

Origin of carbon dioxide and evolution of CO₂-rich waters in the West Carpathians, Poland

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ABSTRACT:

LEŚNIAK, P.M. Origin of carbon dioxide and evolution of CO₂-rich waters in the West Carpathians, Poland. *Acta Geologica Polonica*, **48** (3), 343-366. Warszawa.

The research was carried out to determine the origin of carbon dioxide and to track the possible isotopic evolution of carbonated waters of the flysch Carpathians. Carbon isotopic composition ($-9.2\text{‰} < \delta^{13}\text{C}_{\text{CO}_2(\text{g})} < -1.8\text{‰}$, $-7.1\text{‰} < \delta^{13}\text{C}_{\text{TDC}} < +5.4\text{‰}$) of the unusually CO₂-rich, cold waters of various salinity, with bicarbonate as the dominant anion, is characteristic for an CO₂-water open system. It differs from carbon isotopic composition of waters of the closed-CO₂ system with $\delta^{13}\text{C}_{\text{TDC}}$ values reaching up to $+28\text{‰}$, that have chloride as the dominant anion. From the detailed isotopic measurements of CO₂(g) ($\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$) and of the corresponding total dissolved carbonates ($\delta^{13}\text{C}_{\text{TDC}}$) it is found which fluids are in isotopic equilibrium with accompanying CO₂ gas and which are not. Because of the variability of the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values simple assignment of a definite single or multiple CO₂ source(s) is rather ambiguous. To evaluate the main factors which influence the isotopic composition, two limiting models of kinetic fractionation occurring during a vertical advective flow of carbonated solution and/or CO₂ gas are derived. The models suggest that both the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and $\delta^{13}\text{C}_{\text{HCO}_3}$ values can be modified on the way of the CO₂-H₂O mixture to the Earth surface. The model of parallel flow of CO₂(g) and carbonated solution predicts that the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and $\delta^{13}\text{C}_{\text{HCO}_3}$ values can be only slightly changed towards negative $\delta^{13}\text{C}$ values at Damköhler number (Da) equal 1. In the one-phase CO₂ flow model, due to decreasing $C_{\text{CO}_2(\text{g})}/C_{\text{HCO}_3}$ the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and $\delta^{13}\text{C}_{\text{HCO}_3}$ equilibrium values (Da=1) display a clearly declining trend along the vertical profile. Generally, the isotopic shift with respect to the original input value depends mainly on P_{CO₂} gradient, Damköhler number and the difference in the velocity of CO₂ gas and carbonated solution. Because during both the equilibrium or non-equilibrium fluid flow the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values decrease, only the highest $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values can be considered as non-fractionated and may possibly reveal the origin of CO₂. Lower $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values result from isotopic fractionation and are not useful as indicators of CO₂ origin. These findings support the view that low $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values considered sometimes as an evidence of mantle or organic provenance of carbon dioxide in the West Carpathians or elsewhere are in fact significantly modified during the ascendance flux of CO₂ gas to the Earth surface. The common assumption that $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ remains constant during CO₂-H₂O flow to the surface has been shown to be invalid. High $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values around -2‰ suggest that CO₂ gas in the CO₂-charged waters in the West Carpathians is predominantly derived from the thermal decomposition of the carbonate and silicate rocks. In the closed systems with respect to CO₂, ($\delta^{13}\text{C}_{\text{TDC}}$ up to 28‰), carbon dioxide originates from the decarboxylation of acetic acid.

INTRODUCTION

West Carpathian flysch is a province known for the occurrence of the CO₂-rich waters and CO₂ dry exhalations. The purpose of this work is to present the general systematics of the carbonated waters, to identify carbon dioxide source(s) and major geochemical processes involving carbon compounds. The study concerns carbonate chemistry of waters as well as stable carbon isotopes of the CO₂ containing gases and of total dissolved carbonates. It has long been recognized that inorganic CO₂ gas derived from the Earth crust should have higher $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values than CO₂ gas which originates in the Earth mantle (OHMOTO & RYE 1979). However, CO₂ exhalations sampled at the Earth surface in many locations in the world, including Carpathians, display large range of $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values; from about -19 to -2‰ (DEINES 1980, HUEBNER 1981). Therefore, identification of a single or mixed source of CO₂ from the variety of possible choices such as crustal organic, crustal inorganic or mantle is problematic. The $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ value is usually assumed to be constant during CO₂ transport to the surface. This is a fairly good approximation for waters which outgas CO₂ close to the Earth surface, but generally it is not the case. Therefore, the important question is whether and how the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ of the original imprint(s) as well as the $\delta^{13}\text{C}_{\text{TDC}}$ composition ($\delta^{13}\text{C}$ of total dissolved carbonates) can be modified on the way upwards.

The assumption of isotope equilibrium was used previously to elucidate the carbon isotope evolution in groundwaters by DEINES & *al.* (1974), WIGLEY & *al.* (1978) and PEARSON & *al.* (1978) among others. Although the equilibrium assumption is a useful key-reference, it does not explain all data. The application of kinetic methodology to study the evolution of carbon and oxygen isotopic compositions in natural settings was challenged by HENDY (1971), INOUE & SUGIMURA (1985), USDOWSKI & HOEFS (1985), DULIŃSKI & *al.* (1995). Spatial differentiation of $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ or $\delta^{13}\text{C}_{\text{TDC}}$ values in gases and waters in the Earth crust was not of interest in the mentioned works.

Unlike rocks, waters and gases frequently lose their original chemical and isotopic signatures and only recent changes are possible to trace. The kinetic models of isotopic exchange during advective transport of fluids were successful in explaining the past variation of the $\delta^{18}\text{O}$ values in

rocks (LASSEY & BLATTNER 1988, BOWMAN & *al.* 1994) and were applied in this study to interpret the recent evolution of the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and $\delta^{13}\text{C}_{\text{TDC}}$ values in Carpathian CO₂-charged waters.

Carbonated waters in the Outer West Carpathians are very common and several attempts have been made to explain the origin of CO₂ (DOWGIAŁŁO & *al.* 1975). LIS & HAŁAS (1980) as well as LIS (1986) suggested multiple origins of CO₂ according to the different $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values. Therefore, their implicit assumption was that the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values cannot be changed by secondary processes. The present author (LEŚNIAK 1985) tried to set up evidence of uniform crustal origin of CO₂. LIS (1986) attempted to correlate the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ data with major Carpathian faults. DULIŃSKI & *al.* (1995) addressed the problem of carbon and oxygen isotopic equilibrium and kinetics between water, calcium carbonate and carbon dioxide. An interpretation of the $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ data of LIS & HAŁAS (1980) by LEŚNIAK (1985) was based on the results of chemical analyses and of separate pH and alkalinity measurements in the field.

$\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ data, however, give only partial information about $\delta^{13}\text{C}$ of the total dissolved carbonates (TDC) as opposed to direct $\delta^{13}\text{C}_{\text{TDC}}$ measurements made on total carbonates precipitated from solution. These shortcomings were overcome by direct precipitation of barium carbonate performed in the field together with measurements of pH and sampling for chemical analyses as reported in (LEŚNIAK 1989). An extensive and careful field work was necessary to avoid secondary fractionation after sample withdrawal.

The current presentation is based on parallel sampling of both phases: barium (strontium) carbonates were precipitated in the field to obtain the $\delta^{13}\text{C}_{\text{TDC}}$, concomitantly with a free gas sampling for the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ analyses. The present work is an extension and elaboration of some ideas presented in LEŚNIAK (1989). A consistent $\delta^{13}\text{C}_{\text{TDC}} - \delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ data set for CO₂-charged Outer Carpathian mineral waters has never been presented before. It is important to note that the obtained $\delta^{13}\text{C}_{\text{TDC}}$ and $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values are representative for the Earth surface. Vertical variation of the $\delta^{13}\text{C}_{\text{TDC}}$ and the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values can only be tracked theoretically. The essential problem whether and how the primary $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ signal could be overridden by secondary processes is advanced by applying outgassing and 1-D reactive transport models. There is no

data to quantify the flux of CO_2 or locate in place and time the source of CO_2 ; an answer to these questions is not attempted.

Finally, the CO_2 -charged waters of the Na-Cl- HCO_3 and Na-Cl types which do not exsolve their CO_2 and are assumed not to be externally charged with CO_2 gas (closed CO_2 system) are shown to have an entirely different origin of CO_2 .

GEOLOGICAL SETTINGS AND GENERAL HYDROCHEMISTRY

The Carpathian flysch of the Outer West Carpathian arc (Text-fig. 1) fills in a longitudinal depression compressed as a result of the collision of the Pannonian microplate and the Eurasian plate in Savian and Styrian events. Outer Carpathians are poor in carbonates and are mainly composed of shaly sandstones, sandstones and shales up to

10 km thick. Strike-slip faults form the tectonic contact of the Outer Carpathians with the very narrow tectonic structure of the Pieniny Klippen Belt which contains several carbonate facies.

The Pieniny Klippen Belt extends from the Vienna Basin to Poiana Botizei (Romania) separating the Outer and Inner Carpathians through a system of strike-slip faults. Deep seismic sounding indicates that the Moho Discontinuity rises southwards from the Pieniny Klippen Belt (PKB) by about 15 km (UCHMAN 1973). Geoelectric studies reveal the existence of a zone of resistivity as low as $1 \Omega\text{m}$ at a depth of about 16 km along the curved and narrow structure of the PKB. Among the other working hypotheses the existence of a reservoir of hot water has been suggested to explain the anomalous resistivity (LEFELD & JANKOWSKI 1985), however no positive heat flux anomaly in this region has been reported. The heat flux is even lower than predicted

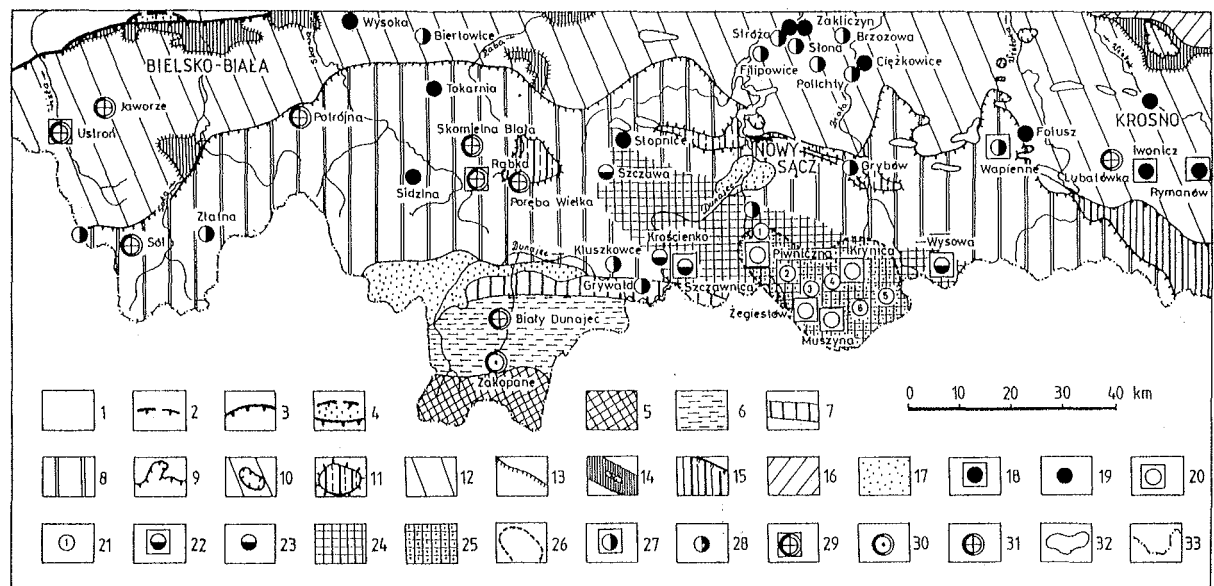


Fig. 1. Geological sketch-map of the Outer-West Carpathians, Poland (after CHRZĄSTOWSKI & WĘCŁAWIK 1992)
 1 – pre-Quaternary sediments of Carpathian foreland, 2 – margin of Carpathian nappes below Miocene sediments, 3 – exposed margin of the Carpathian nappes reflected in morphology, 4 – folded Miocene sediments along outer margin of the Carpathian nappes, 5 – Tatra Mts., 6 – Podhale Flysch (Eocen), 7 – Pieniny Klippen Belt, 8 – Magura Nappe, 9 – margin of the Magura nappe, 10 – tectonic outliers of the Magura nappe upon the Silesian nappe, 11 – tectonic windows, 12 – Silesian nappe, 13 – margin of the Silesian nappe, 14 – Subsilesian nappe, 15 – Dukla nappe, 16 – Skole nappe, 17 – unfolded miocene sediments, 18 – mineral waters of Cl-Na type (spas), 19 – other Cl-Na mineral waters, 20 – CO_2 -charged mineral waters without chloride (spas), 21 – wild CO_2 -charged mineral waters, 22 – CO_2 -charged, chloride mineral waters, 23 – Cl-Na- HCO_3 , CO_2 -charged mineral waters, 24 – Cl-hydrochemical zone, 25 – Cl-absent hydrochemical zone, 26 – dry CO_2 exhalation, 27 – sulfide waters (spas), 28 – other sulfide waters, 29-30 – thermal waters, 31 – thermal waters from the basement of the Magura nappe, 32 – oil-field waters, 33 – state boundary. Encircled numbers indicate localities: 1 – Głębockie, 2 – Łomnica, 3 – Wierchomla, 4 – Złockie, 5 – Tylicz, 6 – Powroźnik

for the continental lithosphere being 40-65 mW/m² (PLEWA 1976). ROKITYANSKI & *al.* (1975) suggested that the Carpathian resistivity anomaly results from regional metamorphism of the flysch complex at a depth below 10 km. Intensive dehydration of rocks could abnormally lower the resistivity. According to ROKITYANSKI & *al.* (1975) at a depth of about 20 km the flysch rocks could have descended only as subducted crust. Recently, ŻYTKO (1997) has suggested that the Carpathian geoelectric anomaly could be generated by the occurrence of graphitized zones associated with deep faults.

