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The origin of chloride waters at Wysowa, West Carpathians. Chemical and isotopic approach.

ABSTRACT: Investigation of chloride subsurface waters occurring in the Carpathian flysch suggests that they should be considered as a mixture of flysch sediments connate water, metamorphic water and meteoric water. Dissolved solids consist for the most part of sodium bicarbonate and sodium chloride which can be related to water-rock-carbon dioxide interaction and to the presence of the connate water respectively. High $^{18}O/^{16}O$, D/H ratios and probably high boron concentration are due to the presence of metamorphic water. Concentration of calcium, magnesium, strontium and probably other divalent metals as well as silica seems to be governed by mineralogical control, being in this case the form of buffering by solid carbonates. Alkaline metals fit rather perfectly the dilution pattern, though, it is modified by rock dissolution and other geochemical processes. The behaviour of halogens follows the trend of alkaline metals dilution. Slope 1, on the pH—pHCO$_3$ plot impose that the Wysowa mineral water system is open to the large reservoir of carbon dioxide of constant chemical potential (pCO_2=const).

INTRODUCTION

Several kinds of mineral water occur in flysch rocks of the Polish Carpathians, namely Cl-Na *, Cl-HCO$_3$-Na, HCO$_3$-Cl-Na and Cl-Na waters (Fig. 1). Their spatial distribution was mapped by Dowgiałło, Płochniewski, Szpakiewicz (1974). The dissolved solids content amounts up to 30 g/l. As far as stable isotopes of oxygen and hydrogen are concerned the $\delta^{18}O$ values vary between 6.7 per mille to -10 per mille and these of δD between -20 per mille and -70 per mille.

The origin of these waters and of their chemical composition as well as the origin of the gas phase CO$_2$ is still unclear, though considerable effort has been made to resolve this problem. (Świdziński 1965, Węcła-

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This paper is based on the author's Ph. D. thesis prepared at the Laboratory of Hydrogeology, Institute of Geological Sciences, Polish Academy of Sciences, Warszawa.

* Every ion mentioned in the formula contributes at least 20 per cent miliequivalents. Sum of cations or anions is taken as equal to 100 per cent.

wik 1967a,b, Kolago & Płochniewski 1971, Dowgiałło 1973, 1976, 1978, Cortecchi & Dowgiałło 1975, Dowgiałło & Sławiński 1978).

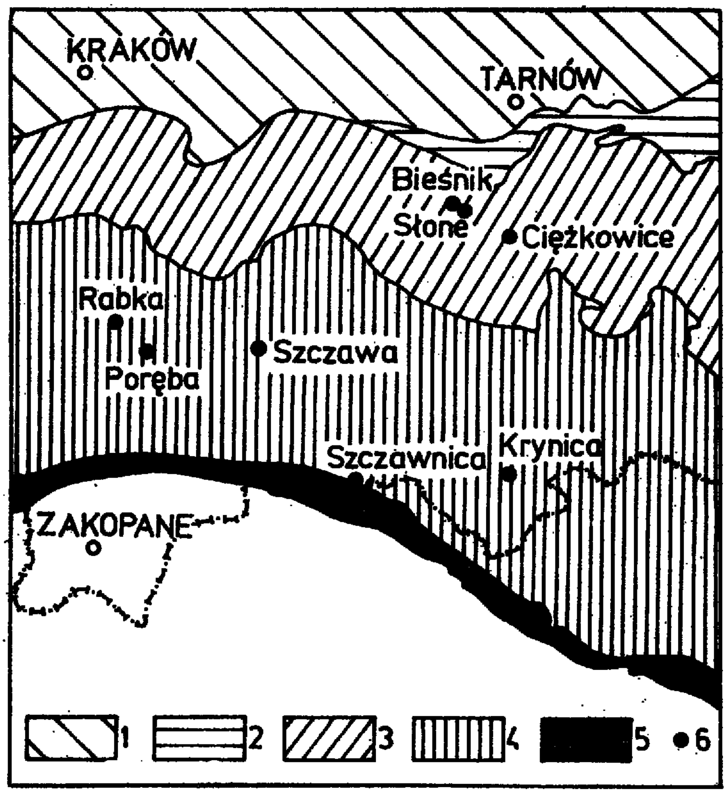

Fig. 1. Tectonic sketch of the central part of the Polish Carpathians and the locations of the mineral waters of interest

1 Carpathian foredeep, 2 Skole unit, 3 Silesian unit, 4 Magura unit, 5 Pieniny Klippen Belt, 6 Location of the mineral waters of interest

The purpose of this study was to elaborate a consistent and comprehensive model of the origin and evolution of the Wysowa mineral waters and their solutes including carbon dioxide on the base of repeated chemical and stable isotopes measurements, and to compare them with other Carpathian waters.

It is also of practical importance to know what the origin of mineralized waters in the neighbourhood of the Carpathian petroliferous provinces is, whether the resources of these mineral waters are renewable, what kind of water-mineral-gas ractions formed their chemical composition and how the fluid migrates. The knowledge of the corrosive properties of water is also in need.

The investigations were carried out at the Wysowa-Spa nappe where on the area of a few square kilometers several wells not exceeding

100 m in depth provide acidoulous HCO_3-Cl-Na waters for medicinal purposes.

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METHODS OF STUDY

Waters discharging from shallow wells were collected during the period 1961—1977 in poliethylene bottles and delivered to the laboratory where complete chemical analyses were performed. In 1976—77 special attention was given to the field measurements of pH, redox potential and alkalinity. The procedures used were recommended by Barnes (1964) and Orion Research Co. In the same period samples for measuring at monthly intervals the isotope ratios $^{18}O/^{16}O$, D/H and tritium concentration were also collected. Isotope analyses were performed at the Laboratory of Physics and Nuclear Technics, Academy of Mining and Metallurgy, Kraków. Some of oxygen-18 and tritium measurements were performed at the Laboratory of Dynamic Geology, Maria and Pierre Curie University, Paris. Chemical analyses were carried out at the Laboratory of the "Balneoproject" Enterprise, Warszawa.

GEOLOGICAL SETTING

The Magura nappe of the Polish flysch Carpathians is the uppermost tectonic unit overthrusted upon its basement consisting of other units. The sediments occurring under the flysch are not known, though in the north the Miocene formations have been found in deep drillholes. It is a question of considerable importance how far they extend towards the south.

The surrounding Wysowa area is composed of a suite of sedimentary rocks deposited in the flysch basin and belonging to the Magura nappe. This area was mapped by Węcławik (1967, 1972) (Fig. 2).

Four rock complexes were distinguished here on the ground of palaeontological and lithological investigations (Węcławik 1969, Ślączka 1970):

1. The Inoceramus beds consisting mainly of micaceous shales. Illite, muscovite, biotite have been recognized in this suite. This complex is dated to the Campanian and the Maestrichtian.

2. The variegated shale beds are also composed mostly of shales. Clay minerals like illite and chlorite were found here in addition to quartz, plagioclase and muscovite. They were deposited during the Palaeocene—Eocene period. In the neighbourhood of Wysowa some bentonites were discovered. Their presence might be related to submarine volcanic activity in the flysch basin. Calcic montmorylonites and illite predominate here (Sikora 1970, Koszarski & Wieser 1960).

3. The Beloveza beds are composed of sandstones and shales of the Eocena age (Węcławik 1969).

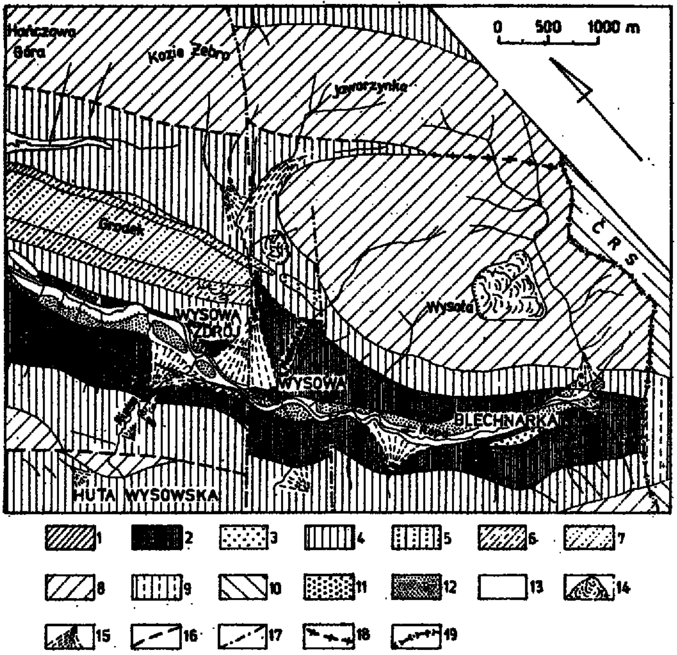

Fig. 2. Geological map of the Wysowa area (after Węcławik 1969)
1 Inoceramus Beds, *2* Variegated Shale Beds, *3* Lenticle of sandstones, *4* Beloveza Beds, *5* Lower Magura Beds, *6* Intermagura Beds, *7* Upper Magura Beds, *8* Undivided Magura Beds, *9* Beloveza Beds of the Raca unit, *10* Zborów Beds of the Raca unit, *11* upper terraces, *12* low terraces, *13* River alluvia, *14* landslides, *15* alluvial fans, *16* longitudinal faults, *17* cross faults, *18* anticline axis *19* State's border

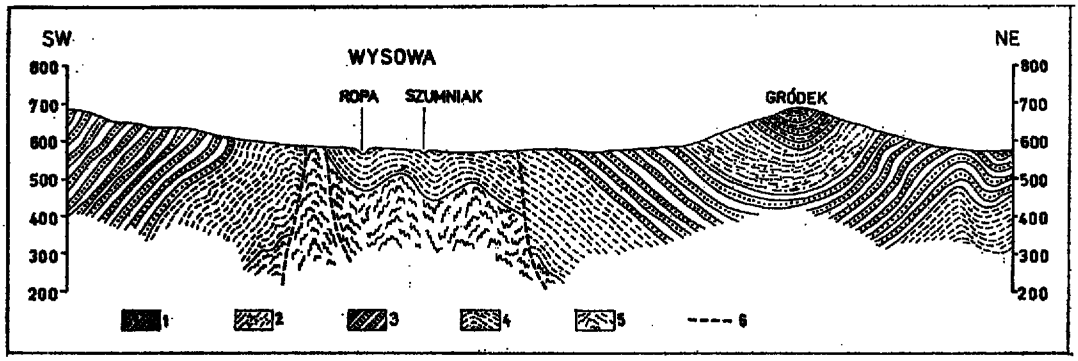

Fig. 3. Geological section-across the Wysowa Hańczowa anticline (generalized)
1 Inoceramus Beds, *2* Variegated Shale Beds, *3* Lenticle of sandstones, *4* Beloveza Beds. *5* Inoceramus Beds, *6* —{ overthrust plane

4. The Magura beds are represented mainly by thick bedded sandstones. They are considered to be the youngest Tertiary sediments in the area under consideration.

The tectonic of the Wysowa area is complicated. The main structure here is an anticline (Fig. 3) crossovered by faults of the NW—SE direction (Fig. 2). The Wysowa valley is developed in the axial zone of this anticline. A perpendicular fault called the Cigelka—Wysowa fault crossovers the anticline and is supposed to provide acidoulous waters of interest.

CHEMICAL MODEL — DILUTION TREND AND EQUILIBRIUM RELATION

For the purpose of this work the following groups of mineral waters within the Carpathians have been distinguished by their equivalent content of major elements. Chemical analyses (Table 1) were taken from Jarocka (1975).

The depths of wells tapping the waters under consideration do not exceed a few hundred meters except those of Poręba and Krynica where the intake depths amount to 1800 m and about 900 m respectively.

