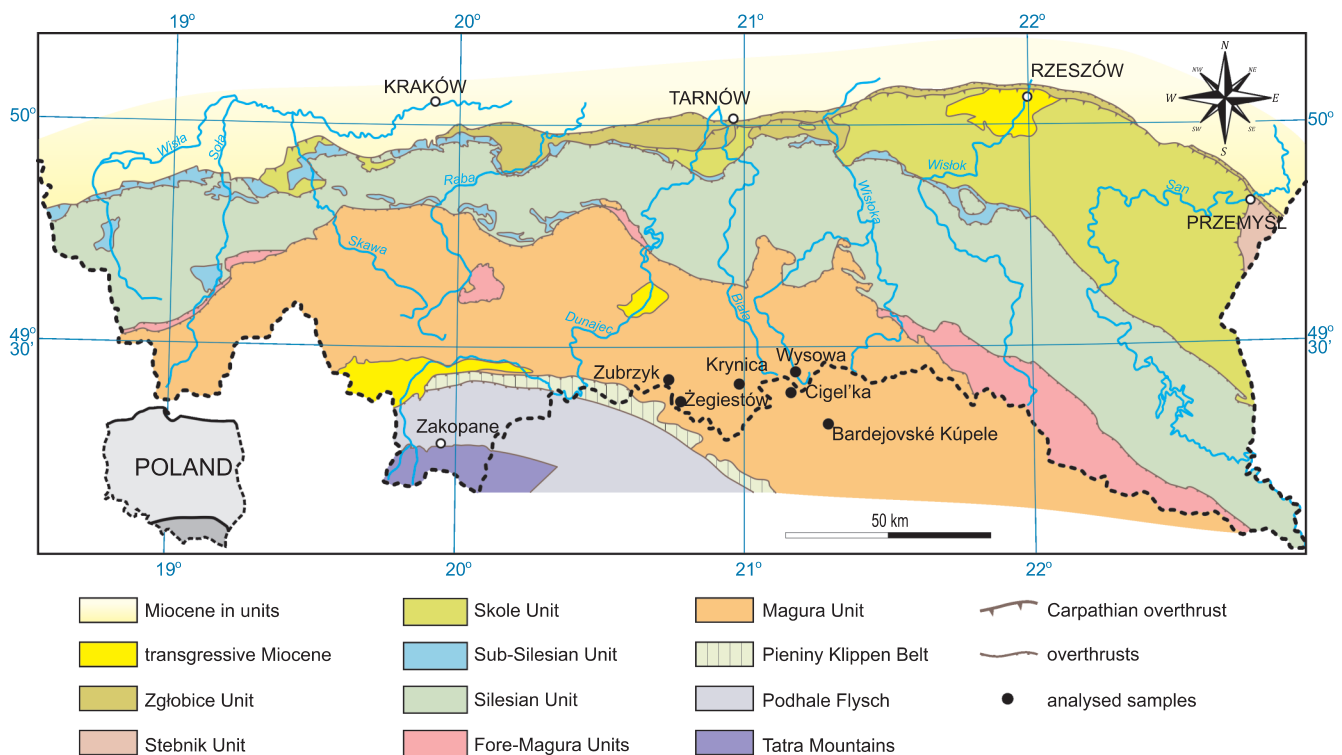

Fig. 1. Location of the sampling points on the geological map of the Carpathians
(Oszczypko et al., 2008, modified)

ring in the groundwaters. Some hydrochemical coefficients such as $r\dfrac{Na^+}{Cl^-}$ and $\dfrac{Cl^-}{Br^-}$ were also applied to add physico-chemical detail.

The chlorine stable isotope analyses were done at the Mass Spectrometry Department, Institute of Physics of the Maria Curie-Skłodowska University in Lublin. The $^{37}Cl/^{35}Cl$ isotope ratio in a given sample (R_{sample}) was measured in relation to the Standard Mean Ocean Chlorine (R_{SMOC}), as follows:

$$Cl = \frac{R_{sample} - R_{SMOC}}{R_{SMOC}} \cdot 1000$$

where: $\delta^{37}Cl$ in ‰.