The chemical composition of CO₂-rich mineral springs (Text-fig. 1) was reported in several geochemical studies (ŚWIDZIŃSKI 1972, WĘCŁAWIK 1979, SZPAKIEWICZ 1980). These waters have a uniform temperature of about 10°C and P_{CO₂} ≈ 0.1 MPa (Tables 1-2). Most of the waters of the Ca-(Mg)-HCO₃ type are derived from relatively young atmospheric precipitations. Other waters of the rare type (Na-HCO₃, Na-HCO₃-Cl) have a complex and controversial origin. Another type of waters containing CH₄-CO₂ gases contain prevalently Na-Cl (Na-Cl-HCO₃) ions with variable total dissolved solids not exceeding 30 g/l. The more concentrated solutions do not contain tritium at all.

At some sites such as Wysowa, Rabka, Szczawnica, the sodium content and alkalinity of waters are linearly correlated with chlorides which has to be interpreted as mixing of saline component with groundwaters. The mixing behaviour also applies to K, Br, HBO₂, Li, and I concentrations (LEŚNIAK 1980). The relative enrichment in these conservative elements with respect to Cl (molar scale) i.e., [X/Cl]_{sample}/[X/Cl]_{seawater} is 1.6, 1.8, 260, 383, 490, respectively, where X denotes concentration of a particular constituent. A mixing process is also strongly suggested by a linear dependence between the most concentrated solutions of high δ¹⁸O_{H₂O} and δD_{H₂O} values extending up to +6.7 and -20‰, respectively (a non-meteoric end-member) and the present day precipitations characteristic for the local mountainous terrain with average values of -10.7‰ for δ¹⁸O and -72‰ for δD.

The non-meteoric end-member was supposed to have a composition similar to that of seawater (DOWGIAŁŁO 1973). Further chemical and isotopic studies added another possible component to that mixture: metamorphic water (LEŚNIAK 1980). However, GRABCZAK & ZUBER (1985) ar-

gue that mixing is possible between two end-members: meteoric and metamorphic waters. One reason for the difference in opinions is in the definition of metamorphic water. While LEŚNIAK (1980) takes it as a pure H₂O solvent derived from OH⁻ structural groups in minerals, GRABCZAK & ZUBER (1985) stress that metamorphic water must be enriched in several constituents including chloride.

It is noteworthy that in the Inner Carpathians, Slovakia, CO₂-rich waters have similar carbon isotope compositions to these in the Outer Carpathians. However, chloride components exceeding 500 mg/l and positive δ¹⁸O waters have not been encountered there according to the data of FRANKO & *al.* (1975) and BARNES & O'NEIL (1976), respectively.

Although there are several sites throughout the world where CO₂-rich waters have been reported, there is a striking similarity in the chemical and isotopic compositions of the fluids in the Carpathian flysch and those known in the Coast Ranges of California. Both sites are past accretion or subduction zones. The similarity of the sites appears in an increasing concentration of conservative elements such as K, Br, HBO₂, Li, and I with increasing Cl concentration, high concentrations of boron, similar δD-δ¹⁸O pattern and positive δ¹³C values of total dissolved carbonates (WHITE & *al.* 1973, PETERS 1993, DAVISSON & *al.* 1994).

EXPERIMENTAL

The important quantity used throughout the work is total dissolved carbonates concentration (calculated quantity):

$$\text{TDC} = \text{CO}_2(\text{aq}) + \text{HCO}_3^- + \text{CO}_3^{2-} \quad (1)$$

where CO₂(aq) ≡ CO₂(aq) + H₂CO₃. This abbreviation is justified because more than 99% of CO₂ in groundwater exists as 'dissolved gas' and less than 1% as true carbonic acid (STUMM & MORGAN 1981). Alkalinity is defined as:

$$\text{Alk} = \text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^- - \text{H}^+ \quad (2)$$

and represents a deficit of charge in solution.

The most common and recommended method for measurements of δ¹³C of total dissolved carbonates (δ¹³C_{TDC}) is by direct precipitation in the field by reaction with saturated SrCl₂ + NH₄OH

or $\text{BaCl}_2 + \text{NaOH}$ (GLEASON & *al.* 1969, DEINES & *al.* 1974, TRUESDELL & HULSTON 1980).

A recent critical review by BISHOP (1990) confirmed this method as highly reliable. In the precipitation method uncertainty may even be lower than $\pm 0.2\text{‰}$, although results with an uncertainty of $\pm 0.7\text{‰}$ are not uncommon in the literature (FRITZ & *al.* 1981). The precipitation method has been criticised by GRABER & AHARON (1991) as inadequate for waters containing more than 300 mg/l of sulphate. Carpathian CO_2 -rich waters are, however, either devoid of sulphate or sulphate is from 50 to 400 times less abundant than the total dissolved carbonates.

Water pH and temperature were measured and samples for chemical analyses were taken at several sites in the Western Carpathians in Poland (Textfig. 1). For the field pH measurement, an ORION 407 ionmeter was used. The pH electrode was an ORION 9105 with an internal AgCl reference electrode. The uncertainty of 0.1 unit in pH measurements translates to the uncertainty of about 23% in hydrogen ion activity and to the related quantities such as total dissolved carbonates concentration (TDC) and partial pressure of CO_2 (P_{CO_2}).

At the same time when pH measurements were made, samples were collected for the $\delta^{13}\text{C}_{\text{TDC}}$ determinations by BaCO_3 precipitation ($\delta^{13}\text{C}_{\text{TDC}}$ in the range -5.9 to $+5.4\text{‰}$). In another field trip, gas samples of CO_2 were taken for isotope analyses of carbon in $\text{CO}_2(\text{g})$. This sampling was also accompanied by precipitation of SrCO_3 for the $\delta^{13}\text{C}_{\text{TDC}}$ determinations. Isotopic analyses show that the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values are similar to the results reported by LIS (1986). The difference in $\delta^{13}\text{C}$ for particular sites do not exceed 0.3‰ and enables one to conclude that the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ is constant against time.

For the purpose of CO_2 sampling, syringes with manifold stopcocks were used to separate gas from water. Gas was separated from water by displacement with a syringe, then sucked into the evacuated sampling bottle. The analyses were performed at the Institute of Fossil Fuels, Academy of Mining and Metallurgy, Cracow. Samples precipitated in the field were washed and dried at 105°C . Because of the large quantity of carbon this procedure does not modify the isotopic composition of the precipitates. CO_2 was extracted on a vacuum line, purified according to the standard procedure (MCCREA 1950) and the $^{13}\text{C}/^{12}\text{C}$ ratio was measured. All results are given as δ (‰) against an internationally accepted V-PDB standard for carbon

and V-SMOW for oxygen. A familiar δ notation used throughout the paper is defined as: $\delta^{13}\text{C} = (\text{R}/\text{R}_s - 1) \cdot 10^3$ where R stands for the ratio of heavy to light isotopes ($^{13}\text{C}/^{12}\text{C}$) in sample (R) and in standard (R_s).

In some studies concerning CO_2 -charged waters (CORNIDES & KECSKES 1982, 1987) there is an incorrect assumption that the isotopic composition of precipitated carbonates is isotopically equivalent to the isotopic composition of HCO_3^- . Actually in some cases of low pH, low carbonated CO_2 -charged waters, $\text{CO}_2(\text{aq})$ contributes as much as 80% to the measured TDC values and this is directly reflected in the $\delta^{13}\text{C}$ values (LEŚNIAK 1989, 1994). The other species contributing to the TDC concentration is HCO_3^- . CORNIDES & KECSKES (1982, 1987) who sampled CO_2 -charged waters mostly in the Inner Carpathians interpreted their results in terms of $\delta^{13}\text{C}_{\text{HCO}_3^-}$ values, though frequently $\text{CO}_2(\text{aq})$ contributes more than 50% to the total dissolved carbonates (TDC) in these waters. In the limiting case, if TDC concentration is close to $\text{CO}_2(\text{aq})$ concentration the $\delta^{13}\text{C}_{\text{CO}_2(\text{aq})}$ value can be even more positive than $\delta^{13}\text{C}_{\text{TDC}}$, but not more than the difference of the δ values ($\Delta \approx \delta^{13}\text{C}_{\text{CO}_2(\text{aq})} - \delta^{13}\text{C}_{\text{CO}_2(\text{g})}$) known as the fractionation factor between $\text{CO}_2(\text{aq})$ and $\text{CO}_2(\text{g})$. At 10°C this fractionation is equal to -0.83‰ (DEINES & *al.* 1974), -1.13‰ (MOOK 1986) being close to the latest data -1.26‰ of ZHANG & *al.* (1995).

RESULTS AND DISCUSSION

The results of chemical and isotopic measurements are given in Tables 1 and 2. Generally, high alkalinities up to 300 meq/l are accompanied by high $\delta^{13}\text{C}_{\text{TDC}}$ values up to $+5.4\text{‰}$, and high $\delta^{13}\text{C}$ of $\text{CO}_2(\text{g})$ up to -1.8‰ .

The $\delta^{13}\text{C}_{\text{TDC}}$ values reported in Tables 1 and 2 were obtained by direct measurements and those in LEŚNIAK (1985) were calculated: this is the main reason for some discrepancies of the results.

The $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ measurements made on the samples of CO_2 of the deep well Zuber-1 gave different results. The $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ value of a sample taken from the CO_2 separation device was -1.9‰ and that of another CO_2 gas sample simultaneously separated from the associated water was -2.3‰ . It seems that in some cases the isotopic

No.	Name	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	H ₄ SiO ₄	B
	<u>Krynica</u>									
1	Zuber 1	5850	210	128.3	465.3	726.8	45	17503	36.9	7.8
2	Zuber 2	4500	145	176	759	266	45	16100	64	8.9
3	Zuber 3	6900	350	144	321	1152	63	19003	44.8	7.8
4	Zuber 4	6500	250	160.3	500.8	798	123	19512	35.2	3.3
5	Jan-A	12.5	1.7	132.1	25.5	23	55	466.8	38.4	n.d.
6	Słotwinka	340	12.5	252	287	7	3	3186	32	2.8
7	Tadeusz	12	3.3	783	79	3.6	15	2996	115	n.d.
8	Józef	11.5	1.5	199	31.1	16	75	685.8	38.4	0.7
9	K-18	75	8	830.5	185	5	2.5	3732	88.4	n.d.
10	K-10	270	12	802	896.4	7	1	779	122	n.d.
11	Mieczysław	390	33	430	163	10.6	1.0	3211	80	3
12	Milusia	370	25	279	376	10.6	10	3711	35.2	2.2
	<u>Muszyna</u>									
13	Antoni	300	20	301	936	9	1	6428	56	11.4
14	Piotr	150	12	319	164	10.6	10	2151	33.6	1.1
15	Anna	25	2	268	74	5.3	15	1283	43.1	n.d.
	<u>Złockie</u>									
16	Kolejarz-1	710	25	407	536	7	4	5881	64	4.5
17	Metalowiec-3	7.5	2	270	53	7	18	1068	57.6	0.6
18	Szczawnik-1	480	13	248	102	7	2.6	2571	48	1.7
	<u>Żegiestów</u>									
19	Anna Z.	16	2.3	442	121	5	30	1962	51	1
20	Żegiestów-2	1350	42	294	1191	94	2	10419	70.4	6.2
21	Zofia	520	21	286	278	35.5	20	3584	54.4	3.4
	<u>Piwiczna</u>									
22	Piwiczna-1	160	24	356	139	7	1	2291	51.2	2.8
23	Piwiczna-2	85	11.5	230	75.5	9	15	1306	32	1.7
	<u>Głębokie</u>									
24	Kinga-1	515	15.5	305	114	12	2	2937	32	7.8
25	Kinga-2	465	13.5	298	102	14.2	2	2677	35.2	7.3
	<u>Wysowa</u>									
26	Aleksandra	6880	112	282	27	3896	7.4	13015	9.6	198
27	Bronisława	1400	36.6	87.8	26.6	674	11	3066	12.8	61
28	W-12	1200	15.6	169	99	667	3	3123	12.8	10.2
29	W-14	5050	80	201	47.8	2754	8	9769	n.d.	n.d.
30	Józef-1	360	10.5	119	46	263	31	1099	16	37
	<u>Szczawnica</u>									
31	Jan	1000	32.5	136.6	38.5	528.3	1	2435	n.d.	n.d.
32	Magdalena	5500	90	104	175	4277	7.5	8314	32	284
33	Szymon	550	18	180	36.5	425.4	15	1477	32	28.4
34	Pitoniakowka(F)	1482	50	96	62	1336	78	2216	n.d.	n.d.
	<u>Cigel'ka</u>									
34	Cigel'ka P-1	8460	145	233	92.1	3794	0.1	15587	21.4	n.d.
	<u>Luhacovice</u>									
35	Vincentka 1	2320	106	220	22	1525	19.6	4351	5.2	n.d.
36	Vincentka 2	-	-	-	-	-	-	-	-	-
	<u>Bardejov</u>									
37	Bardejov BV-9	1120	27	166	52.8	469	22.8	2957	28.8	n.d.