Table 1

Selected constituens and $\delta^{18}O$ values of some Carpathian mineral waters (in g/l and ‰ respectively)

	N., Locality and name	Year of sampling	TDS	Na	Cl	HCO_3	$\delta^{18}O$
I	1. Rabka Krakus	1974	20.832	7.500	11.130	1.422	+4.1
	2. Rabka Warzelnia	1974	15.113	5.650	8.297	1.338	−0.7
	3. Rabka *R-18*	1974	25.684	9.350	13.942	1.598	+6.4
	4. Rabka *IG-1*	1974	22.412	8.125	12.096	1.457	+4.3
	5. Rabka *R-19*	1974	18.973	6.875	10.203	1.425	+2.2
II	6. Ciętkowice *IG-1*	1973	12.474	4.240	4.393	3.103	—
	7. Poręba Wlk. *IG-1*	1977	21.590	7.400	7.843	5.553	—
	8. Słone *I*	1973	8.383	2.625	3.097	1.945	—
	9. Słone *II*	1973	4.802	1.500	1.629	1.328	—
	10. Bieśnik-Łazienka	1973	5.653	1.725	1.925	1.566	—
III	11. Szczawnica Jan	1975	5.346	1.230	0.664	2.979	—
	12. Szczawnica Magdalena	1974	26.304	7.500	5.686	11.584	+4.4
	13. Szczawnica Stefan	1974	7.263	1.263	1.297	3.564	—
	14. Szczawnica Szymon	1974	2.567	0.485	0.351	1.402	—
	15. Szczawnica Wanda	1974	8.565	2.200	1.603	4.099	−5.1
	16. Szczawa *2*	1974	25.504	7.325	5.957	10.699	+5.8
	17. Szczawa Hanna	1974	7.234	1.900	1.472	3.173	−0.4
	18. Szczawa Dziedzilla	1974	5.346	1.390	1.035	2.497	−6.0
IV	19. Wysowa Aleksandra	1974	25.673	7.000	3.856	13.275	+6.5
	20. Wysowa Bronisława	1974	4.185	1.000	0.519	2.183	−7.0
	21. Wysowa Józef *1*	1974	1.619	0.290	0.165	0.905	—
	22. Wysowa Józef *2*	1974	4.593	0.860	0.424	2.475	—
	23. Wysowa *W-13* (Anna)	1974	15.321	4.220	2.260	8.125	−0.8
	24. Wysowa *W-14* (Franciszek)	1974	20.579	5.460	3.082	10.269	+3.7
V	25. Krynica Zuber *1*	1974	24.992	5.700	0.708	17.537	—
	26. Krynica Zuber *2*	1974	22.932	4.400	0.242	16.938	—
	27. Krynica Zuber *3*	1974	27.991	6.850	1.018	19.177	—
	28. Krynica Zuber *4*	1974	23.258	6.550	0.893	19.676	

$\delta^{18}O$ data do not correspond to the years of sampling for chemical analyses.

An interesting feature may be observed when plotting the total dissolved solids versus chloride concentration of the known Carpathian waters (Fig. 4). Waters from Rabka (group I) fit the line TDS=1.805Cl which characterize the World Ocean (Alekin 1965, Horne 1969). This relationship suggests that large dilution caused by fresh water of undefined origin was involved in the evolution of the chemical composition of the Rabka water. The same concerns other groups which have been moreover largely influenced by carbon dioxide, as the bicarbonate content amounts up to 90 per cent miliequivalents of anions (Krynica — group V). This factor has changed the waters position on figures 4 and 7 along the axis of total dissolved solids. All groups decline to the point (O;O) according to a process which is called here the local dilution step. It might be referred to paleoinfiltration or to the influence of recent local precipitation. as it will be shown below, taking Wysowa as an example.

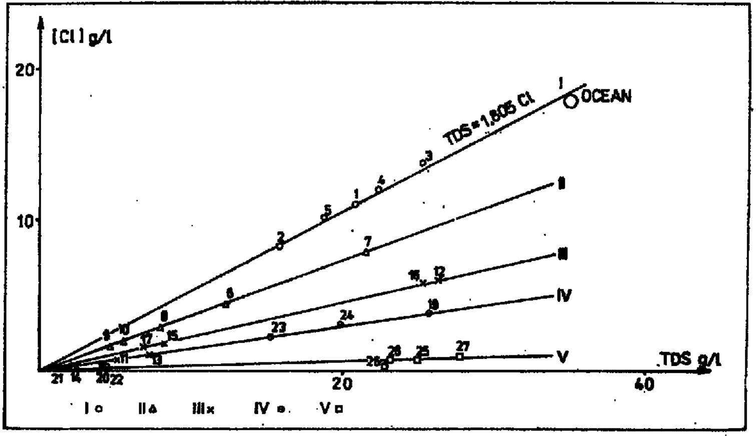

Fig. 4. Relation between dissolved solids and chloride concentration in some Carpathian mineral waters and in the Ocean

Roman numerals denote the following set of waters: *I* Cl—Na waters from Rabka; *II* HCO_3—Cl—Na waters from Poręba, Ciężkowice, Słona, Bieśnik; *III* HCO_3—Cl—Na acidoulous waters from Szczawa and Szczawnica; *IV* HCO_3—Cl—Na acidoulous waters from Wysowa; *V* HCO_3—Na acidoulous waters from Krynica (so called Zuber waters)

Solids lines are best fit lines. Arabic numerals correspond to the names of waters in Table 1

In order to verify the dilution hypothesis the model of Carpenter and Miller (1969) has been applied. It has been assumed that during the process a decreasing concentration of a chosen element should be accompanied by decrease of chloride concentration in the way that:

$$\frac{[X]}{[Cl]} = K \text{ thus } \log [X] = \log K + \log [Cl]$$

where [X] and [Cl] stand for analytical concentrations of the chosen element and the chloride concentrations respectively, and K is a constant.

The above equation plotted on the logarythmic scale forms a straight line of a slope 1.

Some discrepancy with the model might be due to:

1. dissolution or precipitation of minerals other than chloride salts;
2. dilution by water containing non negligible amounts of dissolved solids;
3. uncertainties of chemical analyses (the variation of chloride concentration resulting from dissolution or precipitation of chloride salts has been excluded because of the absence of evaporites in the flysch rocks).

If one relates sodium and bicarbonate concentrations to chloride (Figs 5—6) it is clear that the dilution model is fit rather perfectly for the Carpathian waters, though some deviations should be considered.

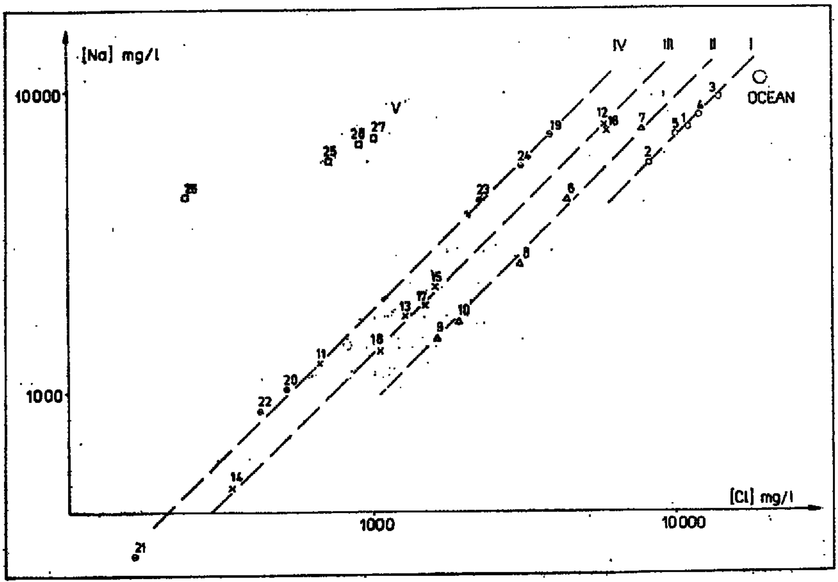

Fig. 5. Relationship between sodium and chloride concentration in some Carpathian mineral waters. For other explanations see Fig. 4

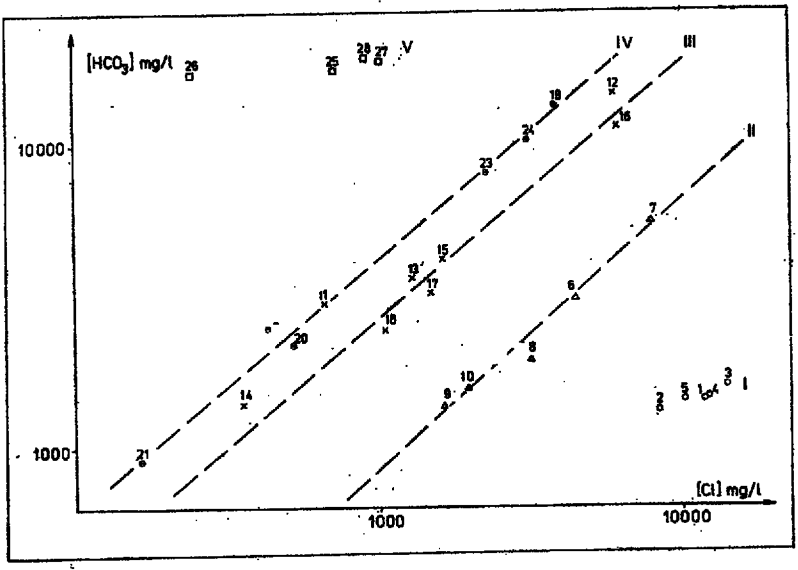

Fig. 6. Relationship between bicarbonate and chloride concentration in some Carpathian mineral waters. For other explanation see Fig. 4

Group V (Krynica) is beyond this relation especially on HCO_3/Cl graph. Though this discordance might be partly due to the large departure from the equilibrium state with respect to the minerals, more careful research should be carried out to resolve this behaviour. It is also clear that variations in sodium and bicarbonate concentrations are proportional to the chloride concentration within the groups, but inversely proportional among the groups.

It should be also remarked that variations in chloride concentration within a given group exceed considerably variations among different groups, so it is equivalent to say that the local variation in chloride concentration is greater than the regional one which was stressed by Kolago & Płochniewski (1971).

This relation found in the Carpathian waters empose two steps of dilution pattern — the first which was followed by increasing in alkalinity, alkaline metals, and some halogens, and the second one which will be investigated carefully within the Wysowa waters (group IV) (Fig. 7, Tab. 2).