The chlorine isotope analyses was done by applying the most common method used in chlorine isotope ratio analysis which employs the conversion of a chlorine sample to chloromethane (CH_3Cl) prior to the mass spectrometric analysis. Chloromethane is very convenient for mass spectrometry as it has no memory effect in vacuum systems and additionally could be easily obtained from a chlorine sample and transferred from the preparation line to the inlet system of a mass spectrometer since its melting point is –97.7°C.

In chloromethane preparation, the following three steps are applied (Long et al., 1993; Eggenkamp et al., 1995; Eggenkamp, 2004):
– precipitation of silver chlorine,
– reaction of silver chlorine with iodomethane,
– cryogenic separation of chloromethane from iodomethane.

In the first step, to the 10 ml amount of natural sample (solution of chlorine), 4 ml of a 1M solution of KNO_3 and 2 ml of Na_2HPO_4 – a citric acid buffer solution – were added. These substances are added to reach a high ionic strength and to attain of low pH of 2.2, which results in the formation of small AgCl crystals and prevents the precipitation of unwanted salts (e.g., phosphates), respectively. The solution obtained is then heated to ~80°C. In the next step, 1 ml of a 0.2 M AgNO$_3$ solution is added to the warmed solution and AgCl starts precipitating instantaneously. The precipitated silver chlorine is then filtered over a glass fibre filter and dried for a day at 80°C. The filter with AgCl is loaded into an ampoule with a teflon stopcock (Hałas and Pelc, 2009).

The ampoule with the sample is attached to the preparation line and evacuated from air. Then 200 ml iodomethane is cryogenically transferred into the ampoule and frozen. In the next step the ampoule is pumped down following disconnection from the vacuum line. Then ampoule is placed in an oven at 75°C for 48 hours. In the oven, an exchange reaction between the iodomethane (CH_3I) and silver chlorine takes place. This reaction requires at least a 10-fold molar excess of CH_3I to AgCl, which results in a difficult purification procedure of the CH_3Cl obtained from the residual CH_3I due to the similarity in their physical properties. In our case the cryogenic separation/purification method of chloromethane is used. The ampoule with the mixture of CH_3Cl and CH_3I is then again connected to the preparation line. The chloromethane obtained is cryogenically separated from the iodomethane using three traps (one with butyl acetate and two with trimethylpentane). At the end of this procedure the pure chloromethane is transferred to another ampoule which is then connected to the inlet system of the mass spectrometer (Hałas and Pelc, 2009).

The mass spectrometer measures the chlorine isotope ratio. In the analysis of $\delta^{37}Cl$ a negative ion mass spectrometer, which retains all the best features of IRMS, including a dual inlet system with changeover valve, dual collector assembly and CH_3Cl gas as analyse, was used. In the modified ion source only $^{35}Cl^-$ and $^{37}Cl^-$ ions are produced and their ion currents are measured and used for the $\delta^{37}Cl$ determination. The method's precision is better than 0.01‰ (Pelc and Hałas, 2008; Hałas and Pelc, 2009).

RESULTS

The hydrogeochemical studies indicate that the waters investigated can be classified as chloride CO$_2$-rich waters. This means that the amount of free CO$_2$ is >1000 mg/l and Cl$^-$ concentration should be >20% meq. However, despite the fact that some of the waters analysed do not contain Cl$^-$ in amounts of >20% meq they still can be considered as chloride CO$_2$-rich waters. That is because the primary, easily soluble chlorine compounds have been leached as a result of meteoric water influx.