Table 1. Representative chemical compositions of some of the CO₂-charged waters in the Outer West Carpathians (mg/l)
(JAROCKA & *al.* 1976)

No.	Name	t	pH	TDS	Alk.	P _{CO2}	TDC	$\delta^{13}\text{C}_{\text{TDC}}$	pH ^f	TDC ^f	α	$\delta^{13}\text{C}_{\text{TDC}}^f$
		°C		mg/l	meq/l	10•MPa	mmol/kg	‰		mmol/kg		‰
	<u>Krynica</u>											
1	Zuber-1	10.3	6.8	25010	286.6	1.73	371.5	5.4	6.96	346.7	0.9928	5.9
2	Zuber-2	7.9	6.75	22080	263.6	1.74	355.8	4.6	6.92	323.8	0.9929	5.2
3	Zuber-3	8.6	6.8	18980	311.2	1.85	406.3	5.1	6.99	371.3	0.9927	5.8
4	Zuber-4	8.8	6.9	27940	319.5	1.50	397.3	4.5	7.00	380.2	0.9925	4.9
5	Jan-A	10.5	5.2	754	7.643	2.39	129.6	-3.7	5.50	69.87	0.9999	-3.7
6	Słotwinka	9.2	5.95	4169	52.17	2.52	184.1	-1.9	6.27	113.8	0.9971	-0.5
7	Tadeusz	8.3	5.85	4075	48.84	2.97	209.0	1.5	6.25	110.6	0.9974	3.2
8	Józef	8.7	5.6	1057	11.23	1.35	83.91	-2.4	5.66	73.39	0.9970	-2.4
9	K-18	8.9	6.1	4959	61.11	2.03	168.1	1.1	6.33	122.5	0.9965	2.2
10	K-10	9.9	6.55	9932	127.5	1.36	196.4	3.4	6.61	188.1	0.9942	3.6
11	Mieczysław	9.2	6.05	4318	52.58	2.03	159.0	-0.4	6.28	114.2	0.9968	0.7
12	Milusia	11.1	6.4	4829	60.78	1.03	111.8	-3.1	6.33	122.2	0.9956	-3.5
	<u>Muszyna</u>											
13	Antoni	9.4	6.4	8077	105.2	1.62	188.5	-2.7	6.53	166.1	0.9948	-2.1
14	Piotr	10.5	6.35	2855	35.22	0.69	70.31	-3.3	6.12	96.99	0.9965	-4.4
15	Anna	11.0	5.9	1732	21.01	1.23	82.94	-2.2	5.91	83.01	0.9983	-2.2
	<u>Złockie</u>											
16	Kolejarz-1	10.8	6.7	7661	96.41	0.77	134.8	0.0	6.51	157.4	0.9942	-0.9
17	Metalowiec-3	11.2	6.1	1496	17.78	0.67	51.25	-3.6	5.84	79.84	0.9980	-4.5
18	Szczawnik-1	9.5	6.20	3490	42.15	1.19	104.2	-0.9	6.20	103.9	0.9968	-0.9
	<u>Żegiestów</u>											
19	Anna	10.9	6.05	974	11.05	1.27	95.89	-2.6	6.08	93.92	0.9974	-2.6
20	Żegiestów-2	10.3	6.05	13486	170.6	1.27	233.9	-1.3	6.72	230.9	0.9935	-1.2
21	Zofia	8.3	6.65	4802	58.69	0.55	88.69	0.0	6.32	120.2	0.9950	-1.5
	<u>Piwniczna</u>											
22	Piwniczna-1	11.1	6.15	3042	37.53	1.19	96.88	-2.8	6.14	99.29	0.9970	-2.9
23	Piwniczna-2	10.6	6.0	1769	21.38	1.00	72.20	-3.7	5.92	83.41	0.9981	-4.0
	<u>Głębokie</u>											
24	Kinga-1	9.3	5.75	3961	48.09	3.79	246.5	-5.9	6.25	109.8	0.9976	-4.0
25	Kinga-2	8.7	5.75	3634	43.83	3.46	228.6	-5.6	6.21	105.6	0.9978	-3.9
	<u>Wysowa</u>											
26	Aleksandra	12.5	6.85	25127	213.1	1.12	267.1	2.6	6.83	272.4	0.9930	2.5
27	Bronisława	10.2	6.2	5583	50.20	1.41	122.1	-1.5	6.27	111.7	0.9965	-1.2
28	W-12	10.0	6.35	5346	51.14	1.00	102.3	-0.7	6.27	112.6	0.9960	-1.1
29	W-14	9.9	6.7	16339	100.7	1.21	213.7	1.6	6.71	212.8	0.9936	1.6
30	Józef-1	11.5	5.85	2099	18.00	1.21	77.75	-3.2	5.85	79.98	0.9986	-3.2
	<u>Szczawnica</u>											
31	Jan	8.5	6.06	4326	40.26	1.60	126.3	-3.1	6.18	102.0	0.9972	-2.5
32	Magdalena	10.8	7.1	18820	136.1	0.42	157	1.2	6.64	195.5	0.9930	-0.3
33	Szymon	9.2	6.2	2764	24.18	0.70	61.10	-4.3	5.97	86.03	0.9974	-5.2
	<u>Cigelka</u>											
34	Cigelka V-99	10.2	6.9	28345	258.5	1.21	314.5	4.3	6.90	314.6	0.9927	4.3
	<u>Luhacovice</u>											
35	Vincentka-1	12.2	6.1	8570	71.63	2.44	186.9	-0.5	6.40	132.1	0.9962	0.8
36	Vincentka-2	12.0	6.5	8570	71.63	0.97	117.6	-0.4	6.40	132.1	0.9951	-1.0
	<u>Bardejov</u>											
37	Bardejov BV-9	20.0	6.0	4856	48.61	2.35	139.1	-0.9	6.25	110.0	0.9970	-0.2

Table 2. The results of chemical and isotopic measurements in the CO₂-charged waters in the Outer West Carpathians; TDC concentration is given in mmol/kgH₂O, $\alpha \approx 1/\alpha_{\text{TDC,CO}_2(\text{g})}$ stands for average equilibrium fractionation between the initial value (at field conditions) and final values (TDC^f, pH^f, $\delta^{13}\text{C}^f$) at 0.12 MPa, 10°C

signal of fluids such as $\delta^{13}\text{C}$ could be modified if gas separators are used for collecting CO_2 gas on the headspace of the wells.

Several sample duplicates were taken to make sure the results are reliable. At the site W-12 (Wysowa), when gas separation was done in a syringe, an immediate separation and separation requiring several minutes gave similar isotopic values: $\delta^{13}\text{C}_{\text{CO}_2(\text{g})} = -4.4$ and -4.5% and $\delta^{18}\text{O}_{\text{CO}_2(\text{g})} = -7.0$ and -6.9% (V-PDB). Similar comparisons were made on waters from Z-II, Złockie exhalation, Głębokie K-2: all $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and $\delta^{18}\text{O}_{\text{CO}_2(\text{g})}$ values were within the range of 0.3% .

Systematics of carbon isotopes distribution

Because of the elevated P_{CO_2} pressure in the Carpathians and other sites where CO_2 -charged waters occur, the total dissolved carbonates concentration (TDC) at depth consists mainly of $\text{CO}_2(\text{aq})$ and only partially of HCO_3^- concentration. On the contrary, at the Earth surface the $\text{CO}_2(\text{aq})$ content is much less than at depth as it is converted directly to CO_2 gas during ascent. A general assumption is made: on the way upward, when major geochemical processes such as mineral dissolution which supplies additional cations have been completed, alkalinity is considered to be constant for a given water because the net charge balance of ions is not affected by CO_2 gas dissolution or outgassing. Although the precipitation of carbonates can sometimes appreciably change the alkalinity of groundwaters, carbon loss in $\text{CO}_2(\text{g})$ of CO_2 -rich waters close to the Earth surface highly overweighs the mass of carbon precipitated as CaCO_3 . Therefore, it is assumed that the alkalinity in outgoing springs is not influenced by carbonate precipitation. However, only waters devoid of tritium are subject to this assumption because it is valid only in the absence of mixing. For other waters a provision should be made for the mixing effect.

When waters saturated with gases rise to the surface, the loss of hydrostatic pressure enables separation of the CO_2 gas phase. In consequence, TDC concentration decreases because of the loss of $\text{CO}_2(\text{aq})$ while pH increases.

In all Carpathian carbonated waters sampled at the surface, bicarbonate concentration and pH increase proportionally (Text-fig. 2). This suggests that a unique external reservoir of CO_2 con-

trols the water pH according to the reaction: $\text{CO}_2(\text{g}) + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^-$. At equilibrium the following relation applies (Text-fig. 2):

$$\text{pH} = \log\{\text{HCO}_3^-\} - \log K_{\text{H}} K_1 - \log P_{\text{CO}_2} - \log\{\text{H}_2\text{O}\} \quad (3)$$

where K_{H} designates the gas hydration constant, and K_1 indicates the first dissociation constant of carbonic acid (PLUMMER & BUSENBERG 1982). Curled brackets are for ionic activities. The general estimation of P_{CO_2} at depth prior to degassing can be obtained from measurements of pH and carbonate alkalinity in waters of the lowest dissolved carbonates concentration (SARAZIN & *al.* 1986). Although waters of high TDC concentration have pH by two orders higher than the waters of the low TDC concentrations, all of them display in fact similar P_{CO_2} at the Earth surface. This suggests that pH is not significantly affected by outgassing. Therefore, combining the carbonate speciation for waters of high TDC concentration (~ 400 mmol/kg H_2O) with pH equal to 5.5, typical for water of the lowest TDC concentration (~ 100 mmol/kg H_2O), allow for P_{CO_2} estimation prior to outgassing (at depth). It is 45 times higher than at the surface at 10°C , i.e. 4.5

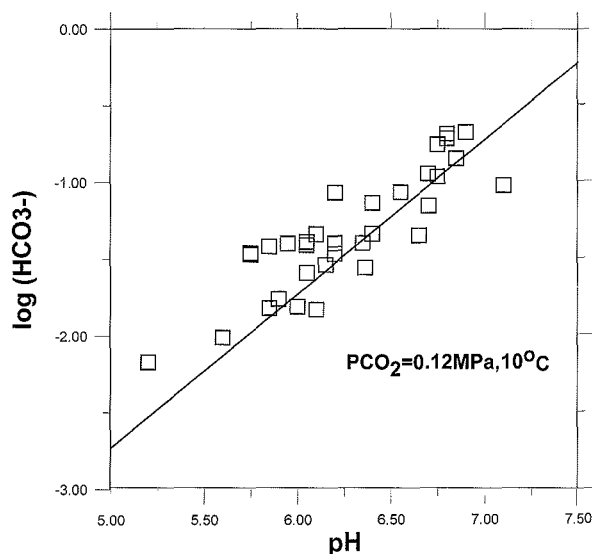


Fig. 2. pH values measured in the field versus negative logarithm of bicarbonate activity; equilibrium line corresponds to $P_{\text{CO}_2}=0.12$ MPa at 10°C ; observe a wide range of pH at which a relationship holds; this relationship represents a common pattern in CO_2 charged waters in Carpathians

MPa. That generalized estimation agrees with the maximum CO_2 pressure measured at the closed well-head of some of the Zuber wells.

There is an important difference between the process of carbon outgassing and distillation which results in fractionation of oxygen and hydrogen isotopes in clouds. While the fractionation factor of oxygen and hydrogen isotopes is dependent only on temperature (therefore it is constant

at isothermal condition), the carbon isotope fractionation between $\text{CO}_2(\text{g})$ and total dissolved carbonates (TDC) (equilibrium fractionation or fractionation) depends on temperature and on the distribution of carbonate species in solution.

An isotopic equilibrium in an open system can be expressed by the non-linear relationship between $\delta^{13}\text{C}_{\text{TDC}}$ and the TDC concentration, where the $\delta^{13}\text{C}_{\text{TDC}}$ is a function of P_{CO_2} and $\delta^{13}\text{C}_{\text{CO}_2}$ (Text-fig. 3). The relationship is given by previously derived equation (LEŚNIAK 1985):

$$\delta^{13}\text{C}_{\text{TDC}} = (10^3 + \delta^{13}\text{C}_{\text{CO}_2(\text{g})}) \frac{[\alpha_0/\gamma_0 + \alpha_1 K_1/(\gamma_1 H) + \alpha_2 K_1 K_2/(\gamma_2 H^2)]}{[1/\gamma_0 + K_1/(\gamma_1 H) + K_1 K_2/(\gamma_2 H^2)]} - 10^3 \quad (4)$$

where α_0 , α_1 , α_2 designate fractionation factors between $\text{CO}_2(\text{aq})$ and $\text{CO}_2(\text{g})$, HCO_3^- and $\text{CO}_2(\text{g})$, CO_3^{2-} and $\text{CO}_2(\text{g})$, respectively. K_1 and K_2 stand for the first and the second dissociation constants of carbonic acid, H abbreviates hydrogen ion (H^+) activity, γ_0 , γ_1 and γ_2 indicate ion activity coefficients of $\text{CO}_2(\text{aq})$, HCO_3^- and CO_3^{2-} , respectively, calculated by Davies equation. Fractionation factors used throughout the present work are those of DEINES & *al.* (1974) which are similar to the latest values given by ZHANG & *al.* (1995).