For this purpose the following mineral water component have been considered: Na, K, Li, Br, J, HBO_2, TDS. Their concentrations were plotted versus chloride on the logarythmic diagram. Statistical tests were perfomed to calculate correlation

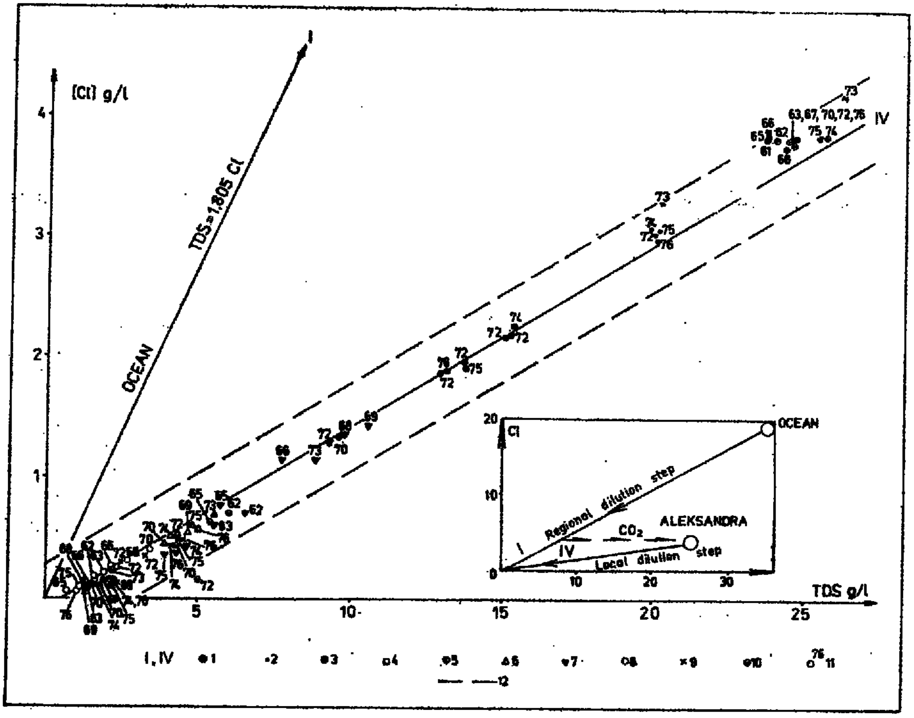

Fig. 7. Comparison of total dissolved solids and chloride concentration in the Wysowa waters and in the Ocean

Roman numerals *I* and *IV* indicate set of waters as given in Fig. 4. Set *IV* represents least square fitting line of the data points of waters from Wysowa area, namely: 1 — Aleksandra, 2 — W—14 (Franciszek), *3* — W13 (Anna), *4* — Na Skrypinie, *5* — W—11 (Henryk), *6* — Bronisława, *7* — Józef—2, *8* — W—12, *9* — Słone, *10* — Józef 1, *11* — arabic numerals at points indicate year of sampling, e.g.1970—70. Dashed lines represent 95 per cent confidence limit. The insert gives the essential feature concerning chemical evolution path of the Carpathian fluid

Table 2

Chemical composition of the Wysowa mineral waters (sampled and analysed by Balneoprojekt Enterprise in 1977, concentracion unit is mg/l)

	1	2	3	4	5	6	7	8	9	10
pH_{field}	6.9	6.9	6.67	6.45	6.3	6.35	6.5	6.1	5.95	6.05
pH_{lab}	7.1	6.9	—	6.53	6.45	6.49	6.42	6.41	5.7	5.65
$Na_T{}^+$	6800.	5500.	3650.	1875.	1700.	1425.	1050.	910.	300.	335.
$K_T{}^{+}{}_{2+}$	135.	105.	77.	50.	41.	37.	28.	20.	18.5	12.
$Ca_T{}^{2+}$	276.	233.9	172.	134.	125.	92.3	172.	252.	125.	112.
$Mg_T{}^{2+}$	37.	42.4	35.	27.	56.	23.5	48.2	74.3	33.5	34.4
$Sr_T{}^{2+}$	—	0.25	1.2	0.35	0.65	—	0.6	—	0.3	0.52
$Li_T{}^+$	9.	7.5	5.4	1.9	2.9	1.96	1.7	1,4	0.3	0.5
$NH_{4T}{}^+$	1.6	9.4	—	4.7	0.8	1.2	0.6	0.4	1.0	0.3
$Br_T{}^-$	21.3	17.3	10.5	5.6	7.3	3.9	4.0	4.3	1.13	1.3
$J_T{}^-$	4.6	4.0	2.5	1.3	0.84	0.95	0.32	0.3	0.21	—
F_T	0.9	0.43	—	0.07	0.4	0.31	0.37	0.3	0.25	0.25
$Cl_T{}^-$	3852.	3014.	1934.	773.	903.	702.	476.2	545.	90.	160.
$HCO_{3T}{}^-$	12798.	10600.	7237.	4415.	3918.	3056.	2815.	2668.	1258.	1098.
$SO_{4T}{}^{2-}$	3.	3.	3.5	trace	trace	20.	2.	10.	10.	60.
HBO_{2T}	989.	810.	580.	292.	584.	203.	181.	110.	55.3	55.1
H_2SO_{3T}	9.1	11.7	11.1	13.	11.7	12.4	11.7	11.7	17.6	13.
TDS	24980.	20388.	13728.	7650.	7425.	5596.	4804.	4620.	1931.	1894.

Arabic numerals at the top denote as follows: 1 — Aleksandra, 2 — *W-14* (Franciszek)), 3 — *W-13* (Anna), 4 — Na Skrypinie, 5 — *W-11* (Henryk), 6 — Bronisława, 7 — Józef-*2*, 8 — *W-12*, 9 — Słone, 10 — Józef-*1*. pH values in the field were measured by means of portable N-511 pehameter (Polymetron)

coefficients, regression equations and slopes of the curves (Tab. 3—4). These curves deviate in the same pattern from the theoretical dilution model for all of the elements mentioned. This deviation is studied by means of the chemical equilibrium theory (see Garrels & Christ 1965) as it is probably due to water-mineral interaction.

Table 3

Equations relating some of the elements and total dissolved solids in function of chloride concentration, δD in functions of $\delta^{18}O$ of the Wysowa mineral waters

Equation	Concentration unit	Period of sampling	Relative enrichment *A*/*B*
$LogNa = 0.925 logCl + 0.514$	mg/l	1961—1977	3.6
$logK = 0.654 logCl - 0.289$	,,	,,	1.6
$logLi = 0.689 logCl - 0.552$	,,	,,	383.
$logBr = 0.807 logCl - 1.655$	,,	,,	1.8
$logJ = 0.820 logCl - 2.313$	,,	,,	490.
$logHCO_3 = 0.716 logCl + 1.515$	,,	,,	—
$logHBO_2 = 0.785 logCl + 0.042$	,,	1969—1977	260.
$TDS = 6.521 Cl + 0.729$	g/l	1961—1977	—
$\delta D = 2.567 \delta^{18}O - 43.07$	‰	1976—1977	—

A stands for element-chloride relation in Wysowa waters mean values from the period of observations, *B* stands for element-chloride relation in Ocean (Horne 1969)

Table 4

Statistical parameters of regression equations

	n	logCl	logX	σ_X^2	σ_{Cl}^2	k	r
Na	90	2.819	3.119	0.3296	0.2858	0.93	0.99
K	82	2.821	1.556	0.3312	0.1700	0.65	0.91
Li	54	2.854	0.415	0.3507	0.2340	0.69	0.84
Br	77	2.849	0.644	0.3138	0.2404	0.81	0.92
J	80	2.891	0.057	0.3097	0.2277	0.82	0.96
HCO_3	89	2.816	3.520	0.3332	0.1771	0.72	0.98
HBO_2	41	2.898	2.317	0.3207	0.2340	0.79	0.92
TDS	75	1.361	9.604	1.9813	74.0719	6.52	0.99
D	89	−4.46	−54.51	28.6655	192.2275	2.57	0.99

Two last lines are calculated without logarithmic transformation. They relate $\delta D = f(\delta^{18}O‰)$ and TDS=f (Cl g/l) respectively. n stands for observation number, σ^2 stands or squared standard deviation, r stands for correlation coefficient

Ions activity and saturation factors in the Wysowa waters have been calculated by the "Equil" computer programme described by Fritz (1975). Total concentration of elements, pH, redox potential and temperature were taken into account to relate three types of equations in the programme: mass balance relationship, mass action expression and electroneutrality equation. A set of 120 minerals and aqueous species were considered in the programme.

The equations of mass action are of the type:

$$K = \frac{[H_3SiO_4^-]\,\gamma_{H_3SiO_4}\,10^{-pH}}{[H_4SiO_4]\,\gamma_{H_4SiO_4}}$$

where terms in square brackets stand for molalities and γ for activity coefficients. Mass balance relationship includes all forms of elements in the solution.

$$[Si_T] = [H_4SiO_4] + [H_3SiO_4^-] + \ldots$$

The following equation makes it possible to conserve the electroneutrality of the solution:

$$[Na_T] + 2[Ca_T] + 2[Mg_T] + \ldots = [Cl_T] + 2[SO_{4T}] + [HCO^3{}_T] + \ldots$$

The activity coefficient is computed by applying the following equation (Helgeson, 1969):

$$\gamma = \frac{Az_i^2\sqrt{I}}{1 + B\mathring{a}\sqrt{I}} + bI$$

where A and B stand for the Debye-Hückel coefficient, z_i is the charge of the species, a_i — its diameter, I — ionic strenght and b is the deviation function.

The computation of activity distribution species requires repeating loops, as the activity coefficients are the internal function of ionic strenght which in turn depends on the concentrations of individual species. As the ionic strenght is converged to the true value, it means that at n-step, it does not differ from n-1 step more than by 0.5 per cent, the computation is stopped and activity distribution species at equilibrium for given temperature and 1 atmosphere of total pressure is known. Saturation state of minerals and particular gases considered are computed by Gibbs free energy difference. A brief review of the result is presented in Table 5.

Table 5

pH field-values. ionic strenght, partial pressure of CO_2, activity and ion activity ratios in the Wysowa mineral waters

	pH	IS	$\log pCO_2$	$\log\{H_4SiO_4\}$	$\log\frac{\{Na\}}{\{H\}}$	$\log\frac{\{K\}}{\{H\}}$	$\log\frac{\{Ca\}}{\{H\}}$	$\log\frac{\{Mg\}}{\{H\}}$
1. Aleksandra	6.9	0.3029	0.052	−3.93	6.20	4.27	10.88	10.33
2. *W-14* (Franciszek)	6.9	0.2481	−0.020	−3.83	4.11	4.17	10.78	10.43
3. *W-13* (Anna)	6.7	0.1689	0.065	−4.07	5.73	3.82	10 .28	9.96
4. Na Skrypinie	6.45	0.0938	0.097	−3.77	5.25	3.43	9.86	9.50
5. *W-11* (Henryk)	6.3	0.0912	0.192	−3.81	5.05	3.21	9.73	9.53
6. Bronisława	6.35	0.0709	0.050	−3.80	5.04	3.21	9.57	9.29
7. Józef *2*	6.5	0.0622	−0.131	−3.82	5.07	2.89	10.16	9.92
8. *W-12*	6.1	0.0640	0.234	−3.82	4.60	2.71	9.53	9.31
9. Słone	5.95	0.0265	0.092	−3.65	4.02	2.55	9.06	8.77
10. Józef *1*	6.05	0.0271	−0.066	−3.78	4.16	2.47	9.21	8.97

Complete analyses are given in Table 2

These results could be referred rather to the near-surface condition than to the deep water reservoir mainly because of the temperature difference.

Data limitation except thermodynamic data (see Fritz 1975) concerns especially the determination of non-conservative species in their ionic forms as Al, Fe, Mn, Si, though even classical alkalinity determination (Barnes 1964) without flushing the carbon dioxide of the sample by neutral gas, is subjected to inaccuracy due to the high pressure of CO_2.

In Figures 7 and 8 relating sodium and chloride concentration based on 90 analyses (carried out since 1961) one can see a perfect correlation ($r = 0.99$). The slope of the regression line is equal to 0.93 indicating the validity of dilution hipothesis. The Wysowa waters are enriched* in sodium about three times as compared to sea water (Table 3). As mentioned above this enrichment should be referred to the regional evolution of Carpathian saline waters which is simultaneous to the increasing in alkalinity, from CO_2 attack on silicate rock and H consumption. Therefore deviation from ideal dilution pattern is due to water-sodium bearing minerals interaction which supplies sodium inte the solution. The evolution path can be followed also on the activity diagram for a portion in the system $Na_2O—Al_2O_3—SiO_2—H_2O$ (Fig. 9). More diluted Wysowa waters are located in the lower part of the diagram within the kaolinite stability field, waters of higher ionic strenght are likely to fall into sodium aluminosilicate stability field. It is apparent that dilution process is responsible for such scatter of points representing the Wysowa waters.