The waters investigated show a wide range of mineralisation, ranging from 1722.2 to 28535.6 mg/l (Table 1). They differ in free CO$_2$ concentration, which varies from 1501 to 3437 mg/l and Cl$^-$ concentration which ranges from 35.5 to 4148.3 mg/l (Table 1). The hydrogeochemical types of chloride CO$_2$-rich waters examined change from HCO$_3$-Cl-Na, through HCO$_3$-Cl-Na-Ca and HCO$_3$-Na-(Mg)-(Ca), to HCO$_3$-Na (Fig. 2). However, the prevailing waters are of HCO$_3$-Cl-Na and HCO$_3$-Na type that show the highest salinities. Besides the mineralisation and free CO$_2$, specific components such as iodine and ferrous ion are present in some waters. The content of iodine exceeds the minimum threshold for therapeutic waters (1 mg/l) in waters from five boreholes (in ascending order): Władysław, CH-1, Napoleon, Alžbeta and Aleksandra, while ferrous ion concentrations exceeding 10 g/l were recorded in waters from the following five intakes (in ascending order): Władysław, Słone, Napoleon, Aleksandra and Alžbeta.

Based on the analyses, the water from the CH-1 borehole in Cigel'ka has the highest mineralisation, reaching 28.5 g/dm^3 and its hydrogeochemical type was determined as HCO$_3$-Cl-Na+CO$_2$+I. In terms of mineralisation, next are waters from the Aleksandra well in Wysowa, rising to 24.3 g/l and classified as HCO$_3$-Cl-Na+CO$_2$+I+ Fe. The CO$_2$-rich waters from the Zuber I and Zuber III boreholes in Krynica have similar mineralisations, respectively 23.1 and 24.4 g/l, and they represent a HCO$_3$-Na+CO$_2$ water type. A similar water type, though enriched with magnesium ions and less saline, reaching 11.5 g/l, was encountered in the Z-3* borehole in Zubrzyk. In the Zofia II well in Żegiestów the HCO$_3$-Na-Mg-Ca+CO$_2$ water type was found with mineralisation of ~4.5 g/l. The mineralisation of waters from the Henryk and Władysław boreholes in Wysowa reach 3.6 and 4.4 g/l and their water type is HCO$_3$-Cl-Na-CO$_2$ and HCO$_3$-Cl-Na-Ca+CO$_2$+I+Fe, respectively. The waters sampled from Bardejovske Kupele, that is Alžbeta and Napoleon, were defined as HCO$_3$-Cl-Na+CO$_2$+ I+Fe and their mineralisation is 3.9 and 3.5 g/l, respectively. The lowest value of mineralisation, reported in Słone water from Wysowa, reaches 1.7 g/l and was defined as of HCO$_3$-Na-Ca+CO$_2$+Fe type (Table 1)

The $\dfrac{Cl^-}{Br^-}$ ratio and molar ratio of Na$^+$ to Cl$^-$ ($r\dfrac{Na^+}{Cl^-}$) were used to identify the origin of salinity in the waters investigated. It was observed that the $\dfrac{Cl^-}{Br^-}$ ratio in all waters analysed is lower than in sea water (Table 2). The highest ($r\dfrac{Na^+}{Cl^-}$) r values were

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Chemical composition of the waters analysed