P_{CO_2} controls pH by virtue of Eq.1 and is implicitly incorporated in equation 2 through the equilibrium constant K_1 . The $\delta^{13}\text{C}_{\text{TDC}}$ values versus TDC concentrations of the Carpathian carbonated waters were superimposed to the curves (Text-fig. 3) based on the Eq. 2. The points correspond to the results shown in Table 2. In the TDC reported concentration range there is an apparent trend of the points to mimic the shape of the curves. Generally however, the points are scattered. Ideally, in an open system P_{CO_2} could be equal in all sites, but in fact it is different because of the variation in hydrostatic pressure as well as of other less identified reasons. The isotopic compositions at particular sites have been adjusted by recalculating all pairs of the TDC and the $\delta^{13}\text{C}_{\text{TDC}}$ values to correspond to the condition of $P_{\text{CO}_2} = 0.12 \text{ MPa}$ and 10°C . For this purpose PHREEQE program (PARKHURST & *al.* 1980) and a separate isotopic routine CABIST written by author were used. The latter procedure calculates the $\delta^{13}\text{C}_{\text{TDC}}$ values at $P_{\text{CO}_2} = 0.12 \text{ MPa}$ and 10°C taking account of an average fractionation $\alpha_{\text{CO}_2(\text{g})-\text{TDC}} = \sum_i \alpha_{\text{CO}_2(\text{g})-i} X_i$ between initial and final solutions, where $\alpha_{\text{CO}_2(\text{g})-i}$ denotes fractionation factor between $\text{CO}_2(\text{g})$ and designated species and X_i is for the con-

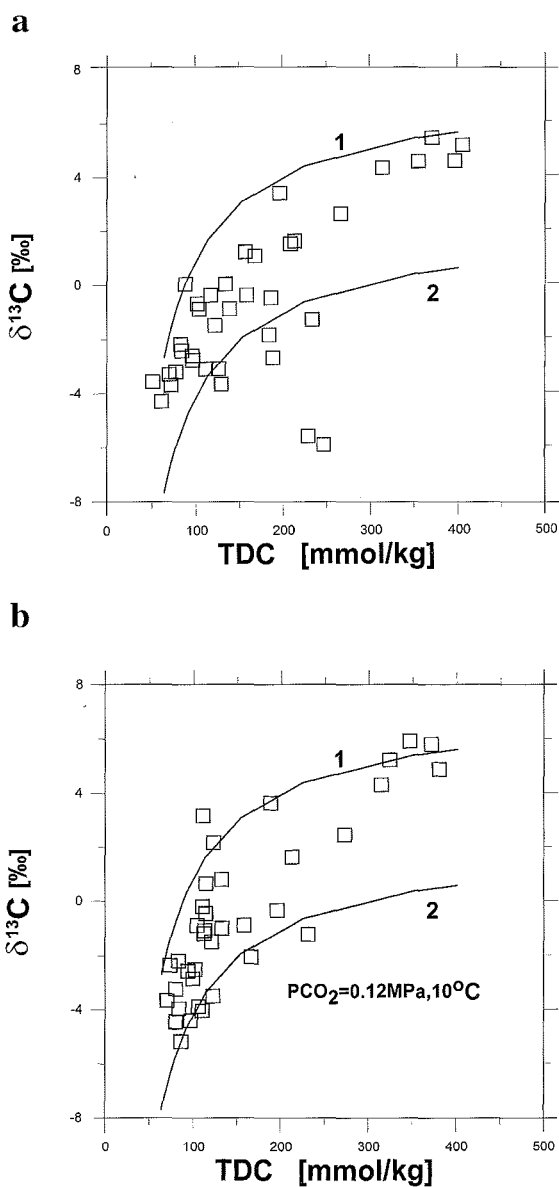


Fig. 3a, b. Relationship between the $\delta^{13}\text{C}_{\text{TDC}}$ values and TDC concentrations in CO_2 -charged waters; (a) at field pH's and temperatures, (b) at $P_{\text{CO}_2} = 0.12 \text{ MPa}$ and 10°C ; isotopic equilibrium curves are for $\delta^{13}\text{C}_{\text{CO}_2(\text{g})} = -2\text{‰}$ (1) and -7‰ (2)

tribution of carbonate species to the TDC concentration. In order to minimize the error associated with the average fractionation, the outgassing/in-gassing process was divided into several steps.

No single CO₂ gas phase is in isotopic equilibrium with all waters (Text-fig. 3a). In high TDC waters with δ¹³C_{CO₂(g)} values close to -2‰ isotopic equilibration between CO₂(g) and dissolved carbonates is most likely, but low TDC waters could be in equilibrium with CO₂ gas with δ¹³C close to -7‰. At the same P_{CO₂} and temperature, waters in Text-fig. 3b show considerably less scatter of δ¹³C_{TDC} values than at original field conditions.

Test for isotopic equilibrium

The measurements of both δ¹³C_{TDC} and δ¹³C_{CO₂(g)} values were made at several sites

(Table 3). When δ¹³C_{TDC}, pH and temperature are measured and chemical analyses are made at the same time as the total dissolved carbonates are precipitated, it is possible to calculate the δ¹³C_{HCO₃} values in order to verify if there is an isotopic equilibrium between bicarbonate and CO₂ gas. Such a calculation depends on temperature and carbonate species distribution. Results of the calculation performed using program PHREEQE and isotopic routine CABIST are denoted as δ¹³C_{HCO₃}^{*}.

Much less error is associated with the δ¹³C_{HCO₃} values calculated from δ¹³C_{CO₂(g)} and the fractionation factor between CO₂ gas and bicarbonate:

$$\delta^{13}\text{C}_{\text{HCO}_3}^{**} = [(\delta^{13}\text{C}_{\text{CO}_2(\text{g})} + 1000) / \alpha_{\text{CO}_2(\text{g})-\text{HCO}_3}] - 1000. \quad (5)$$

Name	temp °C	P _{CO₂} 10·MPa	X[CO ₂ (aq)]	X[HCO ₃]	δ ¹³ C _{TDC} ‰	δ ¹³ C _{CO₂(g)} ‰	δ ¹³ C _{HCO₃} [*] ‰	δ ¹³ C _{HCO₃} ^{**} ‰
<u>Krynica</u>								
Zuber1	10.3	1.73	0.22	0.78	5.4	-1.9	7.74	7.26
Zuber2	7.9	1.74	0.25	0.75	5.7	-1.8	7.34	7.60
Zuber 4	8.8	1.5	0.19	0.81	5.4	-1.8	6.56	7.51
Główne	8.8	1.33	0.48	0.52	-3.7 [#]	-3.5	1.47	5.8
K-18	8.9	2.03	0.63	0.37	1.3	-3.25	7.92	6.04
K-9	8.8	1.14	0.53	0.47	-2.6 [#]	-3.8	3.12	5.49
<u>Muszyna</u>								
Antoni	9.4	1.62	0.44	0.56	-2.8	-7.4	2.01	1.8
<u>Żegiestów</u>								
Anna	10.9	1.27	0.66	0.34	-2.6 [#]	-5.6	4.36	3.47
Żegiestow 2	10.3	1.27	0.62	0.38	-2.0	-6.40	5.29	2.72
<u>Głębokie</u>								
Kinga 2	8.7	3.46	0.8	0.2	-7.1	-9.2	3.04	0.05
<u>Wysowa</u>								
Aleksandra	12.5	1.12	0.2	0.8	3.3	-3.9	4.67	5.03
W-12	10.0	1.0	0.5	0.5	-0.7 [#]	-4.4	4.63	4.77
W-14	9.9	1.21	0.28	0.72	2.3	-4.2	4.59	4.98
<u>Szczawnica</u>								
Magdalena	10.8	0.42	0.13	0.87	-0.4	-5.5	2.57	3.58
Jan Szczawnica	8.5	1.60	0.68	0.32	-3.3	-8.9	4.27	0.37
Pitoniakowka	10.0	1.20	0.53	0.47	-6.5	-6.9	-0.88	2.25
<u>Szczawa</u>								
Szczawa 2	10.0		0.48	0.52	1.1	-6.0	6.22	3.15

Table 3. Calculated δ¹³C_{HCO₃} values for waters where both phases CO₂ gas and solution were taken at the same time for δ¹³C_{CO₂} and δ¹³C_{TDC} analyses; X designates contribution of specified carbonate species to TDC concentrations, P_{CO₂} is given in 10·MPa, [#] δ¹³C_{TDC} is taken from Tab. 2, * δ¹³C_{HCO₃} values calculated from carbonate chemistry and δ¹³C_{TDC}; ** δ¹³C_{HCO₃} values calculated from δ¹³C_{CO₂(g)} and fractionation factor between CO₂ gas and bicarbonate

If we assume the temperature of discharge as the temperature of equilibration, the $\delta^{13}\text{C}_{\text{HCO}_3^*}$ values often do not agree within $\pm 1\text{‰}$ with the $\delta^{13}\text{C}_{\text{HCO}_3^{**}}$ values. The difference between these two values can be a measure of departure from isotopic equilibrium. Generally, the CO_2 gases in waters of Wysowa, in two of the three Zuber wells, and in Muszyna (Antoni) are found to be close to isotopic equilibrium with dissolved carbonates. For other waters disequilibrium is apparent at the discharge temperature. In Tylicz, DULIŃSKI (1995) found that the precipitation of CaCO_3 which accompanies degassing had occurred under conditions close to the carbon isotopic equilibrium.

The uncertainties involved in these calculations are mainly due to estimating carbonate species concentrations which, in turn, are based on pH measurements. The error also propagates in the calculations. It is proportional to the TDC concentration as was shown by Monte Carlo method (LEŚNIAK 1989). Highly carbonated waters in which $\text{CO}_2(\text{aq})$ concentration contributes less than 50% to the TDC concentration seem more likely to be in isotopic equilibrium with their $\text{CO}_2(\text{g})$ (Table 3). The CO_2 -charged water system in Carpathians resembles the laboratory experiments conducted by LEŚNIAK & SAKAI (1989) where CO_2 at 0.1 MPa was bubbled through a 300 mmol/l NaHCO_3 solution. There, the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ signature was apparently constant and the $\delta^{13}\text{C}_{\text{HCO}_3}$ value evolved to the equilibrium state during 3 days. In the natural systems like Carpathians, however, a continuous CO_2 bubbling through years seems to be equally efficient in the attainment of equilibrium.

Local mixing and outgassing

The fluids whose composition result from deep geochemical processes such as rock dissolution, precipitation etc., are usually mixed with near-surface groundwaters. This last event is best recognized in Wysowa in terms of chemical and isotopic tracers such as $\delta^{18}\text{O}$, δD and tritium (LEŚNIAK 1980). A more detailed understanding of the mixing and degassing processes occurring over the area is possible by integrating the actual geochemical and isotopic features within the framework of the idealised carbonate system $\text{CO}_2\text{-H}_2\text{O}$.

Typical groundwater with $\text{Alk} \approx 1.0$ meq/l at $\text{pH}=7$ and $\delta^{13}\text{C}_{\text{TDC}} \approx -13\text{‰}$ (DEINES & *al.* 1974) cannot be a candidate for a dilute end-member in the present mixing model. It must be a solution which contains much more carbon and that carbon must be enriched in the ^{13}C isotope in comparison to the typical groundwater. Starting from the above groundwater composition, a dilute end-member solution with alkalinity of 1.0 meq/l, at $P_{\text{CO}_2} = 0.12$ MPa and 10°C was modelled using a PHREEQE program. An addition of CO_2 moves pH of the solution down to 4.2 and raises TDC concentration up to 64 mmol/kg H_2O . The $\delta^{13}\text{C}_{\text{TDC}}$ value was obtained using subroutine CABIST which utilises the chemical output of PHREEQE and calculates $\delta^{13}\text{C}$ of the respective carbonate species based on the isotopic equilibrium of carbonate system. For $\delta^{13}\text{C}_{\text{CO}_2(\text{g})} = -4\text{‰}$ (close to an average found for Wysowa), if there is no fractionation at the gas input (usual case) the resulting $\delta^{13}\text{C}_{\text{TDC}} (\approx \delta^{13}\text{C}_{\text{CO}_2(\text{aq})})$ value of the CO_2 -rich dilute end-member will be close to that of the charging gas i.e., -5‰ . The CO_2 attending

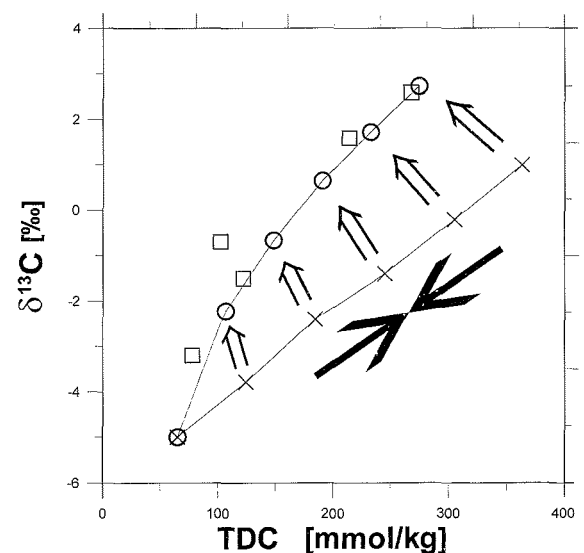


Fig. 4. Model of mixing and outgassing processes in $\delta^{13}\text{C}_{\text{TDC}}$ and TDC co-ordinates; mixing line between two end-members: $\delta^{13}\text{C}_{\text{TDC}} = 1\text{‰}$, TDC = 363 mmol/kg ($P_{\text{CO}_2} = 0.3$ MPa, 10°C) and $\delta^{13}\text{C}_{\text{TDC}} = -5\text{‰}$, TDC 64 mmol/kg ($P_{\text{CO}_2} = 0.12$ MPa, 10°C) is given by crosses and the curve designated by circles corresponds to TDC concentrations and $\delta^{13}\text{C}_{\text{TDC}}$ at $P_{\text{CO}_2} = 0.12$ MPa and 10°C (after outgassing); open squares are for the actual $\delta^{13}\text{C}_{\text{TDC}}$ values and TDC concentrations in Wysowa waters (Table 2); black arrows indicate mixing and white arrows show changes in compositions due to outgassing

water has an overwhelming influence on the $\delta^{13}\text{C}_{\text{TDC}}$ values of groundwater end-member. In fact, such a CO_2 -rich solution can not be considered as a typical groundwater because of its low pH, high TDC concentration and high $\delta^{13}\text{C}_{\text{TDC}}$ values. Waters of this type are known exclusively in areas penetrated by CO_2 of deep origin. An example of a permanent spring discharging such CO_2 -rich solution with $\text{pH}=4.3$ is known in Příbislíná in the Slovak Republic.