One can observe similar behaviour within the potassium subsystem $K_2O—Al_2O_3—SiO_2—H_2O$ (Fig. 10) where the Wysowa waters of high ionic strenght ten to be located closer to kaolinite-muscovite boundary. As the waters of interest are more diluted, they are relatively more enriched in potassium as the muscovite and illite are unstable phases in the environment. This remark is confirmed by slope K/Cl of the dilution line equal to 0.91 (Fig. 11).

High, nearly 400-fold relative enrichment in lithium was ascertained in the Wysowa waters. It follows the dilution pattern as the elements mentioned above

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* The enrichements is calculated in the following way: $X/Cl_A : X/Cl$ where X denotes the analitical concentration of a chosen element and. A denotes the water under consideration.

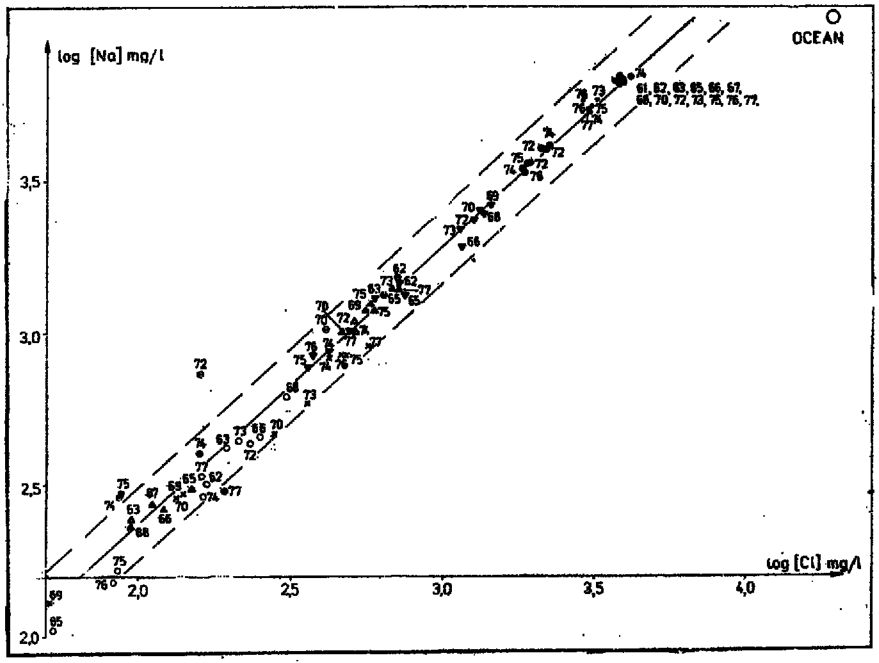

Fig. 8. Relationship between sodium and chloride concentration in the Wysowa mineral waters. Other explanation are the same as given in Fig. 7

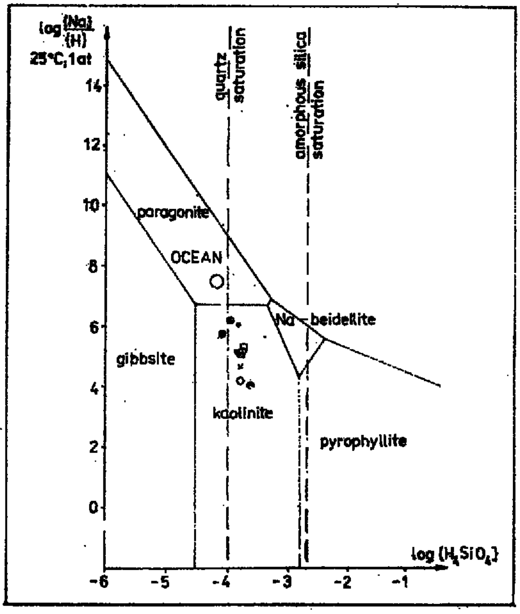

Fig. 9.
The Wysowa mineral waters on the stability field of some minerals in the Na_2O-Al_2O_3-SiO_2-H_2O system. Data points are the same as given in Fig. 7

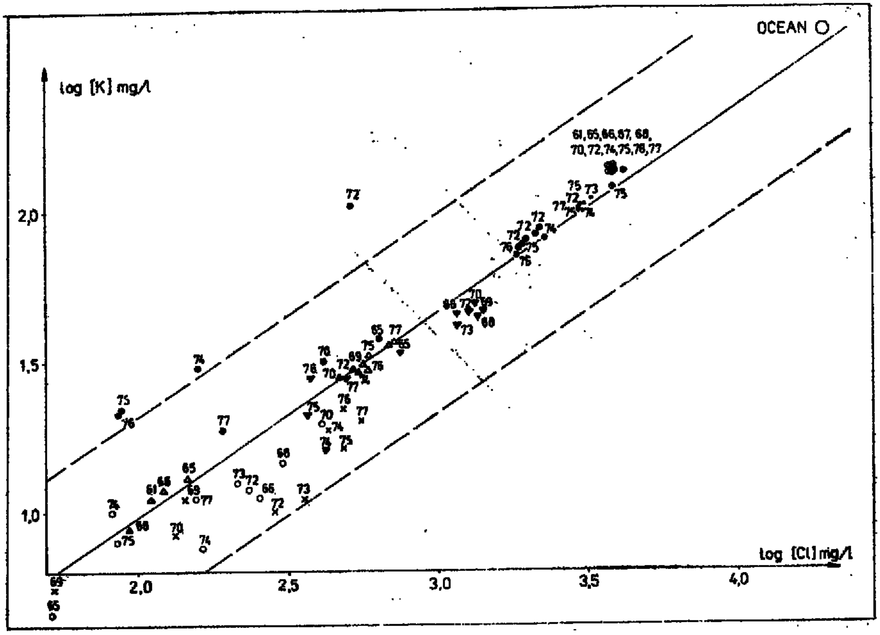

Fig. 10. The Wysowa mineral waters on the stability field of some minerals in the K_2O-Al_2O_3-SiO_2-H_2O system. Data points are the same as given in Fig. 7

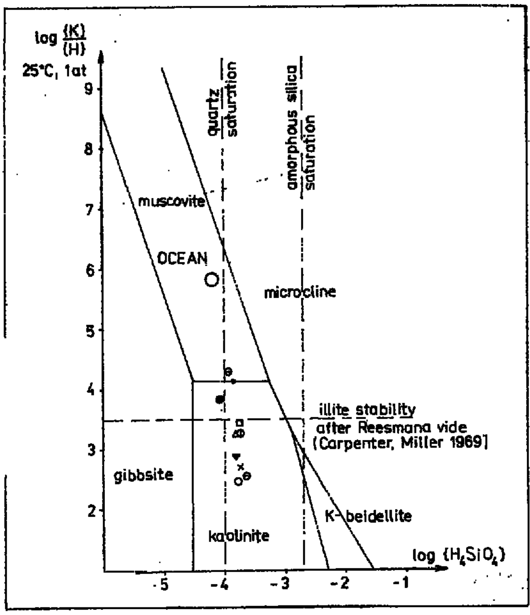

Fig. 11.
Relationship between potassium and chloride concentration in the Wysowa mineral waters. Other explanations are the same as given in Fig. 7

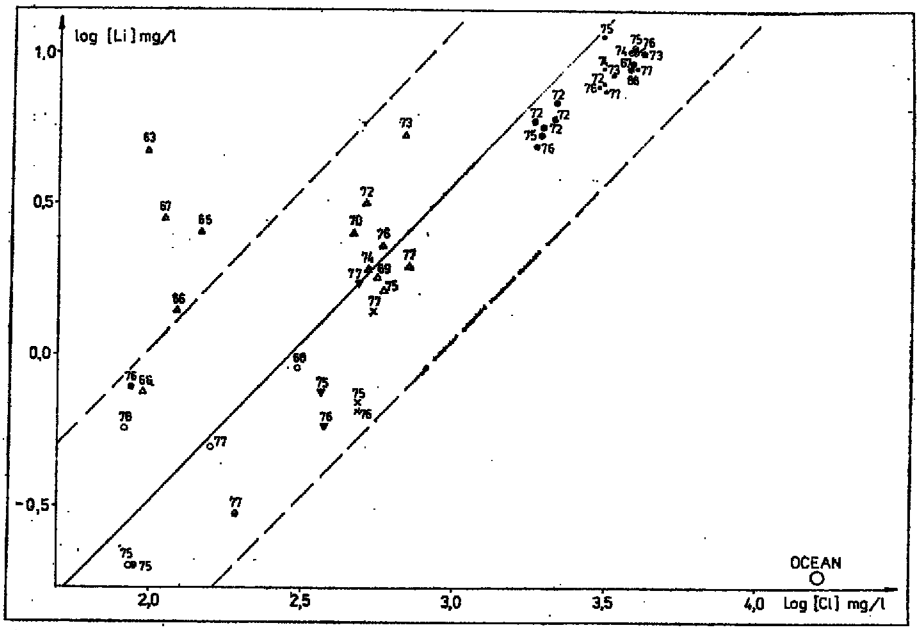

Fig. 12. Relationship between lithium and chloride concentration in the Wysowa mineral waters. Other explanation are the same as given in Fig. 7

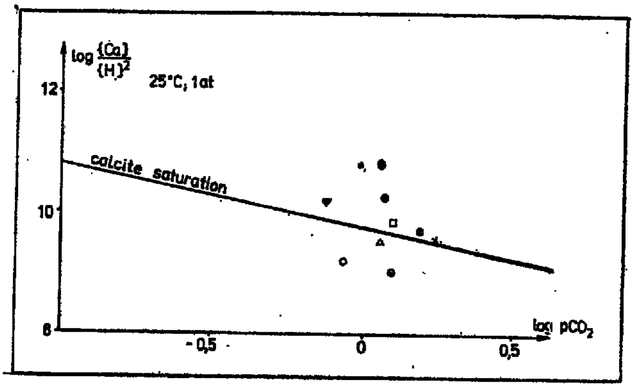

Fig. 13. Comparison of the saturation state of the Wysowa mineral waters with respect to calcite. Data points are the same as given in Fig. 7

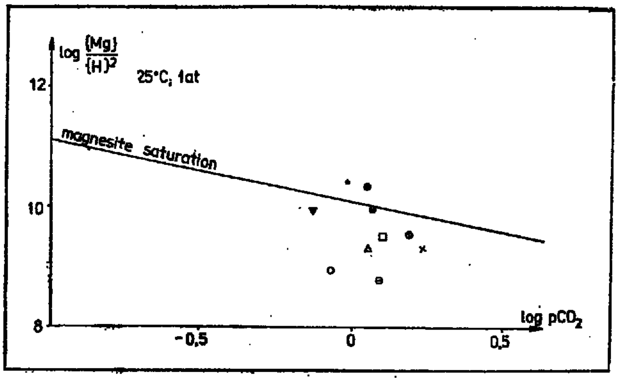

Fig. 14. Comparison of the saturation state of the Wysowa mineral waters with respect to magnasite. Data points are the same as given in Fig. 7

do. Similar behavior can be probably explained by incorporation of lithium into sodium and potassium mineral lattices (Fig. 12).

Concentrations of calcium and magnesium do not follow the dilution model. A constant concentration level of these elements may be elucidated by the buffer properties of carbonate minerals near equilibrium state (Figs 13—14) according to reaction

$$Me^{2+}+2H^{+}=Me^{2+}+CO_2+H_2O$$

where Me^{2+} stands for Mg or Ca. Concentrations of other divalent metals like Ba, Sr are probably buffered in this way.

It can be also seen that this buffer mechanism is more efficient in the case of water having high ionic strenght.