Location	Cigel'ka	Bardejovske Kupele		Krynica		Żegiestów	Wysowa				Zubrzyk
Borehole	CH-1	Napoleon	Alžbeta	Zuber I	Zuber III	Zofia II	Słone	Henryk	Aleksandra	W-12	Z-3*
Depth [m]	202.5	330.4	329.1	810	935.7	60.6	16.5	50	100	40	60
pH	7.32	5.71	5.74	7.22	7.02	6.06	5.96	6.27	6.91	6.29	6.75
T [°C]	10.50	19.30	19.20	9.50	10.40	9.60	10.83	10.40	9.38	10.15	10.10
CO_2	1647	1986	1917	2146	1501	3437	2366	2217	1939	2552	2726
M	28525.6	3476.3	3926.0	23094.4	24425.1	4504.9	1726.2	3601.2	24338.0	4366.1	11518.6
Na+	8011.6	735.0	844.6	5662.7	6733.8	444.1	235.4	793.5	6606.5	903.7	2326.7
K+	155.70	21.01	23.51	196.31	308.00	21.10	13.57	21.16	128.81	15.82	37.47
Li+	12.10	1.61	1.83	20.48	27.69	1.83	0.45	1.19	10.83	1.26	3.71
Ca^{2+}	158.6	129.2	136.4	181.7	156.3	261.2	137.5	129.7	279.8	227.1	138.2
Mg^{2+}	75.3	32.8	32.6	410.5	246.7	219.2	42.1	37.2	30.3	67.2	420.9
Fe^{2+} [mg/l]	1.2	19.6	22.7	1.8	2.0	4.8	11.8	6.2	20.7	10.5	10.7
Cl^-	4148.3	312.0	345.8	686.3	1140.6	35.5	151.0	386.1	3618.5	499.5	98.7
Br^-	22.4	2.4	2.8	3.3	7.5	0.2	0.4	1.4	13.2	2.7	0.7
I^-	1.6	2.1	3.1	0.6	0.2	0.2	0.1	0.7	3.5	1.1	0.0
SO_4^{2-}	10.5	5.5	7.2	36.6	40.3	15.4	3.0	15.9	3.5	4.1	3.0
HCO_3^-	15298.8	2083.8	2363.1	15834.4	15701.0	3434.3	1075.9	2082.9	12732.5	2497.2	8357.0
HBO_2	604.25	98.44	110.44	14.31	14.26	6.17	32.41	113.33	868.79	118.70	45.17
H_2SiO_3	18.40	28.12	27.14	42.01	40.67	55.12	20.06	9.64	11.74	14.11	19.32

found in the chloride CO_2-rich waters from the following boreholes (in ascending order): Zofia II, Zuber I, Zuber III and Z-3*. The value calculated in the latter borehole is surprisingly high, reaching 36.4 (Table 2).

The measured $\delta^{37}Cl$ values in the CO_2-rich waters analysed extend from –1.15 to –0.26‰ (Table 2), so all water samples are depleted in the ^{37}Cl isotope with respect to the standard (sea water). As can be seen from the plot (Fig. 3), $\delta^{37}Cl$ values and borehole depths are weakly correlated. The regression line for the waters considered fulfills the equation:

$$\delta^{37}Cl = -0.0008CD - 0.4581$$

with correlation coefficient R5 = 0.49; D – depth [m]

DISCUSSION

The chloride CO_2-rich waters occurring in the area discussed are formed under the influence of various geomorphological, geological, hydrological and hydrogeological conditions. Based on physicochemical analyses, we observed that in all water samples the chlorine concentrations are lower than in sea water, which may be the result of diluting the diagenetic waters from the flysch strata by addition of meteoric waters. The presence of a non-meteoric component, in the form of diagenetic waters, can be also shown by r ratio. For all waters analysed, the r values are >1 (Table 2), which indicates an additional source of Na, that might proceed e.g. during the diagenesis of clay-rich deposits (Macioszczyk, 1987). The calculated ratios (Table 2) are lower than the values observed in sea water (~288). This may indicate that the rocks in which the waters analysed had been trapped, were compacted during diagenesis and bromine was released from organic-rich deposits or that evaporatic processes played an important role (Edmunds, 1996). The research showed that the waters investigated have a high content of dissolved solids and their chemical compositions reflect at least a two-component mixture of meteoric waters and diagenetic waters. Nonetheless, the processes noted above do not satisfactorily explain the high chlorine concentrations in the waters tested.