A second end-member was chosen to be similar in composition to the Aleksandra water, the most concentrated solution in the area (Table 1). The $\delta^{13}\text{C}_{\text{TDC}}$ of the Aleksandra water is $+3.3\text{‰}$ at CO_2 pressure about 0.1 MPa at the Earth surface. It was assumed that at some depth, at elevated pressure, its $\delta^{13}\text{C}_{\text{TDC}}$ is lower. The $\delta^{13}\text{C}_{\text{TDC}}$ value equal to $+1\text{‰}$ was arbitrarily assigned to account for higher CO_2 pressure (0.3 MPa) prior to the outgassing (equivalent to the TDC concentration of 363 mmol/kg H_2O at $\text{Alk} = 213$ meq/l), an assumption consistent with the decreasing P_{CO_2} gradient towards the Earth surface.

Mixing between the specified end-members provides a linear pattern in the $\delta^{13}\text{C}_{\text{TDC}}$ and TDC co-ordinates because total carbonate concentration is conserved in the mixing process. If the obtained mixed solutions are outgassed to reach a similar pressure (0.12 MPa at 10°C), $\delta^{13}\text{C}_{\text{TDC}}$ versus TDC forms a convex curve which approximately fits the true mixing curve (Text-fig. 4) as opposed to a straight line obtained from simple mixing.

The intermediate isotopic compositions for the mixed solutions were obtained via Rayleigh distillation for one output system (WIGLEY & al. 1978):

$$\delta^{13}\text{C}_{\text{TDC}}^f = (10^3 + \delta^{13}\text{C}_{\text{TDC}}^i) F^{(\alpha-1)} - 10^3 \quad (6)$$

where $\delta^{13}\text{C}_{\text{TDC}}^i$ and $\delta^{13}\text{C}_{\text{TDC}}^f$ designate isotopic composition at the beginning and at the end of the process, α indicates the average isotopic fractionation between $\text{CO}_2(\text{g})$ and TDC concentration over the reaction step and F stands for the fraction of the TDC concentration left.

Although the choice of parameters in the model is arbitrary, the above scenario reproduces quite sufficiently the isotopic and geochemical paths of the carbonate system (Text-fig. 4). The model seems to integrate most of the parameters which control chemical and isotopic compositions of waters of interest and predicts the correct

direction of change of the quantities such as TDC and $\delta^{13}\text{C}_{\text{TDC}}$.

The close coincidence between the measured $\delta^{13}\text{C}_{\text{TDC}}$ values and the derived curves in Text-figs 3 and 4 indicates that mixing and outgassing, as described on a local scale in Wysowa, can also be responsible for changes in the chemical and isotopic water composition on a regional scale.

The $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ evolution

The CO_2 degassing at the Earth surface seems to have no apparent effect on the quantity of carbon dissolved in waters and CO_2 gas within the flysch rock.

Gas may flow to the surface in one of the following ways:

- 1) direct flow of the gas to the Earth surface ("dry" flow);
- 2) one-phase flow of water with dissolved CO_2 through the aquifer followed by separation of liquid and gaseous phases close to the Earth surface;

Neglected is the flux from biogenic soil CO_2 to the atmosphere due to elevated P_{CO_2} in soil.

In the first case at different periods of year the atmospheric precipitation may locally leak through the soil supplying dry CO_2 discharges with water. These temporary dry emissions of CO_2 gas in Złockie and Krynica-Tylicz areas have $\delta^{13}\text{C}$ values between -2 and -1‰ . Most probably, however, these exhalations represent CO_2 phase separated from waters close to the Earth surface.

The second case is common in CO_2 -charged springs. If CO_2 -charged water flows laterally through the aquifer, the constant P_{CO_2} fixes TDC concentration and $\delta^{13}\text{C}_{\text{TDC}}$; at high P_{CO_2} at depth TDC concentration consists mostly of the $\text{CO}_2(\text{aq})$ species unless the solution advects in the carbonate aquifer. During an ascendent flow to the surface the $\text{CO}_2(\text{g})/\text{H}_2\text{O}$ volume ratio increases but the $\text{CO}_2(\text{g})/\text{TDC}$ molal ratio – due to the outgassing – decreases (Text-figs 5a, b). When the CO_2/TDC carbon molal ratio is approaching 1 ($\text{CO}_2/\text{H}_2\text{O}$ volume ratio exceeding 300), the conditions are highly favourable for isotopic exchange to occur between phases. The available data show that at a depth of about 500 m the measured CO_2 pressure in the Zuber-3 well was about 4.5 MPa at 16°C (ŚWIDZIŃSKI 1972) which is

equivalent to 2.13 molal solution or 3.8% of CO₂ by volume. Calculations performed by PHREEQE (PARKHURST & *al.* 1980) show that if this carbonated solution is outgassed, then the CO₂(aq)/TDC molal ratio (CO₂(aq) is directly proportional to CO₂(g)) is reduced by 50%,

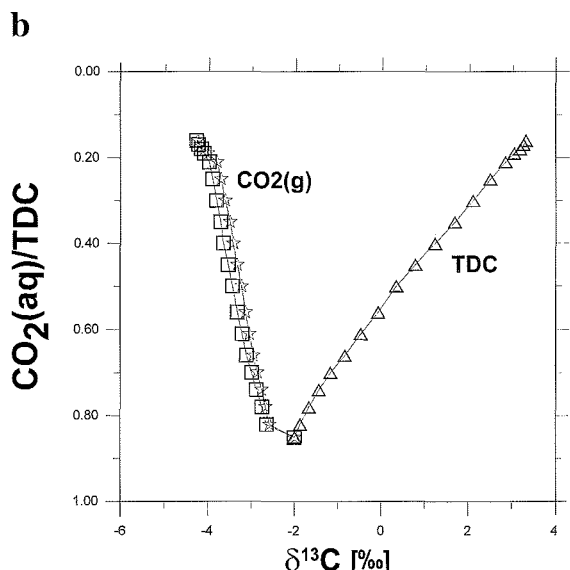
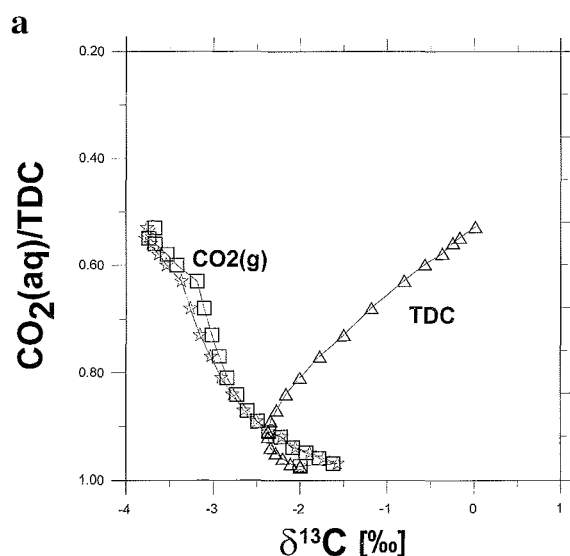


Fig. 5a, b. $\delta^{13}\text{C}_{\text{TDC}}$ values versus $\text{CO}_2(\text{aq})/\text{TDC}$ ratio in the model of outgassing of: (a) water of high alkalinity 328.6 meq/l – Zuber-3, (b) water of low alkalinity 51.4 meq/l – K-9; initial condition are 4.6 MPa, 16°C, $\delta^{13}\text{C}_{\text{CO}_2(\text{g})} = -2\text{‰}$; asterisks indicate evolving compositions of isolated CO₂ (instantaneous product), squares designate evolving composition of accumulated CO₂ while triangles stand for δ values of residual TDC concentrations

which is equivalent of converting half of the total dissolved carbonates to the gas phase (Text-fig. 5a). In the case of low alkalinity waters, the CO₂(aq)/TDC molal ratio is reduced by 70% through degassing under similar initial conditions (4.5 MPa at 16°C; Text-fig. 5b).

The coexistence of two phases, CO₂ and H₂O, is possible up to temperatures of 150°C and pressures above 2 kbars. The addition of salts, as little as 5%, extends the boundary of immiscibility up to 300°C (GEHRIG 1979).

Equation 6 predicts a response of the $\delta^{13}\text{C}_{\text{TDC}}$ value to degassing. The $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ depends on the way of accumulation of CO₂(g) after separation from a parent solution. The CO₂ phase can be isolated from a parent solution (trapped CO₂, instantaneous CO₂ product) or continuously accumulated forming a two-phase system. The $\delta^{13}\text{C}$ of the isolated CO₂(g) is:

$$\delta^{13}\text{C}_{\text{CO}_2(\text{g})} = [(10^3 + \delta^{13}\text{C}_{\text{TDC}})/\alpha] - 10^3 \quad (7)$$

where α stands for fractionation between CO₂(g) and TDC, $\delta^{13}\text{C}_{\text{TDC}}$ – is the remaining reactant given by (6). The accumulated CO₂(g) remains in contact with the solution and $\delta^{13}\text{C}$ of that CO₂(g) is calculated by the Rayleigh distillation formula (FRITZ & FONTES 1980):

$$\delta^{13}\text{C}_{\text{CO}_2(\text{g})}^f = (10^3 + \delta^{13}\text{C}_{\text{TDC}}^i) (1-F)^\alpha / (1-F) - 10^3 \quad (8)$$

where F is a fraction of degassed CO₂, superscripts i and f indicate initial and final compositions, respectively.

In the simple model of degassing of high and low alkalinity waters the calculations indicate, that the $\delta^{13}\text{C}$ of both isolated and accumulated CO₂(g) decrease with CO₂ loss (Text-fig. 5). The process yields similar $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values of about -3.7‰ at different CO₂(aq)/TDC ratio. In the case when the remaining dissolved carbonates may be considered as belonging to an infinite or continuously replenished reservoir with respect to the quantity of the released gas, the $\delta^{13}\text{C}$ of CO₂(g) does not change with CO₂(aq)/TDC ratio. The comparison of the present $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ data and that of LIS (1986) indicate that, for a given site, Carpathian $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ signatures are essentially constant with time. The reason of dissimilar $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values at different localities can be investigated in more details through the space dependent one dimensional model of CO₂(g) and carbonated solution advection coupled to isotope exchange.

One-dimensional advective transport and isotopic exchange

A model of the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ evolution is more instructive when exchange of carbon isotopes between $\text{CO}_2(\text{g})$ and HCO_3^- is coupled to: 1) the advective flow of $\text{CO}_2(\text{g})$ and carbonated solution; 2) $\text{CO}_2(\text{g})$ advection through stagnant carbonated solution. As it was evidenced above, the equilibrium outgassing does not allow for the formation of CO_2 with the low $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values as it occurs in several sites including Carpathians (Tab. 2). However, within the assumed initial and boundary conditions, the occurrence of such low $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values is possible as predicted by the model of advective flow of the gas through stagnant solution. In a natural setting the situation tends to be in between the two extremes (one-phase and two-phase flow model) because bubbling CO_2 gas usually lags behind the flowing carbonated solution.

The essential questions are: how long does it take for an isotopic equilibrium to be established for carbon in CO_2 -rich groundwater system and what is the time and space distribution of the isotopic composition of carbon in the main carbonate solutes? DULIŃSKI & al. (1995) indicate 40s as a minimum equilibration time for carbon isotopes in CO_2 - H_2O system. They noted that in the open CO_2 system the time for equilibration becomes considerably longer.

The derived rates of a change of $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and $\delta^{13}\text{C}_{\text{HCO}_3^-}$ are based on the development made in the field of carbon, sulfur and oxygen isotope exchange in the homogenous and heterogeneous systems (MILLS & UREY 1940, OHMOTO & LASAGA 1982, CHIBA & SAKAI 1985, COLE & al. 1983, CRISS & al. 1987, LASSEY & BLATTNER 1988, MCKIBBIN & ABSAR 1989). The starting equation is a mass conservation equation for a fluid:

$$\partial(\rho_f \phi) / \partial t = -\nabla q \rho_f \quad (9)$$

where q stands for Darcy velocity of the fluid, t is for time, ϕ indicates porosity and ρ_f designates density of fluid. In the 1-D space, when the density of the fluid ρ is replaced by concentration C (^{12}C), considering a CO_2 -rich fluid with main carbonate species $\text{CO}_2(\text{g})$, $\text{CO}_2(\text{aq})$ and HCO_3^- , this equation is transformed into a mass conservation equation for heavy isotope ^{13}C :

$$\begin{aligned} \partial[(C_{\text{CO}_2(\text{g})} R_{\text{CO}_2(\text{g})} + C_{\text{CO}_2(\text{aq})} R_{\text{CO}_2(\text{aq})} \\ + C_{\text{HCO}_3^-} R_{\text{HCO}_3^-}) \phi] / \partial t = \\ - q \partial(C_{\text{CO}_2(\text{g})} R_{\text{CO}_2(\text{g})} + C_{\text{CO}_2(\text{aq})} R_{\text{CO}_2(\text{aq})} \\ + C_{\text{HCO}_3^-} R_{\text{HCO}_3^-}) / \partial z \quad (10) \end{aligned}$$