In the subsystem $CaO—Al_2O_3—SiO_2—H_2O—CO_2$ (Fig. 15) the Wysowa waters, as it might be supposed, fall into kaolinite stability field as they do in the subsystem $MgO—Al_2O_3—SiO_2—H_2O—CO_2$ (Fig. 16). The dilution trend is less distinct as in the case of sodium and potassium subsystems.

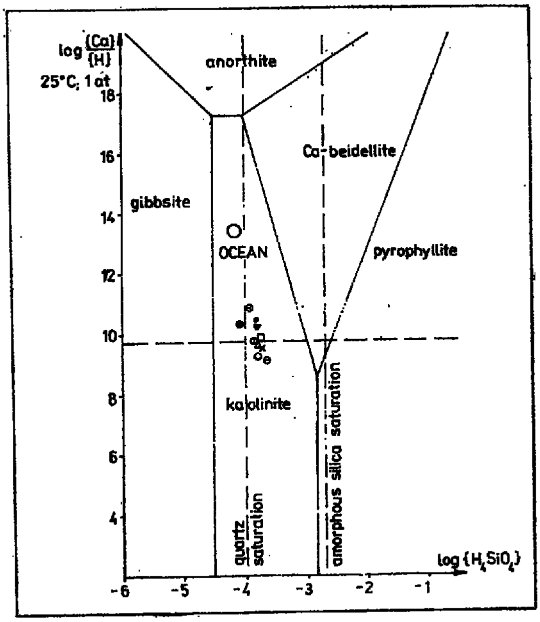

Fig. 15.
The Wysowa mineral waters on the stability field of some minerals in the $CaO-Al_2O_3-SiO_2-H_2O-CO_2$ system. Data points are the same as given in Fig. 7

Jodide and bromide in the Wysowa waters have a similar dilution slope which is equal to 0.81 (Figs 17—18) respectively, but their relative enrichment differs about 300 times, being 500 times greater in the case of jodide (Table 3) as compared to sea water.

The probable source of jodine and bromine seem to be flysch rocks with organic matter content, if the latter has had the chance to be preserved during a long geological period.

Little is known about the sulfate-sulfide subsystem in the Wysowa waters. Sulfate is not abundant and sometimes does not exceed 3mg/l. Its variability is probably related entirely to near-surface redox condition.

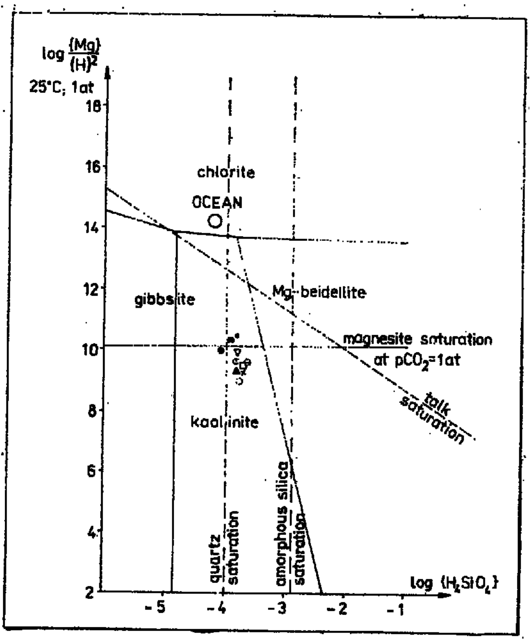

Fig. 16.
The Wysowa mineral waters on the stability field of some minerals in the $MgO-Al_2O_3-SiO_2-H_2O-CO_2$ system. Data points are the same as given in Fig. 7

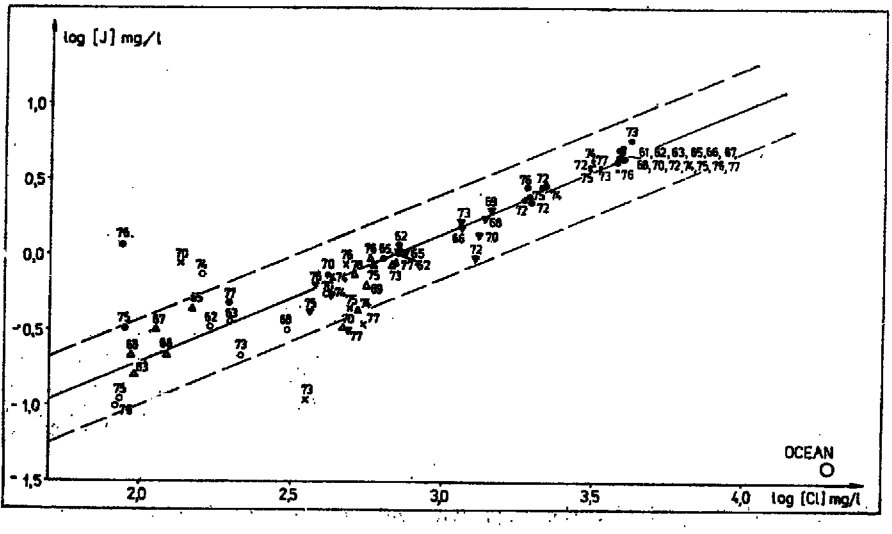

Fig. 17. Relationship between iodide and chloride concentration in the Wysowa mineral waters. Other explanations are the same as given in Fig. 7

One of the most uncommon features in the Carpathians is the boron concentration. In the Wysowa waters it reaches as high value as about 900mg/l (as HBO_2). The concentration of boron is subjected to local dilution trend with a slope of 0.8 in relation to chloride, correlation coefficient being close to 0.92 (Fig. 19). This high boron concentration assigns 200 fold enrichment in relation to sea water. In the Carpathian waters it roughly increases from group I to IV but

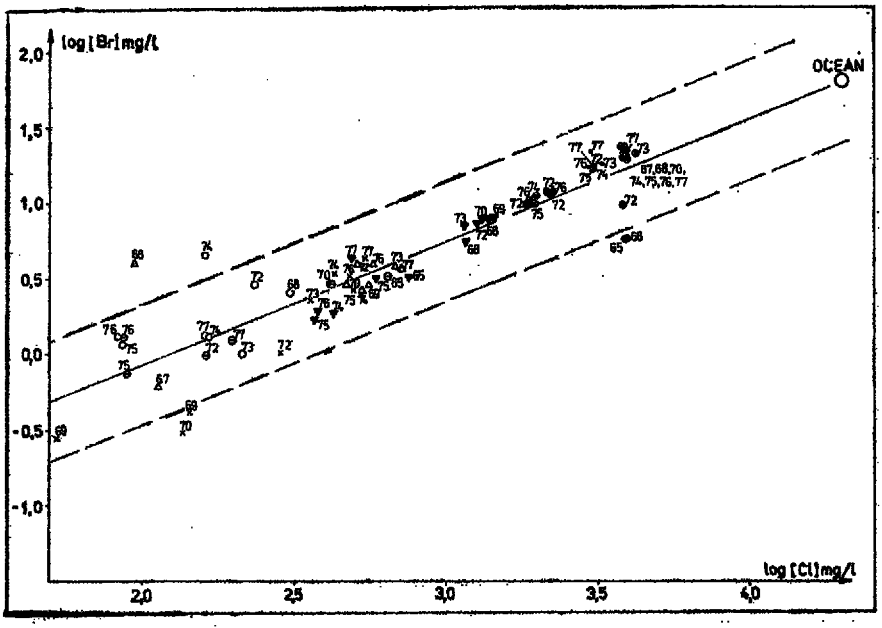

Fig. 18. Relationship between bromide and chloride concentration in the Wysowa mineral waters. Other explanations are the same as given in Fig. 7

it is only 14 times greater in group V (Krynica). High boron concentration corresponds rather to positive values of $\delta^{18}O$ in the Carpathian waters.

The provenance of boron can be derived directly from sedimentary rocks which are the main reservoir of this element. Durkovic & Čicel (1966) reported

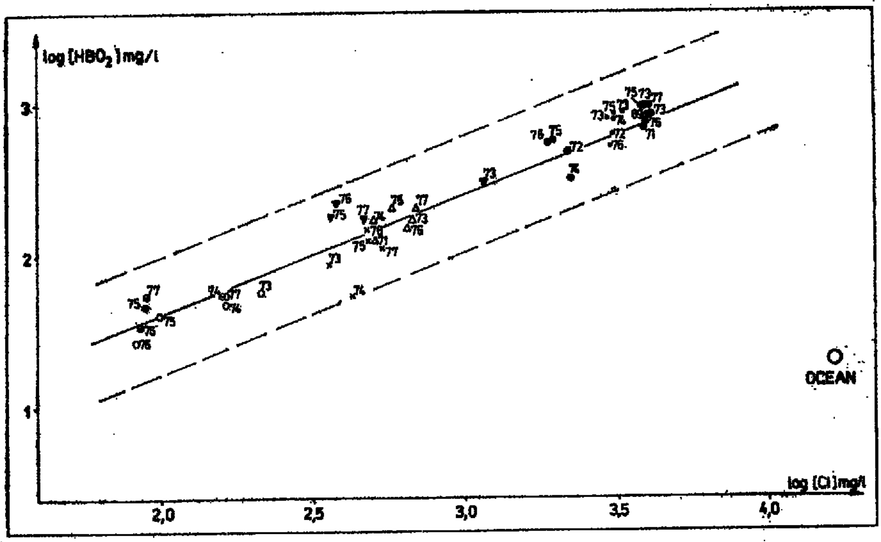

Fig. 19. Relationship between boron and chloride concentration in the Wysowa mineral waters. Other explanations are the same as given in Fig. 7

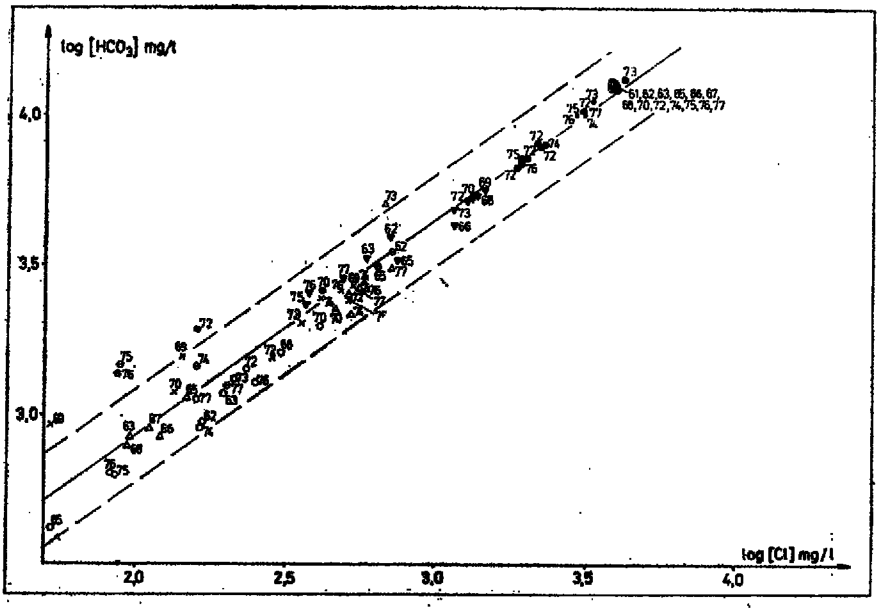

Fig. 20. Relationship between bicarbonate and chloride concentration in the Wysowa mineral waters. Other explanations are the same as given in Fig. 7

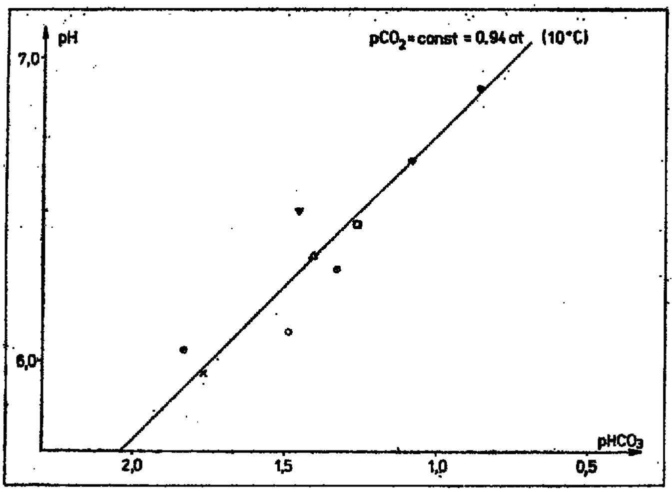

Fig. 21. Relationship between pH and bicarbonate activity in the Wysowa mineral waters. Data points are the same as given in Fig. 7

600 ppm of boron within sedimentary rock complex on the Slovakian territory. Illite is always suspected to be the main boron-bearing mineral (Lerman 1966 Harder 1970, Perry 1972).