As reported by Leśniak (1980) a high chloride concentration may be the result of an additional component if metamorphic waters, apart from connate and meteoric waters, were involved in water mixing. According to that author, metamorphic water is a pure H_2O solvent derived from OH^- structural groups in clay minerals undergoing dehydration (White et al., 1973). Trying to solve the problem of chlorine ion origin, Dowgiałło (1980) proposed another mixing model. In his concept, the Cl^- contents are inferred to result from connate waters, high-temperature dehydration waters and meteoric waters. However, Oszczypko and Zuber (2002) ruled out the existence of a metamorphic component, while they indicated the non-meteoric genesis of the Cl^- ion and its high concentrations were explained via diagenetic processes. Alternative hypothesis for the origin of the chlorides in the CO_2-rich waters in Cigel'ka include inflow of water originating from the basement of the Magura Unit (Bačova et al., 2009).
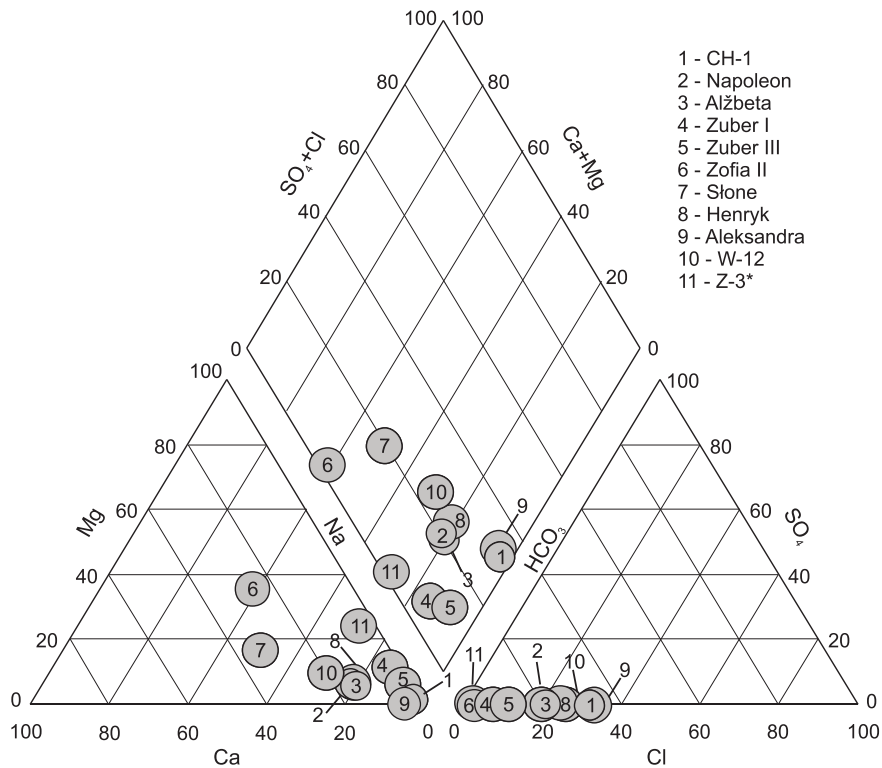
Fig. 2. Piper diagram of the waters investigated

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Hydrogeochemical coefficient values and the results of chlorine isotope analyses

Location	Borehole	Hydrogeochemical type of water (without specific components)	$\frac{Cl^-}{Br^-}$	$(r\frac{Na^+}{Cl^-})$	$\delta^{37}Cl$ [‰]
Cigel'ka	CH-1	HCO₃-Cl-Na	185.1	3.0	−0.51 ±0.01
Bardejovske Kupele	Napoleon	HCO₃-Cl-Na	128.8	3.6	−0.56 ±0.01
	Alžbeta	HCO₃-Cl-Na	124.7	3.8	−1.06 ±0.01
Krynica	Zuber I	HCO₃-Na	205.9	12.7	−1.14 ±0.01
	Zuber III	HCO₃-Na	151.3	9.1	−1.15 ±0.03
Żegiestów	Zofia II	HCO₃-Na-Mg-Ca	143.1	19.4	−0.38 ±0.01
Wysowa	Słone	HCO₃-Na-Ca	337.0	2.5	−0.28 ±0.02
	Henryk	HCO₃-Cl-Na	283.0	3.1	−0.66 ±0.01
	Aleksandra	HCO₃-Cl-Na	275.0	2.8	−0.27 ±0.01
	W-12	HCO₃-Cl-Na-Ca	185.1	2.8	−0.29 ±0.02
Zubrzyk	Z-3*	HCO₃-Na-Mg	150.7	36.4	−1.10 ±0.01
Sea water (standard)		Cl-Na	288	0.86	0.03 ±0.01
					0.02 ±0.01
					−0.02 ±0.01