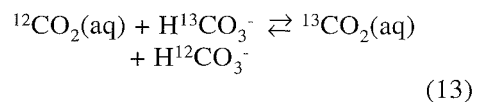
where R_i indicates the ratio of heavy to light isotope $^{13}\text{C}/^{12}\text{C}$ and z is for length. There are two phases considered, $\text{CO}_2(\text{g})$ and an aqueous phase in which two carbonate species $\text{CO}_2(\text{aq})$ and HCO_3^- contribute to TDC. The amount of CO_3^{2-} species is negligible at pH kept (≤ 7) throughout the simulation, hence, changes of $\delta^{13}\text{C}_{\text{CO}_3}$ in time and space were ignored. No source or sinks of ^{13}C in the solid matrix, i.e., no exchange with CaCO_3 is assumed. R_i can be replaced by δ_i ($\delta_i = R_i/R_{\text{st}} - 1$) 10^3 , where δ_i is an abbreviation for $\delta^{13}\text{C}_i$. After dividing the equation by $C_{\text{HCO}_3^-}$ and introducing $\Phi = (C_{\text{CO}_2(\text{g})}/C_{\text{HCO}_3^-}) \sim K_{\text{H}}(C_{\text{CO}_2(\text{aq})}/C_{\text{HCO}_3^-})$ where K_{H} indicates hydration constant of CO_2 one obtains:

$$\begin{aligned} \partial[(\Phi \delta_{\text{CO}_2(\text{g})} + K_{\text{H}} \Phi \delta_{\text{CO}_2(\text{aq})} + \delta_{\text{HCO}_3^-}) \phi] / \partial t = \\ - q [\partial(\Phi \delta_{\text{CO}_2(\text{g})} + K_{\text{H}} \Phi \delta_{\text{CO}_2(\text{aq})} + \delta_{\text{HCO}_3^-}) / \partial z] \quad (11) \end{aligned}$$

The equation 10 can be finally written as:

$$\begin{aligned} \partial(\Phi \delta_{\text{CO}_2(\text{g})}) / \partial t = \\ - q / \phi [\delta_{\text{CO}_2(\text{g})} \partial \Phi / \partial z + \Phi \partial \delta_{\text{CO}_2(\text{g})} / \partial z \\ + K_{\text{H}} (\delta_{\text{CO}_2(\text{aq})} \partial \Phi / \partial z + \Phi \partial \delta_{\text{CO}_2(\text{aq})} / \partial z) \\ + \partial \delta_{\text{HCO}_3^-} / \partial z] \\ - K_{\text{H}} \Phi \partial \delta_{\text{CO}_2(\text{aq})} / \partial t \\ - \partial \delta_{\text{HCO}_3^-} / \partial t \quad (12) \end{aligned}$$

It says that the rate of isotope exchange is balanced by the rate at which isotopes are swept away by advection. Considering the isotope exchange reaction:



the rate of change of $\delta^{13}\text{C}_{\text{HCO}_3^-}$ is:

$$\partial \delta_{\text{HCO}_3^-} / \partial t = -k_1 (\alpha_1 \delta_{\text{HCO}_3^-} - \delta_{\text{CO}_2(\text{aq})} + \Delta_1) C_{\text{CO}_2(\text{aq})} \quad (14)$$

and similarly for $\delta_{\text{CO}_2(\text{aq})}$. The abbreviation $\alpha_1 \equiv \alpha_{\text{CO}_2(\text{aq})-\text{HCO}_3^-}$ stands for the fractionation factor and $\Delta_1 = 10^3(\alpha_{\text{CO}_2(\text{aq})-\text{HCO}_3^-} - 1)$ designates the apparent fractionation. The consistent new

data of Zhang & al. (1995) give: $\Delta_1 = 0.119T(^{\circ}\text{C}) - 12.09$ (‰). The abbreviation k_1 stands for the rate of 'isotopic exchange' in reaction (13).

Equations 12 and 14 constitute the coupled differential equations describing isotopic changes of the CO_2 gas in contact with carbonated solution as a function of time and position in one-dimensional porous medium.

For the case when only CO_2 gas advects through a stagnant carbonated solution of constant chemical composition, the previous equation 12 simplifies to the following:

$$\begin{aligned} \partial(\Phi\delta_{\text{CO}_2(\text{g})})/\partial t = & -q/\phi [\delta_{\text{CO}_2(\text{g})}\partial\Phi/\partial z + \\ & \Phi\partial\delta_{\text{CO}_2(\text{g})}/\partial z] \\ & -K_{\text{H}}\Phi \partial\delta_{\text{CO}_2(\text{aq})}/\partial t \\ & -\partial\delta_{\text{HCO}_3}/\partial t \end{aligned} \quad (12')$$

and equation 14 still holds.

The kinetic equation 14 can easily be reduced to equilibrium relation: $\delta_{\text{HCO}_3} = \delta_{\text{CO}_2(\text{aq})} - \Delta_1$. Perhaps the most useful parameter which allows for estimates of the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$, $\delta^{13}\text{C}_{\text{HCO}_3}$ and $\delta^{13}\text{C}_{\text{TDC}}$ variations during flow and reaction is the non-dimensional Damköhler number used commonly in geochemical studies (McKIBBIN & al. 1986, LASSEY & BLATTNER 1988). It is defined as: $Da = k_1 z \phi / q$ where z designates the length of advective flow (m), ϕ indicates the effective porosity (), q stands for Darcy velocity of fluid ($\text{m}^3/\text{m}^2\text{s}$), k_1 is 'isotopic exchange rate' (s^{-1}). The Damköhler number expresses the relative importance of a isotopic exchange rate to advective flux for a given length scale. Low Da number signifies that the flow is reaction controlled, high Da number indicates that the rate of the reaction is high relatively to advection and as a consequence equilibrium is achieved. Diffusion is not included in the equations 12 and 12'. The possible diffusion term written as $D/k_1 z^2$ (D stands for diffusion coefficient of $\text{CO}_2(\text{g})$) is minor in comparison to the advection term expressed as $q/k_1 z \phi$ with data used in simulations: $D=10^{-9}$ m^2/s , $z=100\text{m}$, $\phi=0.1$, $q=10^{-2}$ $\text{m}^3/\text{m}^2\text{s}$ and $k_1=10^{-3}\text{s}^{-1}$. Therefore, balance of isotopes must be found between advection and isotopic exchange. Moreover, the diffusion process is only hardly isotopically fractionating but it demands additional assumptions concerning boundary conditions. Its inclusion in $\text{CO}_2\text{-H}_2\text{O}$ flow model would result in a more flattened shape of isotopic profiles versus time and space.

The models are not intended to predict isotopic changes in a particular type of water or water from an individual well. Instead, they are considered to be general enough to predict the direction and extent of isotopic evolution of the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$, $\delta^{13}\text{C}_{\text{HCO}_3}$ and $\delta^{13}\text{C}_{\text{TDC}}$ along the vertical distance of $\text{CO}_2\text{-H}_2\text{O}$ flow to the Earth surface. Several features applied in the models are similar to those used in the description of groundwater transport of dissolved constituents. However, constituents have been replaced by isotopic quantities and the rate of isotopic exchange between phases is included. Thus, the models are expected to give a quantitative insight into the coupled exchange reaction and advective transport of ^{13}C in carbon dioxide and dissolved carbonate species.

In the models it was assumed that maximum P_{CO_2} is equal to the hydrostatic pressure at a given depth (1 MPa at 100m depth and 0.1 MPa at the Earth surface), therefore a minimum condition for the existence of a distinct CO_2 gas phase is assured. This implies that the distribution of the dissolved carbonate species concentrations depends on P_{CO_2} . To keep the model relatively simple all complexities arising from gas and water flow dynamics (partial saturations changes with time, variation in specific densities and relative phase permeabilities) were ignored. Chemical composition of the solution is constant with time but varies with vertical length and is determined by P_{CO_2} and alkalinity. When modeling the changes of the isotopic composition of carbon the assumption concerning the initial values of the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and the $\delta^{13}\text{C}_{\text{HCO}_3}$ poses a major problem. While it is justified to assume that the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})} = -2$ ‰, because it is a value close to the upper limit of the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ in the area of interest, similar justification is lacking in the case of the $\delta^{13}\text{C}_{\text{HCO}_3}$. It is assumed that the model covers a vertical space close to the Earth surface where all alkalinity changing processes are no longer active. Thus, the initial $\delta^{13}\text{C}_{\text{HCO}_3}$ value cannot depart sharply from the $\delta^{13}\text{C}_{\text{HCO}_3}$ values obtained for the conditions at the Earth surface. This value for the Tylicz water is close to +8.6‰ as evidenced by DULIŃSKI & al. (1995) and may be as high as +10‰ for other waters. The equations were solved for the following set of initial and boundary conditions. The initial $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and $\delta^{13}\text{C}_{\text{HCO}_3}$ values were -2 and +8‰, respectively (close to isotopic equilibrium at 10°C) and the boundary con-

ditions were $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}(z=0, t>0) = -2\text{‰}$, and for the two-phase flow, $\delta^{13}\text{C}_{\text{HCO}_3}(z=0, t>0) = +8\text{‰}$.

The differential equations 12, 12', 14 and the algebraic equations describing carbonate equilibrium in solution with the respective boundary conditions were solved by a method of finite differences using DAE solver DASSL (BRENAN & al. 1989).

The important factor influencing the variation in the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$, $\delta^{13}\text{C}_{\text{HCO}_3}$ and $\delta^{13}\text{C}_{\text{TDC}}$ signatures is the $C_{\text{CO}_2(\text{g})}/C_{\text{HCO}_3}$ gradient in equations 12 and 12'. In fact, it is equivalent to P_{CO_2} gradient because bicarbonate concentration is constant during the simulation. Results of the calculation are displayed as the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$, $\delta^{13}\text{C}_{\text{HCO}_3}$ and $\delta^{13}\text{C}_{\text{TDC}}$ values for comparison with the field data at the Earth surface. Monitoring the variation of $\delta^{13}\text{C}_{\text{HCO}_3}$ and $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values has the advantage of predicting any departure from the isotopic equilibrium between $\text{CO}_2(\text{g})$ and HCO_3^- .

In the first limiting model described by equations 12 and 14, CO_2 gas and carbonated solution of an alkalinity 0.3 meq/l move at the same speed to the top of a vertical rock column of an assumed effective porosity equal to 0.1 at constant temperature (10°C). The $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and $\delta^{13}\text{C}_{\text{HCO}_3}$ values (Fig. 6a, b) tend to be lower than the initial $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and $\delta^{13}\text{C}_{\text{HCO}_3}$ signa-

tures and equilibrium is held within the system ($\text{Da}=1$). At the Earth surface the steady-state is achieved after less than fifty pore $\text{CO}_2\text{-H}_2\text{O}$ fluid volume replacements (Fig. 6a). Low $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values are not achieved. $\delta^{13}\text{C}_{\text{TDC}}$ value increases towards the Earth surface because of the diminishing contribution of $\text{CO}_2(\text{aq})$ to TDC.

In another limiting model defined by equations 12' and 14 (Figs 7a,b), CO_2 bubbles through a stagnant carbonated solution of constant composition. In this model the steady state is established after less than fifty volume replacements (Figs 7a). This is not in contrast with the two-phase flow described above (Fig. 6a). Here, however, at $\text{Da}=1$, although the isotopic equilibrium is kept, much lower $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and $\delta^{13}\text{C}_{\text{HCO}_3}$ values around -12 and -20‰ , respectively, are attained (at $z=100\text{m}$), as a consequence of decreasing $C_{\text{CO}_2(\text{g})}/C_{\text{HCO}_3}$ ratio. At moderate Damköhler number ($\text{Da}=1$) the isotopic equilibrium can therefore be kept in the two-phase and one-phase flow. Low $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and advancing disequilibrium can only be predicted for the case of very low although less realistic Da values.

In the Carpathians to which the model of $\text{CO}_2\text{-H}_2\text{O}$ flow is related, CO_2 gas accompanying carbonated water may have $\delta^{13}\text{C}$ values in the range from -9.2 to -1.8‰ . Thus, accord-

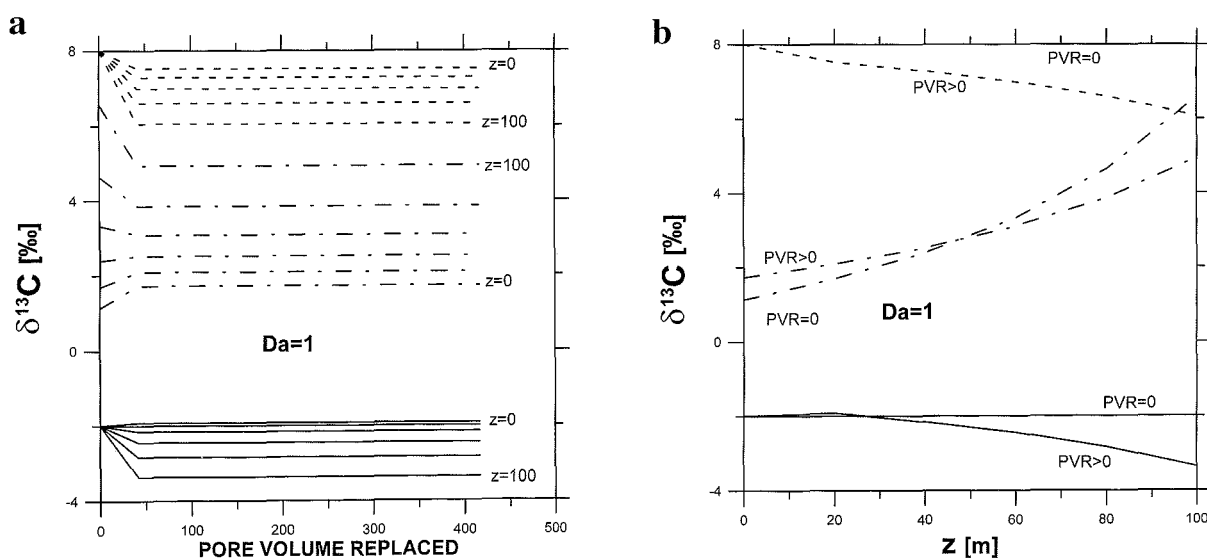


Fig. 6. Evolution of the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$, $\delta^{13}\text{C}_{\text{HCO}_3}$ and $\delta^{13}\text{C}_{\text{TDC}}$ values for the model of two-phase $\text{CO}_2(\text{g})$ and H_2O parallel flow (equal velocities): a) as a function of PVR (pore volume replacements) for fixed levels in 100 m vertical length; b) as a function of z co-ordinate for fixed pore volume replacements (PVR); continuous line is for $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ variations, broken line stands for $\delta^{13}\text{C}_{\text{HCO}_3}$ and dashed-dotted line designates $\delta^{13}\text{C}_{\text{TDC}}$ variation

ing to the models, low $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values are consistent with the model of CO_2 flow through stagnant carbonated solution but higher $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values conform to the model of parallel flow of CO_2 and carbonated solution at $\text{Da}=1$.