A constant concentration level of silica is not surprising (Tab. 2). In the flysch water reservoir where the aluminosilicate minerals predominate and the silica concentration does not exceed several ppm it should be buffered by various silicate phases as suggested for example by Carpenter & Miller (1969). All waters under consideration are saturated with respect to the quartz.

The concentration of bicarbonate, which in the Wysowa waters is believed to be equivalent to the total alkalinity, fits the dilution line though it is declining more slowly than chloride does (Fig. 20). The slope of the HCO_3/Cl line is equal to 0.72. This corresponds to interaction with silicate rocks during their leaching from alkaline and halogen elements.

From the regional point of view higher bicarbonate content is accompanied in the Carpathian waters (Fig. 6) by lower chloride concentration, so it is obvious that the regional dilution step has been associated with high activity of carbon dioxide. This is also manifested by carbonate deposits in flysch rock fractures.

A linear relation between pH and Cl has been found in the Wysowa waters. It means also that pH is proportional to bicarbonate activity with slope 1 and thus imposes that the Wysowa water system is open to carbon dioxide reservoir (pCO_2 = const) (Fig. 21) which can be felt by intuition.

ISOTOPE COMPOSITION

Craig (1961) reported the empirical relationship between oxygen-18 and deuterium activity in the waters of the meteoric cycle. The following equation was proposed:

$$\delta D = 8\delta^{18}0 + 10$$

where δ value stands for enrichment (+) or depletion (—) in deuterium or oxygen, relatively to the standard called SMOW (Standard Mean Ocean Water).

Systematic observation of isotope composition of oxygen and hydrogen in the Wysowa waters has confirmed the Dowgiałło's data (1973) about their high positive $\delta^{18}0$ values, though the interpretation of the results requires revision (Table 6).

The highest value of $\delta^{18}0$ reported from Wysowa reaches +6.7 per mille which is very uncommon even in the World scale (see White & al. 1973, Clayton & al. 1966).

The most negative values of $\delta^{18}0$ vary about —10 per mille in the Wysowa *Józef 1* water. The surface waters do not fall below this value. It should be mentioned that samples were not taken in winter when oxygen in precipitation is the heaviest. Considering the temperature relationship of Dansgaard (1964) the mean annual value of precipitation in the area considered should not be more negative than —11.5 per mille and —82.6 per mille for $\delta^{18}0$ and δD, respectively, if the mean annual temperature at the altitude of 1187m (Ostry Wierch Mt.) is about 3.1°C.

In the Wysowa chloride waters the relationship between $\delta^{18}O$ and δD has a form of equation:

$$\delta D = 2.6\delta^{18}O - 43 \quad \text{(Fig. 22)}$$

correlation coefficient $r = 0.99$ number of samples $n = 89$.

If one compiles the presented data of oxygen and hydrogen isotopes and those reported by Dowgiałło (1973) from Carpathians, it can be supposed that this line, called below the Carpathian waters isotope line, represents at least the know Carpathian chloride waters being a proof of regional geochemical processes which were responsible for isotope composition of the solvent.

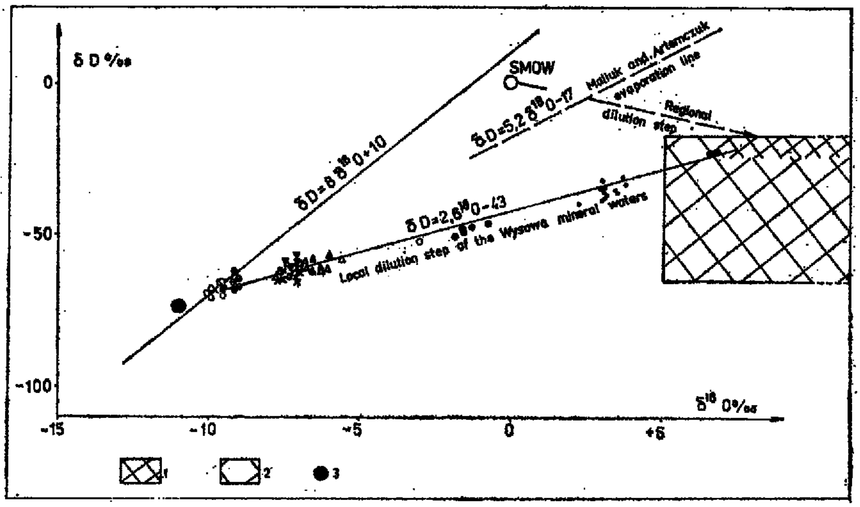

Fig. 22. Relationship between ^{18}O and D in the Wysowa mineral waters on the background of the Craig's meteoric line and Artemczuk's and Maliuk's experimental evaporation line. Data points are the same as given in Fig. 7. Arabic numerals denote as follows: *1* — Carpathian flysch metamorphic fluid, *2* — Taylor's range of metamorphic fluid, *3* — surface water in the Wysowa area

The scatter of the points representing these waters along the Carpathian $\delta D-\delta^{18}O$ line, especially for those with tritium concentration below 4TU, suggests contribution of at least three or more kinds of waters of different origin.

As it has been mentioned, tritium concentration in rich in oxygen-18 and deuterium water does not exceed 4TU. Higher tritium concentration is observed in the W-12 water, but it maintains a rather constant concentration level (Table 6). This constancy can be due to the high water capacity of the underground reservoir.

The most striking is that all waters having such different $^{18}O/^{16}O$, D/H ratios and tritium concentration are tapped in at a depth below 100 m and at a maximum distance of a few hundred meters.

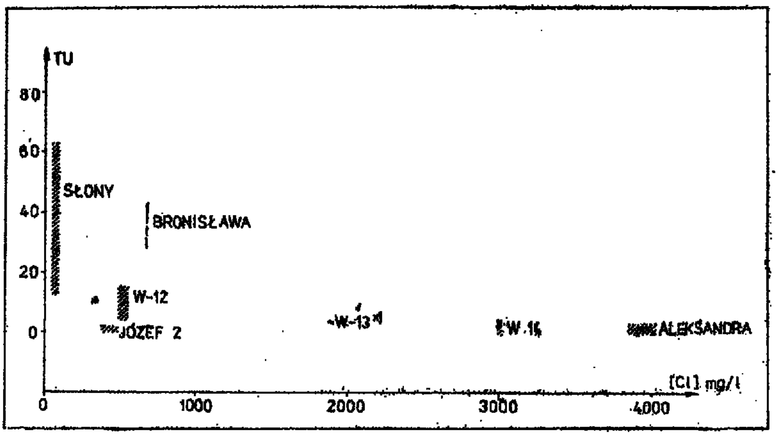

Fig. 23. Relationship between tritium and chloride concentration in the Wysowa mineral waters. x — denotes single determination of chloride

The concentration of tritium in the „Słony" and the „Bronisława" waters reaches 60TU and does not keep at all the constant concentration level. Surface water from the Ropa River and precipitation were in 1977 at a level of about 150TU. Tritium concentration is inversely proportional to the chloride content — — this relation depends on the presence of contemporary precipitation waters (Fig. 23).

The depth at which tritium disappears is about 20 m (Fig. 24—25). Simple calculation has been performed to learn the percentage content of tritium

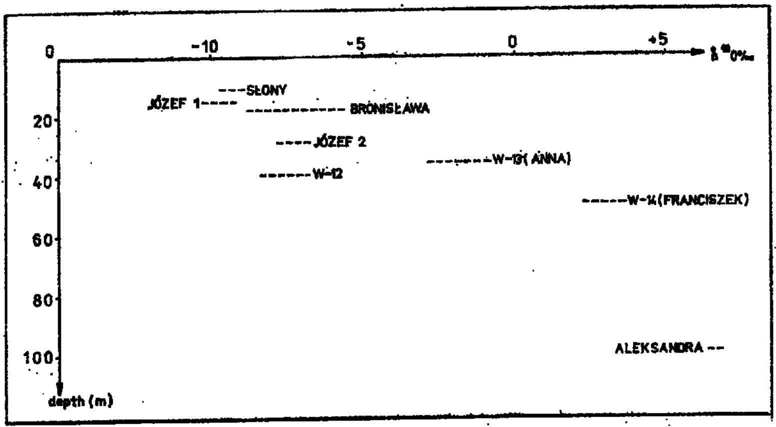

Fig. 24. Relationship between ^{18}O and the depth of wells of the mineral waters at Wysowa

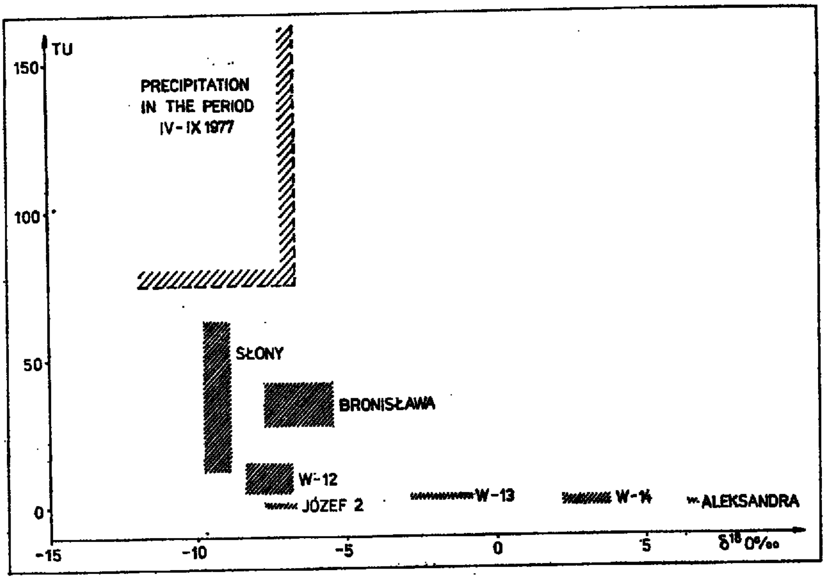

Fig. 25. Relationship between δ^{18}O and tritium concentration in the Wysowa mineral waters

containing water in the mixture. According to the mixing rule it is equal to the ratio of tritium concentration of the sample to the tritium concentration in precipitation

$$X = \frac{TU_{mixture}}{TU_{precipitation}}$$

The „Słony" water contains as much as 25 per cent of contemporary waters (Table 7) if one takes the mean tritium content of water of interest and the tritium concentration in precipitation equal to 150TU, which is in accordance with the field observation.