The research carried out by these authors did not take into account the results of chlorine isotopic analyses as they based their interpretation on physicochemical and oxygen and hydrogen stable isotope analyses. The new data obtained from stable chlorine isotopes analyses reported in this paper allow us to constrain previous hypotheses concerning the origin of the chlorine ion in chloride CO₂-rich waters.

There are two stable chlorine isotopes in nature – ^{37}Cl and ^{35}Cl, which may separate as water flows through rocks. ^{37}Cl is preferentially incorporated over ^{35}Cl into the structure of clay minerals such as e.g. smectites and illites. Then, during diffusion processes through low-permeabilty clay layers, separation of ^{35}Cl and ^{37}Cl isotopes takes place. The lighter ^{35}Cl isotope is more mobile due to its lower atomic mass, and so the waters passing through a low-permeability barrier have lower $\delta^{37}Cl$ values, and are enriched in ^{35}Cl isotope, relative to the original brines from which they formed (Desaulniers et al., 1986; Lavastre et al., 2005).
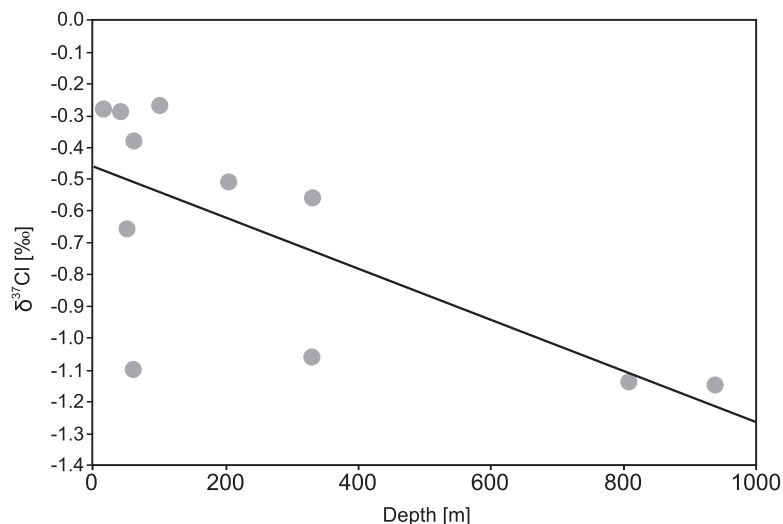
Fig. 3. Relationship between $\delta^{37}Cl$ and borehole depths

Based on its chlorine isotopic composition, we interpret the origin of the water with reference to the ranges of variability proposed by Hoefs (2009). Sea water chloride is isotopically homogeneous throughout the world (Godon et al., 2004) with a $\delta^{37}Cl$ value oscillating around ~0‰ (SMOC). Chlorine isotope variations in groundwater are rather small and usually vary from ~–2 to 2‰. while chlorine released in subduction processes shows the most negative $\delta^{37}Cl$ values from –2 to –7‰ (Fig. 4). Depletion in the ^{37}Cl isotope can also be the result of physical changes to the water e.g. from filtration, diffusion.

Since none of the water samples have been enriched in the ^{37}Cl isotope (Table 2), processes such as water evaporation and leaching of sediments containing chlorine compounds (e.g., NaCl deposits) can be excluded as a main source of chlorine in the waters under question. The negative $\delta^{37}Cl$ values indicate that either an external source of chloride or some isotopic fractionation mechanisms *in situ* played a significant role.