Only a visual observation allowed to select in which site the fluid flow regime approaches more closely the one or two-phase flow pattern. For cases when isotopic equilibrium is found as in Wysowa W-14 well, known for a steady flow and moderate $\text{CO}_2/\text{H}_2\text{O}$ ratio and, to a lesser degree, for Muszyna Antoni well, with low $\text{CO}_2/\text{H}_2\text{O}$ ratio, $\delta^{13}\text{C}$ data seem to be consistent with the modelling results obtained for parallel flow of gas and water (Fig. 6a, b). None of the models fit the $\delta^{13}\text{C}$ at some sites such as in Żegiestow (Z-II) with intermittent exploitation, high $\text{CO}_2/\text{H}_2\text{O}$ ratio and the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and $\delta^{13}\text{C}_{\text{TDC}}$ values close to -6.4 and -2.0‰ , respectively (disequilibrium, see Tab. 3). It is not expected that the results of modelling would match the $\delta^{13}\text{C}$ fluid compositions measured in Zuber 1 to 4 wells in Krynica. Due to their depths, intermittent exploitation and unsteady flow conditions Zuber wells present a special challenge for simulation of their $\delta^{13}\text{C}$ compositions.

The reported measurements for Carpathian fluids (Tab. 3) indicate two cases where appar-

ent fractionations between $\text{CO}_2(\text{g})$ and HCO_3^- are smaller than the respective fractionation factors. Among the variety of factors that could contribute to such cases at least two should be suggested: initial disequilibrium conditions and mixing of different gases and/or waters.

The Geysir-Clear Lake geothermal system is indicated as another potential example for the use of modelling to interpret the distributions of $\delta^{13}\text{C}$ values in carbonated fluids of geothermal system. The $\delta^{13}\text{C}$ values as low as -19‰ were reported by HUEBNER (1981) for the bubbling CO_2 gas. It was suggested that CO_2 gas is derived predominantly from an organic source. Present analysis shows that such definitely low $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values are also possible when CO_2 gas velocity differs distinctly from solution velocity or a two-phase flow is kept at low Damköhler number. This alternative explanation can be attractive in the case when the supply of organic matter can not account for the mass balance in the system of interest.

In Carpathians, apart from some bacterial-mediated reactions yielding high $\delta^{13}\text{C}$ values, which do not seem to be of importance in CO_2 -charged waters, only the highest $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ value (around -2‰) could preserve the original imprint of the CO_2 source. Thus, low $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values do not seem to be due to a different isotopic

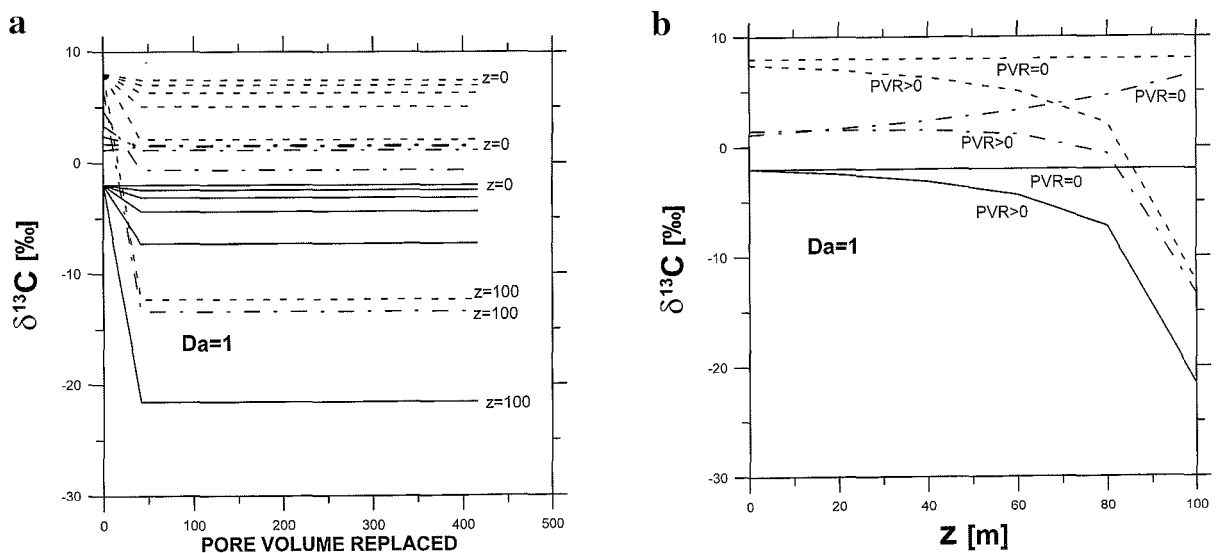


Fig. 7. Evolution of the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$, $\delta^{13}\text{C}_{\text{HCO}_3}$ and $\delta^{13}\text{C}_{\text{TDC}}$ values for the model of one-phase $\text{CO}_2(\text{g})$ flow through a stagnant carbonate solution: a) as a function of PVR – pore volume replacements for fixed levels in 100 m vertical length; b) as a function of z co-ordinate for fixed pore volume replacements (PVR); continuous line is for $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ variations, dashed line stands for $\delta^{13}\text{C}_{\text{HCO}_3}$ and dashed-dotted line designates $\delta^{13}\text{C}_{\text{TDC}}$ variation

imprint of a CO_2 gas source at a particular site but rather to be caused by secondary changes. This is simply an equivalent of diagenetically-induced isotopic changes found in rocks when, for example, the $\delta^{13}\text{C}$ value departs from secular $\delta^{13}\text{C}$ signal of the coeval seawater carbonate deposit.

System closed to CO_2 external reservoir

In the Carpathian flysch there is another different type of carbonated waters less abundant in CO_2 than the CO_2 -charged waters. These waters sometimes occur in the close proximity of oil fields and are of sodium-chloride and sodium-chloride-bicarbonate type with P_{CO_2} pressure lower than 0.1 MPa (Table 4), but still higher than in average soil solution ($10^{-2.5}$ to 10^{-3} MPa). The gas composition of this particular type of waters consists mainly of methane and carbon dioxide. They are considered to be 'closed' with respect to CO_2 as opposed to the open CO_2 system described previously. Though in essence the discrimination between open and closed systems has a thermodynamic rather than genetic connotation, it happens that in the present study open and closed carbonated CO_2 systems have different origins. With their high

$\delta^{13}\text{C}_{\text{TDC}}$ values reaching +28‰ (Table 4) and the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values being close to +20‰, the Na-Cl- HCO_3 waters are isotopically distinctly different from waters of open systems with respect to CO_2 .

Recalculations made by means of the PHREEQE program indicate that if these waters were exposed to CO_2 pressure of 0.12 MPa at 10°C and constant alkalinity, their pH would generally drop below 6 (Table 4), i.e., pH would be distinctly lower than in the case of the CO_2 -charged waters. This is due to the less efficient, lower buffer capacity due to lower TDC concentration than in the case of CO_2 -charged groundwater system. At P_{CO_2} adjusted to 0.12 MPa and temperature adjusted to 10°C , the difference in the $\delta^{13}\text{C}_{\text{TDC}}$ compositions between both systems is significant (Text-fig. 8) and validates different origin of CO_2 .

In order to understand the mechanism of formation of this type of carbonated waters an efficient process capable of generating high $\delta^{13}\text{C}_{\text{TDC}}$ values has to be invoked. The ^{13}C enriched solutions with respect to groundwaters ($\delta^{13}\text{C}_{\text{TDC}} > -13\text{‰}$) are most probably produced by a reaction involving bacteria because inorganic reactions do not provide such an extreme fractionation of the isotopes. As most of the waters occur in the area close to oil-fields and contain a prevailing fraction of methane apart of some carbon dioxide, high $\delta^{13}\text{C}_{\text{TDC}}$ values were probably obtained by the disintegration of aliphatic acid anions, a by-product in the chain of kerogen transformation to methane and carbon dioxide.

The aliphatic acid anions, if present, do contribute a charge to total alkalinity. Gran titrations (STUMM & MORGAN 1981) performed on some of the waters of interest revealed that alkalinity is not different from the carbonate alkalinity. Therefore, aliphatic acid anions do not contribute to the alkalinity of these particular Carpathian waters. In fact, the survey of DOMINIKIEWICZ (1951) did not reveal aliphatic acids in Carpathian waters.

KHARAKA & CAROTHERS (1980) in their study of the oil-field waters correlated the increase in aliphatic acid anion concentrations with a drop in temperature from 150°C to 80°C . Below 80°C the concentration of aliphatic acid anions was negligible as a result of the process of decarboxylation of aliphatic acids by methanogenic bacteria. The schematic reaction is as follows:

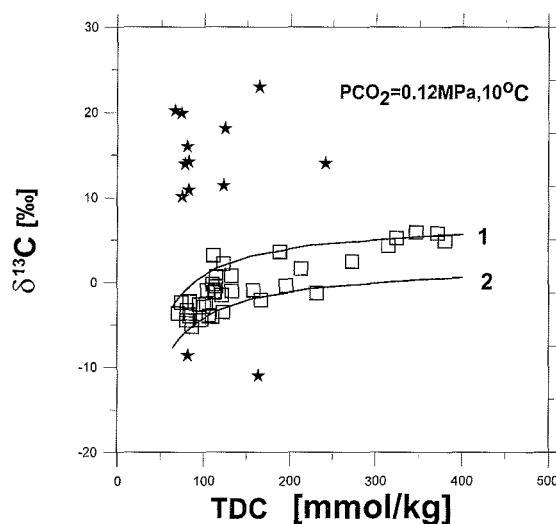


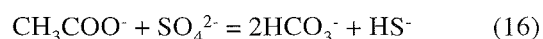
Fig. 8. Comparison of open and closed systems with respect to CO_2 in the Outer West Carpathians ($P_{\text{CO}_2} = 0.12$ MPa, 10°C); isotopic equilibrium curves are for $\delta^{13}\text{C}_{\text{CO}_2(\text{g})} = -2\text{‰}$ (1) and -7‰ (2); open squares designate waters of the open system, asterisks are for waters of the closed system



When ^{12}C isotopes are consumed by the methanogenic bacteria and methane is produced, the enrichment of HCO_3^- in heavy carbon occurs and the $\delta^{13}\text{C}_{\text{HCO}_3}$ and $\delta^{13}\text{C}_{\text{TDC}}$ values are increased. Therefore, if high $\delta^{13}\text{C}_{\text{HCO}_3}$ values are generated through the reaction (15), waters can contain only a trace amount of aliphatic acids. The methanes found in Carpathians belong to two generations. Some are apparently derived at an early stage of the bacterial reduction in the marine environment and have characteristic $\delta^{13}\text{C}_{\text{CH}_4}$ values around -65% and the $\delta\text{D}_{\text{CH}_4}$ values around -185% (KOTARBA 1987, 1992). The second group is attributed to termogenic methanes by virtue of higher $\delta^{13}\text{C}$ values than that found in the previous group ($\delta^{13}\text{C}_{\text{CH}_4}$ from -50 to -35%) and the $\delta\text{D}_{\text{CH}_4}$ between -215 and -130% . The termogenic methanes not associated directly with petroleum are within a narrower field of the $\delta^{13}\text{C}_{\text{CH}_4}$ values extending from -42 to -37% with the $\delta\text{D}_{\text{CH}_4}$ around -150% (KOTARBA 1992; Text-fig. 3) and they accompany the carbonated waters of interest. The presence of methane in localities where waters with high values of the $\delta^{13}\text{C}_{\text{TDC}}$ occur as well as the lack of aliphatic

acid ions strengthened arguments that reaction (15) is responsible for carbonate distribution and its isotopic composition.

Low $\delta^{13}\text{C}_{\text{TDC}}$ values in Poręba water (Table 4) do not seem to conform to reaction (15), however, if there is a sufficient content of sulphate, another concurrent reaction may play a substantial role:



Here, the enrichment of the HCO_3^- ions in the ^{13}C isotope does not occur because there is no other product in the equation 16 which could partition the carbon isotopes as does CH_4 in the equation 15.