Table 7

The portion of contemporary waters in the Wysowa

	Depth (m)	Number of determinations	Mean value (TU)	Portion of recent tritium containing water (per cent)
Aleksandra	100	8	1.2	0.8
Wysowa *14*	50	11	3.2	3.1
Wysowa *13*	36	3	3.8	2.5
Wysowa *12*	40	14	9.0	6.0
„Bronisława"	18	11	32.6	21.8
„Słony"	16.5	13	37.9	25.2

The chloride concentration in the Wysowa water is closely related to $\delta^{18}O$ values (Fig. 26). It can be easily explained up to the range of depth of 20 m where tritium is present. At greater depth where tritium disappears, such relation might be explained only by the presence of old water deprived of Cl and low $\delta^{18}O$, δD values (see also Fig. 25). This observation is in agreement with the scatter of points along the Magura nappe line in the δD — $\delta^{18}O$ coordinates (Fig. 21). This

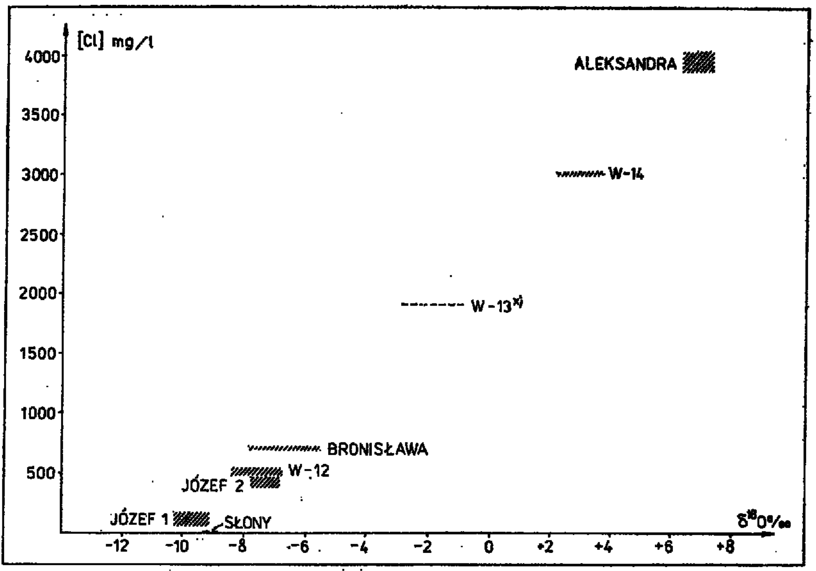

Fig. 26. Relationship between $\delta^{18}O$ and chloride concentration in the Wysowa mineral waters

line crosses the Craig's meteoric line at about —10 per mille and —70 per mille in $\delta^{18}O$ and δD respectively, which point corresponds to recent precipitation water.

However, any conclusions are hardly possible without intensive studies of paleoclimatology, paleogeography as climate and elevation of the flysch massif were decisive in the case of $\delta^{18}O$ and δD control of precipitation. An approach to this problem was done by Dowgiałło (1979, *personal communication*).

MODEL OF WATER-SILICATE ISOTOPE EXCHANGE

This is a question of considerable importance to know in what way ancient flysch Carpathian ocean water has acquired its present high positive $\delta^{18}O$ values. It has been assumed that the isotopic composition of water in the flysch basin was very similar to the present-day ocean water (Taylor 1974).

This constancy is still open to discussion, though it is almost sure that it did not differ in Tertiary times more than by 2 per cent. Therefore isotope exchange between water and silicates might be the unique process by which water could acquire positive value of $\delta^{18}O$ and negative δD value.

Water-isotope exchange was deliberated by Dowgiałło (1973) to be the cause of the oxygen „shift" but finally he leaned to the evaporation process as responsible for the positive value of $\delta^{18}O$.

Silicate and especially clay minerals predominate in the Carpathian flysch system (Książkiewicz 1961, Ślączka 1970, Dominik & al. 1975). The most common minerals in the flysch rocks are illite muscovite, chlorite deposited on the flysch ocean bottom or they may be in part autogenous (Wieser 1970, Sikora 1970).

It results from the structure of clay minerals that it is possible for water to exchange isotopes with either interlayer water, OH groups or aluminosilicate oxygen. Probably in this order decreases accesibility of oxygen-18 and deuterium for isotope exchange (for discussion see O'Neil & Kharaka 1976, James & Baker 1976). Well crystallized illite is hardly accessible for exchanging oxygen at the sedimentary temperature (see op. cit.). Higher temperature is needed to access heavy oxygen located in aluminosilicate framework than in hydroxyl group or interlayer water.

To study the possibility of isotope exchange in the Carpathian flysch system some assumptions have been made. Muscovite has been taken as a representative flysch rock micaceous mineral as the only one for which the fractionation factor for both oxygen and hydrogen are known (O'Neil & Taylor 1969, Suzuoki & Epstein 1976, Friedman & O'Neil 1977). Fractionation factor has been extrapolated from a range 400—650°C to as low as 250°C which seems to be quite justified if one considers that equilibration has been taking place since Tertiary times. The values approximating the fractionation factors are following:

Δ muscovite — $H_2O = 2.38\ 10^6T^{-2} — 3.89$ for oxygen

Δ muscovite — $H_2O = -22.1\ 10^6T^{-2} + 19.1$ for hydrogen

where $\Delta = \delta^f_A — \delta^f_B = 1000\ln\alpha_{A-B}$

α — fractionation coefficient

δ^f_A, δ^f_B stand for δ values after equilibration in phases A and B respectively

T — Kelvin temperature

The model of isotope exchange has been adapted from Sheppard's, Nielsen's, Taylor's (1971) and Taylor's (1974) work to calculate the final isotope composition of water δ^f_w. As stated previously the initial composition of water δ^i_w was taken as 0 per mille for both oxygen-18 and deuterium. The initial assumed $\delta^{18}O$ and δD values of monomineral rock δ^i_r are + 18 per mille and —70 per mille respectively. These values have been taken from Hoefs (1973).

The water-rock ratio must be taken into account as the isotope exchange depends largely on the amounts of water involved in the process. By definition

$$W/R = \frac{\delta^i_r - (\delta^f_w + \Delta)}{\delta^f_w - \delta^i_w}$$

where $\Delta = \delta^r_f - \delta^w_f$ and W/R is the ratio of the atom per cent of oxygen (hydrogen) in water to the atom per cent of oxygen (hydrogen) in a mineral. In turn W/R ratio is related to porosity. As porosity decreases during diagenesis and metamorphism, the W/R does the same, and if temperature is assumed to be constant, W/R is the only parameter that controls δ^w_f. Conversely, if the W/R is kept constant, δ^w_f is determined by Δ which depends exclusively on the temperature (Taylor 1977).

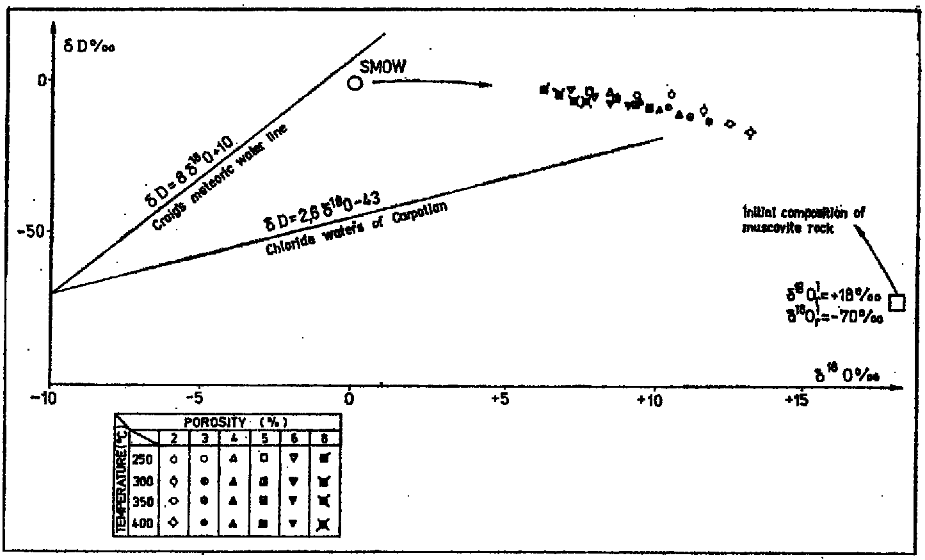

Fig. 27. Evolution of the isotope composition of flysch fluids during equilibration with monomineral muscovite rock along with the temperature and porosity

The results presented in Fig. 27 show the isotope evolution of trapped by sediments flysch ocean water. At the temperature of about 325°C and 2 per cent porosity this connate water attained the Carpathian δD—$\delta^{18}O$ line at values $\delta^{18}O^f_w$ and δD^f_w equal to + 12 per mille and —15 per mille respectively. The same values of $\delta^{18}O^f_w$ and δD^f_w are acquired at the porosity of 3 per cent while the temperature exceeds 400°C. Thus variations in porosity have an apparent influence on the water-mineral isotope equilibration, expecially as far as oxygen is concerned. Although a number of assumptions have been taken into consideration it is quite probable that the Carpathian waters might have been affected by such a process.

EVOLUTION OF ISOTOPE COMPOSITION OF THE CARPATHIAN WATERS

Another hypothesis to explain the enrichment in oxygen 18 and depletion in deuterium relatively to sea water has also been taken into consideration. It may results the presence of the so called "metamorphic water". That is fluid coming from dehydroxylation of hydrous minerals (White 1957).

It is not intentional to differentiate isotope exchange and metamorphic reaction. Laboratory experiments performed so far are "par excellence" at metamorphic or at least at low grade metamorphic temperature (e.g. see O'Neil & Taylor 1969).

The $\delta^{18}O$ value of metamorphic waters have been estimated by Taylor (1974) to be in the range between +5 per mille and 25 per mille and δD −20 per mille to −65 per mille (Fig. 22).

If one considers the initial isotope composition of Carpathian flysch water as very similar to the present-day sea-water and $\delta^{18}O$ — δD range of metamorphic water (see op.cit.) it can be believed that metamorphic fluid could have been responsible for drastic change of isotope composition of trapped flysch water (their dilution).

This isotope path of water in terms of δD — $\delta^{18}O$ values is very similar to that obtained previously by water muscovite exchange model. Considering metamorphic water hypothesis it must be assumed that favorable P,T conditions for such dehydroxylation might have existed in deep-lying bottom of the flysch rocks though even in flysch rocks metamorphic mineral association (greenstones) have been reported by Burtan and Łydka (1978).

The presence of metamorphic water is a more naturalistic phenomenon than pure isotope exchange. It explains large dilution which took place on the so called regional stage. A rough estimate of $\delta^{18}O$ of metamorphic dilution water can be made, if one assumes that the „Aleksandra" water contains neither contemporary water (TU = 0) nor paleoinfiltration water, the latter being more doubtful. The ratio of chloride concentration of the Wysowa water to chloride concentration in sea water will be the portion of connate flysch water, the rest about 80 per cent being metamorphic water. Immediately, one obtains $\delta^{18}O$ of such water equal to +8.4 per mille in the range of lower limit for metamorphic fluid predicted by Taylor (1974). It would be not a good explanation however, if metamorphic Carpathian fluid had uniform isotope composition. Water without paleoinfiltration contribution should have maximum chloride concentration and a high positive value of $\delta^{18}O$. This is the case of Rabka —18 water in the Magura nappe having Cl concentration about 13900mg/l and $\delta^{18}O = +6.4$ per mille. (Fig. 28) As previously $\delta^{18}O$ of metamorphic fluid will be equal to 22.5 per mille value close to the upper limit of the Taylor's range. Therefore the Wysowa water „Aleksandra" should contribute the following portion of fluids of different origin: 50 per cent of connate water ($\delta^{18}O \cong 0$ per mille), 20 per cent of metamorphic water ($\delta^{18}O \cong 23.0$ per mille) and 30 per cent of water from paleoinfiltration ($\delta^{18}O = -10$ per mille).

The latter value of $\delta^{18}O$ is a crude assumption because nothing is known about the nature and origin of this fluid except the suggestion coming from the Carpathian waters δD — $\delta^{18}O$ line which crosses the Craig's line at $\delta^{18}O = -10$ per mille.