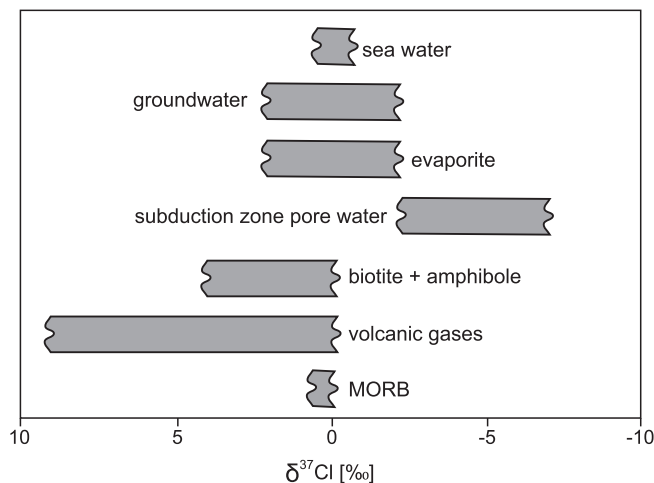Taking into account the relationship between $\delta^{37}Cl$ and mineralisation, it was noted that the CO_2-rich waters analysed cluster into two main groups (Fig. 5). The first group consists of CO_2-rich waters having $\delta^{37}Cl$ values ranging within –0.25 to –0.7‰. The waters with mineralisation <5 g/l were classified into subgroup 1a, while the most mineralized waters, coming from the Aleksandra borehole in Wysowa and the CH-1 borehole in Cigel'ka, belong to subgroup 1b. The second group is represented by samples taken from the Zuber I and Zuber III wells in Krynica, the Z-3* well in Zubrzyk and the Alžbeta well in Bardejovske Kupele, for which $\delta^{37}Cl$ are <–1‰.

It can be assumed that in CO_2-rich waters classified in group 1, in which $\delta^{37}Cl$ values are >–1‰ (Fig. 4 and Table 2), the main chlorine source is primary sea water, in which the chlorine isotopes have slightly fractionated as a result of processes accompanying diagenesis, namely sea water infiltration or diffusion through low-permeability clay layers.

Nonetheless, the waters from the Aleksandra and CH-1 wells may be distinguished from the other waters belonging to group 1. Based on their chemical and isotopic composition they are considered to be the closest to typical diagenetic waters. If we assume, that diagenetic processes are mainly responsible for the depletion of ^{37}Cl in the waters analysed, than the lowest $\delta^{37}Cl$ values will be expected in the CO_2-rich waters tapped from these two boreholes. On the other hand, the chlorine isotope analyses made do not support this hypothesis. Therefore, bearing in mind the Cl^- concentrations, some hydrochemical coefficient ratios and negative $\delta^{37}Cl$ values, it can be inferred that the high chloride ion values in the CO_2-rich waters from the CH-1 and Aleksandra wells may be the result of mixing between diagenetic waters, circulating within the Magura Basin, and brines originating from the rocks underlying the flysch strata, known for instance from the Zboj borehole (Marcin, 1999, 2002). Their hydraulic contact may be possible due to the presence of deep faults and the high pressure prevailing during diagenesis (Bačová et al., 2009).