Origin of CO_2

Though $\delta^{13}\text{C}$ of the gas itself can sometimes provide information on the origin of CO_2 (organic, inorganic), the distinction between mantle and average crustal CO_2 is problematic because both reservoirs have similar isotopic signatures in the approximate range of -2 to -6% (DEINES & GOLD 1973, OHMOTO & RYE 1979, DEINES 1980,

Name	t °C	pH	Alk meq/l	TDC mmol/kg	$\delta^{13}\text{C}_{\text{TDC}}$ ‰	pH ^f	TDC ^f mmol/kg	α	$\delta^{13}\text{C}_{\text{TDC}}^f$ ‰
<u>Sól</u> Sól(spring) ¹	18.5	7.25	14.98	14.98	25.3	5.63	66.11	0.9952	20.2
<u>Rabka</u> Warzelnia ¹	10.3	7.75	14.10	14.46	18.4	5.65	74.53	0.9950	10.1
Krakus ¹	8.2	7.75	15.01	15.36	27.7	5.66	73.38	0.9950	19.9
Krakus	18.5	8.0	22.68	22.46	22.6	5.85	79.91	0.9949	16.0
Rabka-18 ¹	7.2	7.5	19.36	20.04	21.2	5.77	77.36	0.9947	13.9
Rabka-18	18.5	8.4	25.55	24.14	20.7	5.89	81.56	0.9947	14.2
Rabka-19	18.5	8.6	24.06	22.31	17.7	5.89	81.89	0.9948	10.9
<u>Poręba</u> Poręba-1	18.5	8.0	14.98	14.98	28.0	5.63	66.11	0.9952	20.2
<u>Rymanów</u> Klimkówka-27	18.5	8.0	103.5	103.5	26.2	6.54	163.9	0.9931	23.0
Rymanów-5	18.5	8.9	61.66	56.84	16.2	6.35	122.6	0.9938	11.4
<u>Other sites</u> Łęgi-100	18.5	9.0	186.0	153.0	17.4	6.75	240.9	0.9925	14.0
Słone-Kluza	18.5	8.8	20.23	20.38	-1.8	5.88	81.62	0.9951	-8.6
Czarna-4	18.5	8.0	62.91	63.16	22.4	6.35	123.7	0.9938	18.1

Table 4. Chemistry and carbon isotopic compositions of the CO_2 - CH_4 mineral waters; pH values were measured in laboratory before BaCO_3 precipitation, ¹pH measured and BaCO_3 precipitated in the field; the last three locations are not given on the sketch (Text-fig. 1); superscript f stands for δ values at 0.12MPa and 10°C

Name	$\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ ‰	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ‰	$\delta\text{D}_{\text{H}_2\text{O}}$ ‰	T.U.	R/R _A	C/ ³ He
Aleksandra	-3.9	6.4	-34	3	0.97	-
W-14	-4.2	1.7	-42	4	0.37	>2·10 ¹¹
W-12	-4.4	-7.2	-63	7	-	-
Magdalena	-5.5	4.4	-35 ^{&}	0	-	-
Jan-Szczawnica	-8.9	-8.7	-74	39-78	0.35	>2·10 ¹¹
Zuber-3	-1.8	-7.0 ^{&}	-58 ^{&}	0	0.35	>2·10 ¹¹
Zuber-4	-1.8	-8.6	-56 ^{&&}	0	-	-
K-Główne	-4.3	-9.3	-71	15-25 ^{&&}	0.61	>1·10 ¹¹
K-9	-4.3	-11.5 ^{&}	-70 ^{&}	13 ^{&}	0.41	1.2·10 ¹¹
Złockie (gas)	-1.8	-	-	-	0.52	>1.3·10 ¹¹
Żegiestów-2	-6.6	-11.4	-	25	-	-

Table 5. Selected isotopic data of gases and waters

$\delta^{18}\text{O}$ and δD values are given with respect to V-SMOW standard, $\delta^{13}\text{C}$ is expressed relative to V-PDB standard, T.U., designates tritium unit (one atom of ³H per 10¹⁸ atoms of ¹H), R stands for ³He/⁴He, R_A is for helium isotopic ratio in air, [&]DULIŃSKI & *al.* (1987), ^{&&}DOWGIAŁŁO (1973)

MAXWELL & SOFER 1982, PINEAU & JAVOY 1983, SAKAI & *al.* 1984, MATTEY & *al.* 1984, DES MARAIS & MOORE 1984, FINE & STOLPER 1986).

The one-dimensional modelling of the CO₂-charged systems demonstrates that CO₂(g) is easily depleted of the ¹³C during coupled isotope exchange and advective flow to the Earth surface (Text-figs 6 and 7). Apart from some bacterially-mediated processes, CO₂(g) can not be en-

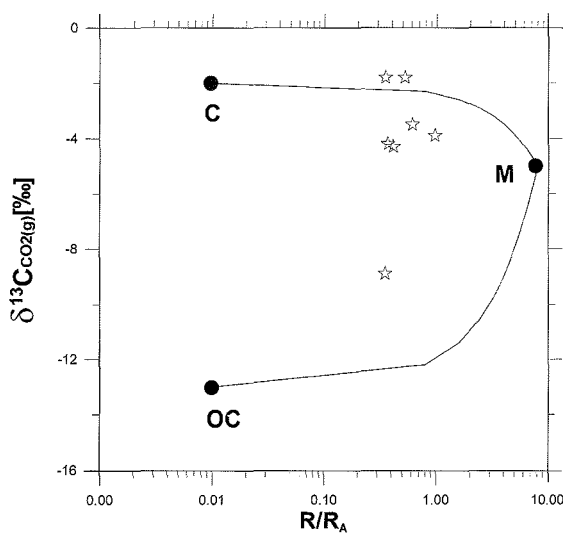


Fig. 9. Comparison of R/R_A ratios and $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values in the Carpathian fluids (after LEŚNIAK & *al.* 1997); the mixing line connects mantle helium component (M) of R_M/R_A = 8 and $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ = -5‰ with crustal helium component (C) of R_C/R_A = 0.01, $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ = -2‰ and crustal organic component (OC) of R_C/R_A = 0.01, $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ = -13‰

riched in the ¹³C isotope in a low temperature environment. Therefore, only the highest $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values preserve a primary signature and are of use to estimate the origin of CO₂. The $\delta^{13}\text{C}$ values around -2‰ may indicate a crustal origin of CO₂ in the Carpathians.

Significant information about CO₂ origin can also be derived from assembling helium isotope data with $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values. Recent data of ³He/⁴He ratios revealed that mantle helium is present in the CO₂-rich gases in the Carpathians (LEŚNIAK & *al.* 1992, 1997). Although the CO₂-CH₄ water at Rymanów (Tytus) has a clear crustal signature of helium R/R_A = 0.03 (where R and R_A is the ratio of ³He to ⁴He in the sample and in the air, respectively), CH₄-dominated water at Rabka (R-18) has an appreciable 5% mantle helium contribution and a distinct sedimentary organic (bacterial) $\delta^{13}\text{C}_{\text{TDC}}$ signature up to +28‰.

In all CO₂-charged waters (open CO₂ system) of the Outer West Carpathians studied so far, mantle helium is present (Table 5) and can contribute as much as 11% to total helium concentration in Wysowa waters. This was calculated assuming a mantle characteristic value R/R_A = 8 (MORB). Recently, it has been suggested that the Euroasian Subcontinental Mantle can have a characteristic R/R_A value of about 6 (DUNAI & BAUR 1995, XU & *al.* 1995), and consequently, the Carpathian fluids should display higher mantle helium content. Secondary processes overriding the primary $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ signal are apparent in Text-fig. 9, where the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values are plotted against the R/R_A ratios for some Carpathian solutions. In spite of the similar R/R_A ratios from 0.3 to 0.9, the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values are varied from -2 to -9‰ for the same waters. Recent estimations of the CO₂/³He ratios around 1·10¹¹ (Table 5) in some of the waters (LEŚNIAK & *al.* 1997), which exceeds the characteristic CO₂/³He ratio of the mantle (2·10⁹), also indicate that CO₂ in the West Carpathians is of crustal origin.

SUMMARY AND CONCLUSIONS

The CO₂-rich waters in the West Carpathians are an example of cold fluids in which carbon of

variable isotopic composition ($-7.1 < \delta^{13}\text{C}_{\text{TDC}} < +28\text{‰}$ and $-9.2 < \delta^{13}\text{C}_{\text{CO}_2(\text{g})} < +20\text{‰}$) is derived from deep crust. The carbon isotopic composition is consistent with the presence of two distinct CO_2 /water systems: an open- CO_2 water system ($\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ in the range from -9.2 to -1.8‰) with bicarbonate as the dominant anion and a closed CO_2 -water system ($\delta^{13}\text{C}_{\text{TDC}}$ up to $+28\text{‰}$) with chloride as the dominant anion. Because of the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ variability, the assignment of a definite single or multiple CO_2 source(s) cannot be made. The $\delta^{13}\text{C}_{\text{TDC}}$ values of an open CO_2 -water system were shown to be also affected by mixing processes and under non-restrictive assumptions the mixing model fits measured $\delta^{13}\text{C}_{\text{TDC}}$ values quite well. The detailed measurements of $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and of the corresponding total dissolved carbonates ($\delta^{13}\text{C}_{\text{TDC}}$) of the waters indicate which fluids are in isotopic equilibrium with accompanying CO_2 gas and which are not. Several models have been tested to resolve the discrepancy between the model derived $\delta^{13}\text{C}$ values and the $\delta^{13}\text{C}$ field data to explore the possible cause of departure from isotopic equilibrium between CO_2 and HCO_3^- . The simple Rayleigh model (equilibrium model) predicts that outgassing may provide two types of carbon dioxide with $\delta^{13}\text{C}$ from -2 to -4‰ depending on whether an instantaneous product or an accumulated product (CO_2) is the result of outgassing. According to this model the isotopic composition of the CO_2 product is similar to that expected to be the $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ signature of degassed crust. However, this model is insufficient to explain $\delta^{13}\text{C}_{\text{TDC}}$ and $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values as low as -9‰ found in CO_2 -charged waters in the Carpathians. A more general and consistent scenario of $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and $\delta^{13}\text{C}_{\text{HCO}_3}$ evolution is obtained by incorporating temporal and spatial variables in a model of CO_2 gas and carbonated water flow to the Earth surface. The slightly negative $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values can be acquired using isotopic models with coupled isotopic exchange and parallel advective transport of $\text{CO}_2(\text{g})$ and carbonated solution. In another limiting model of $\text{CO}_2(\text{g})$ flow through a stagnant carbonated solution $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values as low as -20‰ and $\delta^{13}\text{C}_{\text{HCO}_3}$ values down to -12‰ are obtained due to decreasing $\text{C}_{\text{CO}_2(\text{g})}/\text{C}_{\text{HCO}_3}$ ratio, although isotopic equilibrium between $\text{CO}_2(\text{g})$ and HCO_3 is still kept ($\text{Da}=1$).

If any comparison of the CO_2 -rich waters with respect to the $\delta^{13}\text{C}_{\text{TDC}}$ values is to be made, $\delta^{13}\text{C}_{\text{TDC}}$ should be corrected to correspond to the same CO_2 reference pressure and temperature. It

is proposed that the $\delta^{13}\text{C}_{\text{TDC}}$ correction for CO_2 -rich waters should be made with reference to 0.1 MPa of P_{CO_2} and 10°C . $\delta^{13}\text{C}_{\text{TDC}}$ may be recalculated to correspond to the reference conditions using Rayleigh equations in the form presented by WIGLEY & *al.* (1978).

Apart from organic transformation of kerogen to methane and CO_2 , carbon dioxide can not be enriched in ^{13}C , i.e., $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ values can not increase in the close to the Earth surface environment. Hence, only the highest $\delta^{13}\text{C}$ values of CO_2 can be considered as being not affected by secondary fractionation associated with CO_2 - H_2O flow and can be useful for tracing the origin of CO_2 . These values around -2‰ indicate that CO_2 in the Carpathians is mostly derived from a thermal decomposition of carbonate and silicate rocks of the Earth crust. Carbon dioxide in other waters including those with the most negative values of $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ as low as -9‰ , although modified as the result of secondary isotopic fractionation, is also of crustal origin.

There is a systematic difference in the isotopic composition of carbon in the CO_2 -charged waters (CO_2 -open system) and the carbonated waters which do not exsolve CO_2 (closed CO_2 system). In the latter case the occurrence of dissolved carbonates with characteristic elevated $\delta^{13}\text{C}_{\text{TDC}}$ values ($\delta^{13}\text{C}_{\text{HCO}_3} > +20\text{‰}$) and the prevailing presence of CH_4 indicates that bicarbonate must have been produced by decarboxylation of organic acids.

Summarizing, new quantitative features of interest for the CO_2 -rich systems have been obtained: $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ composition can indeed vary during CO_2 flow to the Earth surface, $\delta^{13}\text{C}_{\text{HCO}_3}$ composition follows $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ decline (equilibrium is held) at moderate Damköhler number, disequilibrium between $\delta^{13}\text{C}_{\text{CO}_2(\text{g})}$ and $\delta^{13}\text{C}_{\text{HCO}_3}$ can develop as the rate of fluid flow exceeds the rate of carbon isotope exchange. The potential of reactive and advective transport theory to elucidate several aspects of the carbon isotopic variation in the CO_2 - H_2O natural system is therefore substantial.

Acknowledgements

I thank Prof. M. BORKOWSKA, the former Director of the Institute of Geological Sciences, Polish Academy of Sciences, Warsaw, for her continuous encouragement during the work. Prof. A. PSZCZÓŁKOWSKI, Director of the Institute of Geological Sciences, is

thanked for critical reading of the manuscript. The work has been completed in the Hydrogeological Laboratory of the Institute headed by Prof. J. DOWGIAŁŁO. A number of the early isotopic data was obtained at the former Institute for Thermal Spring Research in Misasa under Prof. H. SAKAI Directorship. I thank him and his co-workers Drs. F. YANAGISAWA and H. Masuda for support. A helpful assistance with CO₂ sampling was provided by Dr. B. ŁACKA. Prof. M. KOTARBA is thanked for providing access to mass spectrometer for $\delta^{13}\text{C}$ measurements of the CO₂ gas shortly after sampling. Thanks are due to Drs. M. DULIŃSKI, J. Hladikova, and profs. N. OSZCZYPKO, H. SAKAI, late S. WĘCŁAWIK and A. ZUBER for numerous discussions and advices at various stages of the work. Dr. J. HLADÍKOVA is thanked for providing isotopic data from Slovakian springs. Several data were gathered during a joint field-trips with Balneoprojekt team led by Mrs. B. KURKOWSKA. Dr. D. REŠKO and Mr. M. MAČKOWIAK and other Carpathian spas staff, impossible to mention by name, offered uncountable help in the access to the springs and boreholes. Finally, I benefited by critical remarks of journal reviewers: T. PAČES, E. J. REARDON and A. RÓŻKOWSKI. Thanks are due to Dr. I. WALASZCZYK for efficient editorial handling of the manuscript. All the responsibility for ideas presented in this work remains mine. This research was supported by the Committee for Scientific Research (KBN), Warsaw.

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