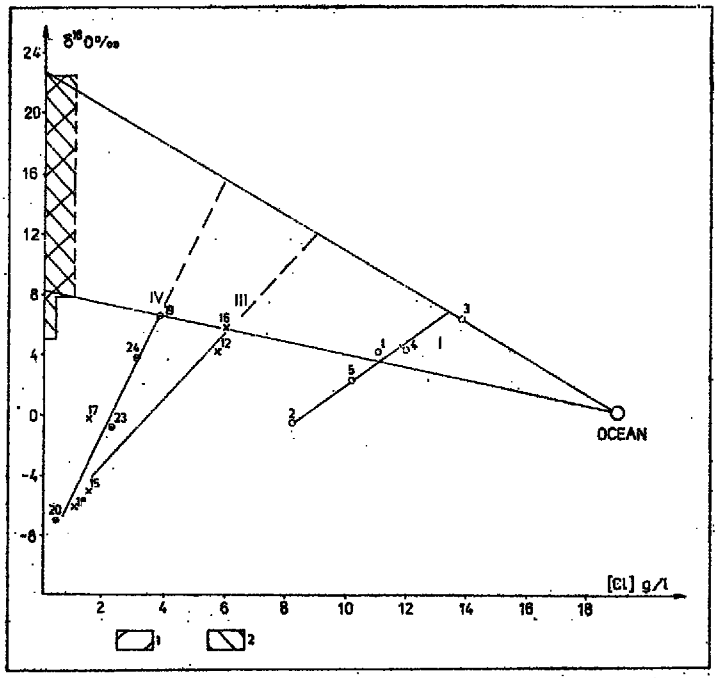

Fig. 28. Evaluation of the Carpathian metamorphic fluid. *1* — Carpathian metamorphic fluid, *2* — Taylor's range ($\delta^{18}O$) of the metamorphic fluid. Other explanations are the same as given in Fig. 4

In Fig. 28 the chloride concentration of the known Carpathian waters was plotted against their $\delta^{18}O$ values to make the calculation more imaginable. Group IV corresponds to the Wysowa waters as in Figs 4—5 being the poorest in Cl and mostly enriched in oxygen-18. Line A represents a changing portion of trapped flysch ocean water (connate) and fluid released during metamorphism. Increasing portion of the latter is accompanied by the rise in bicarbonate concentration on the regional scale. Locally, as it is in the case of Wysowa itself, less cloride concentration conforms to the drop in bicarbonate and $\delta^{18}O$ which is due to the dilution by paleoinfiltration and recent meteoric water.

One can assume that during metamorphism not only water was released from sedimentary rocks but also carbon dioxide. Low grade metamorphism could have generated both the solvent (H_2O) and CO_2 as a result of the following reaction (Vartanian 1978):

1. $6CaCO_3+5Mg_3Si_4O_{10}(OH)_2+4SiO_2=3Ca_2Mg_5Si_4O_{10}OH+2H_2O+6CO_2$
2. $4CaCO_3+3KAlSi_3O_{10}(OH)_8+6SiO_2=2Ca_2Al_2Si_3O_{12}OH+2KAlSi_3O_8+2H_2O+4CO_2$
3. $10CaCO_3+3Mg_5Al_2Si_3O_{10}(OH)_8+2SiO_2=3Ca_5Mg_5Si_4O_{11}(OH)_2+$
   $+2Ca_2Al_2Si_3O_{10}OH+8H_2O+10CO_2$

The metamorphic origin of Carpathian carbon dioxide as a result of carbonate rock metamorphism was suggested by Barnes & O'Neil (1976) who carried out $\delta^{13}C$ research work in Sloviakia. This has been deliberated also by Dowgiałło (1976) and reconsidered by him in 1978 on the ground of $\delta^{13}C$ measurements and gas analyses in the Polish flysch area.

A crude assumption can be made on the quantity of fluids produced by such reaction. From rock volume of 1000km^3 (100 × 10 × 1), 18 per cent of $CO_2 + H_2O$ will be released during the reaction (2), which is equivalent to 165 and 15 cubic kilometers of CO_2 and H_2O respectively. Such amount could supply flysch chloride water system through vast areas of the Carpathians and during geological period of time.

DISCUSSION

The data in this paper represent chemical and isotope approach to the origin of the Wysowa chloride waters, but the comparison with the other Carpathian waters allows to formulate more general hypotheses. Considering these data the former views on the origin of the Carpathian chloride waters has been re-examined.

Dowgiałło (1973) examined two hypotheses to explain high positive $\delta^{18}O$ values of the Carpathian waters. In the first one he excluded the possibility of the water-rock isotope exchange, though he stated, that it is more likely to consider the isotope exchange of these waters with carbonates. Such exchange with silicates is hardly possible because of the temperature factor. In the seconde hypothesis he denotes, that the high positive $\delta^{18}O$ values were acquired by the waters during evaporation in closed flysch basins.

Cortecchi & Dowgiałło (1975) excluded the view that Carpathian waters could have originated from the meteoric infiltration waters subjected to the strong isotope exchange with the wall-rock because of the relatively high δD values of these waters. They concluded also on the background of $\delta^{18}O(H_2O)$ and $\delta^{18}O(SO_4)$ correlation that recent meteoric water is not present in the Carpathian chloride waters. Cortecchi & Dowgiałło (1975) found that the slope of the relationship between $\delta^{18}O$ and δD of the Carpathian waters reflects ultrafiltration. However, this process does not explain at all why waters under consideration have the low content of dissolved solids and low δD values.

Dowgiałło (1976) proposed that the Carpathian waters should be considered as a mixture of the infiltration meteoric waters and relict marine waters, though justification he had done „the higher the content of heavy isotopes, the higher the content of dissolved solids" is not convincing as is explained below. In the case of the Rabka waters Dowgiałło suggested the presence of Miocene formation water which has undergone evaporation as marked by positive $\delta^{18}O$ values.

Dowgiałło & Sławiński (1978) suggested that the Rabka waters originate from the Miocene formation which underlies Carpathian flysch. According to the mentioned authors these waters have come to the surface under high pressure and have undergone ultrafiltration. They extend their interpretation for the large part of the West Carpathians.

These hypotheses can be clearly contradicted if one remembers that the Carpathian waters are enriched in oxygen-18 but depleted in deuterium relatively to the initial composition (Tertiary sea water). Evaporation of the sea water gives the slope of the δD — $\delta^{18}O$ relation equal 5.2 in the temper climate as one can conclude from the work of Maliuk & Artemczuk (1976) (Fig. 22). It can be also as low as 2.6 in the arid climate (Craig & Gordon 1965). Although the latter value is similar to that of the Carpathian waters, the content of dissolved solids in these waters is low and does not correspond to the evaporative conditions. In the evaporation experiments of Maliuk & Artemczuk (1976) the total salt content rose to 170 g/l and corresponding value $\delta^{18}O$ rose to 6.6‰. Such high values have never been encountered in Carpathians.

Though the Carpathian waters have a slope $\delta D/\delta^{18}O$ similar to that obtained by Coplen & Hanshow (1973) during their ultrafiltration experiments, this hipothesis is as before contradicted not only by high oxygen-18 enrichment and deuterium depletion, but also by the low salt content rarely exceeding 25g/l. Much of it is HCO_3 coming from CO_2 attack on silicate rocks, or from oxidation of organic carbon. The rule of the ultrafiltration is that the enrichment (depletion) of heavy isotopes (both oxygen-18 and D) corresponds to the rise (drop) of the salt content (depending on the membrane side).

This chemical — isotope discordancy is convincing and so far there is no proof that the ultrafiltration was a process which governs the isotope and chemical composition of the Carpathian waters.

The origin of the Carpathian waters can be explained by a consistent isotope-chemical model. Initial Tertiary sea water was trapped in the sediments and burried at a greater depth. During low grade metamorphism boron-bearing fluid was released from the sediments, mixed with connate water, which is reflected by the high enrichment in oxygen-18 and depletion in deuterium. By this process relict waters were diluted (regional stage) to different degrees depending on the area and volume of rocks involved in metamorphism. Accompanying generation of CO_2 raised the alkalinity of the resulting fluid (Fig. 7) as well as some alkaline metals and halogens concentration by rocks leaching and dissolution.

The second dilution stage by meteoric waters is shown on fig. 22 to be linear relationship with a slope 2.6 between δD and $\delta^{18}O$. Generally, this pattern corresponds to the five groups of the Carpathian waters on the Cl-TDS concentration plot (Fig. 4).

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PAWEŁ LEŚNIAK

POCHODZENIE WÓD CHLORKOWYCH W WYSOWEJ (KARPATY ZACHODNIE). STUDIUM CHEMICZNO-IZOTOPOWE

(Streszczenie)

Przedyskutowano pochodzenie wód zmineralizowanych i ich składników występujących na obszarze Wysowej w płaszczowinie magurskiej. Ze względu na ścisłe powiązania geologiczne oraz podobny charakter chemiczny i izotopowy, omówiono szerzej niektóre wody występujące na terenie Karpat fliszowych. Skład chemiczny wód Wysowej ustalono na podstawie analiz wykonywanych od 1961 r. Stacjonarne badania składu izotopowego wód (^{18}O, D, T) przeprowadzono w latach 1976—1977.

Analizy chemiczne zostały wykonane przez Laboratorium Balneochemiczne Przedsiębiorstwa Balneoprojekt; analizy izotopowe w Instytucie Fizyki i Techniki Jądrowej w Krakowie i częściowo w Laboratorium Geologii Dynamicznej Uniwersytetu Piotra i Marii Curie w Paryżu.

Interpretacja analiz chemicznych została dokonana w dwóch aspektach: statystycznym, który posłużył do udowodnienia rozcieńczenia wód Wysowej przez meteoryczne wody różnego wieku, oraz równowag chemicznych, które zostały ustalone w wyniku zastosowania programu „Equil" (Fritz 1975). Dzięki temu programowi zdefiniowano różne formy występowania materii (indywiduów) w wodach, oraz stan nasycenia tych wód względem niektórych minerałów i gazów.

Interpretację składu izotopowego wód przeprowadzono z uwzględnieniem identyfikacji procesu, który mógł doprowadzić wody Wysowej (a także wody mineralne występujące w innych punktach Karpat fliszowych) do obecnej wysokiej zawartości ciężkiego izotopu tlenu ^{18}O oraz do obniżenia stężenia deuteru w porównaniu do wyjściowej wody morskiej.

Problem ten rozpatrzono w aspekcie wymiany izotopowej wód z glinokrzemianami oraz obecności tzw. wód metamorficznych pochodzących z dehydroksylacji minerałów. Wielkość stężenia trytu w wodach posłużyła do oceny udziału współczesnych wód infiltracyjnych w wodach Wysowej. Konfrontacja modelu chemicznego, uwzględniającego z jednej strony wnioski statystyczne, z drugiej zaś równowagi chemiczne z modelem izotopowym odnoszącym się do samego rozpuszczalnika (H_2O) doprowadziła do następujących wniosków: w Wysowej występują wody zmineralizowane w skład których wchodzą w różnych proporcjach wody reliktowe zbiornika fliszowego, rozcieńczające je i wzbogacające w ciężki tlen wody pochodzące z przemian metamorficznych skał podłoża lub spągowych partii fliszu oraz wody paleoinfiltracyjne i infiltracyjne współczesne. Obecny system wód mineralnych w Wysowej otwarty jest do nieskończonej pojemności zbiornika dwutlenku węgla, a jego potencjał chemiczny jest niezależny od składników chemicznych systemu fliszowego (pCO_2=const). Gaz ten uwalniany jest równolegle z wodą w procesach metamorfizmu. Wnioski te można uogólnić na obszar Karpat fliszowych, tam gdzie występują tzw. szczawy chlorkowe.