At a depth of ~20 km, the flysch rocks may have descended only as subducted crust (Ney, 1975; Birkenmajer, 1986; Bojdys and Lemberger, 1986; Golonka et al., 2015). The salinity of subduction-zone fluids is 2 to 3 times diluted by comparison with sea water, so the chloride concentration is also lesser.
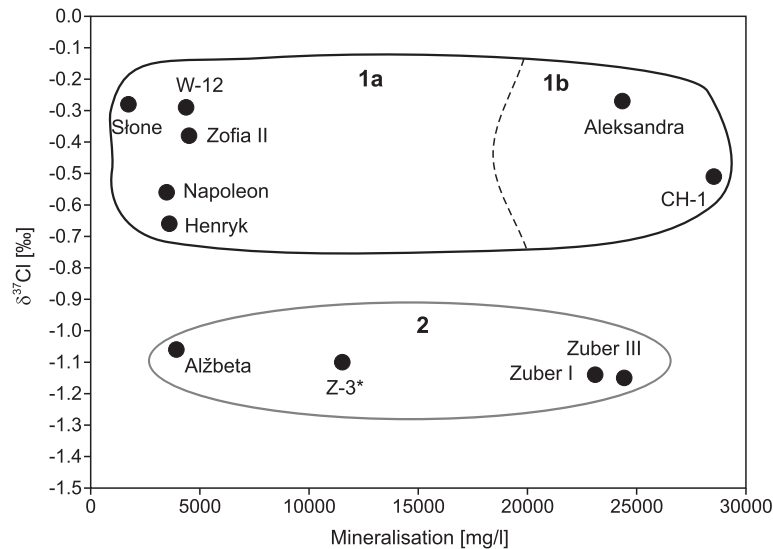

Fig. 4. $\delta^{37}Cl$ variations in various geological reservoirs (Hoefs, 2009)

Fig. 5. Relationship between δ^{37}Cl and mineralisation in the chloride CO$_2$-rich waters analysed

These fluids contain relatively low amounts of Mg, Fe and Al, while Ca silica and alkalis are the dominant solutes (Manning, 2004). Ransom et al. (1995, 1998) and Spivack et al. (2002) have already suggested that δ^{37}Cl values in groundwaters occurring near subduction zones vary from –0.9 to –7.8‰. Such negative values are the result of processes and reactions occurring in subduction zones under the influence of pressure and temperature. The subducting slab includes low-temperature, diagenetically formed, hydrous minerals, such as smectite or illite, enriched in ^{37}Cl, but containing low absolute concentrations. During subduction these minerals react to form higher temperature hydrous minerals (e.g., amphibole, chlorite, serpentine) with significantly higher Cl concentrations. Due to preferentially movement of ^{37}Cl into the solid phase, the solutions in subduction zone environments are depleted in this isotope (Ransom et al., 1998).

After dissolving in water, chlorine along with other gases generated in the subduction zone (e.g., CO$_2$), migrate upwards through networks of faults to areas of lower pressure and higher porosity (Alletti et al., 2009). As noted above, the research area is located near a subduction zone and abounds in tectonic discontinuities; chlorides formed in such subduction zones can mix with deeply circulating waters and subsequently with meteoric waters. Therefore, the chloride CO$_2$-rich waters encountered here, that are taken from different depths, have δ^{37}Cl values <–1‰ (Fig. 3).

In the light of the data presented, the authors presume that in the research area, especially in the waters where the lowest ^{37}Cl values were noted (Zuber I, Zuber III, Z-3*, Alžbeta), the chlorine ion origin might be partially associated with solutions formed in a subduction zone. This interpretation therefore is supported by the occurrence of subduction CO$_2$ present in the waters analysed (Rajchel, 2012). During its upward migration through fault networks, CO$_2$ can adsorb dissolved molecules also formed in subduction zones.

SUMMARY AND CONCLUSIONS

Explaining the processes that control chlorine ion genesis requires correlation of voluminous information – geological, hydrogeological and isotopic. This paper, based on ^{37}Cl/^{35}Cl ratio measurements and previous work, suggests that the chlorides in the waters analysed have different origins. Generally, the chloride CO$_2$-rich waters of the flysch strata of the Carpathians are regarded as a mixture of diagenetic and meteoric waters, so this allows the assumption that the processes accompanying diagenesis, e.g. ultrafiltration or ion exchange, may have caused primary marine waters to be depleted in the ^{37}Cl isotope. The measurements reported show negative δ^{37}Cl values for all waters tested waters. Taking into account the existence of a subduction zone in the bedrock underlying the flysch strata of the research area, we infer that one of possible factors behind such low δ^{37}Cl values, particularly those <–1‰, might be an influx of subduction-zone fluids.

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