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ISTVÁN CORNIDES — ÁRPÁD KECSKÉS*

DEEP-SEATED CARBON DIOXIDE IN SLOVAKIA: THE PROBLEM OF ITS ORIGIN

(Figs. 2, Tabs. 5)

Abstract: The carbon isotope data measured in various areas throughout Slovakia have shown that the deep-seated carbon dioxide appearing in the CO_2 — rich mineral waters in this country is characterized by the carbon isotope ratio $\delta^{13}C = -6.0 \pm 1.5$ ‰ (relative to PDB), and this is indicative for juvenile, i. e. for mantle origin. On the other hand, the CO_2 derived from marine carbonate rocks is found to be a minor component, except the cases of the rather few occurrencies of relatively high $\delta^{13}C$ values. Based on very similar measured isotope data, the same conclusion is valid for all other parts of the Carpathian Basin, in which this type of investigation has been carried out.

Резюме: На основании результатов измерений изотопного состава углерода в двуокиси углерода минеральных вод различных областей Словакии было установлено, что изотопное соотношение глубинной CO_2 находится в узких пределах $\delta^{13}C = -6{,}0 \pm 1{,}5$ ‰. Этот факт указывает на ювенильный характер, т. е. на происхождение из мантии. С другой стороны, двуокись углерода, полученную из морских карбонатных пород, можно считать компонентом сравнительно малой распространенности, который только в довольно редких случаях находят в значительных количествах (при повышенных значениях $\delta^{13}C$). Подобные изотопные соотношения углерода были также найдены в некоторых других областях карпатского бассейна, подтверждающие вышеупомянутые предположения о происхождении глубинной двуокиси углерода.

Introduction

Owing to the numerous and high quality CO_2-rich mineral water springs and also to the dry CO_2 sources available for industrial use, carbon dioxide is one of the significant natural resources of Slovakia. In addition to this economic aspect, a genetic investigation of the crustal carbon dioxide is made desirable also by the fact that it may reveal useful geological informations of more general importance as well.

The deep-seated character of the Carpathian carbon dioxide, involving the necessity of associating its origin with some basic and large-scale geological phenomena, like magmatism and/or metamorphism, was recognized when the first series of carbon isotope data were measured in Hungary (I. Cornides — T. Sült, 1970; I. Cornides, 1970). An important global survey, published in 1978, has clearly displayed the relation between CO_2 discharges and seismicity (I. Barnes — W. P. Irwin — D. E. White, 1978). However, the task of finding and describing the detailed formation mechanism of the deep-seated carbon dioxide, in accordance with the general correlations and also with local geological evidences, is still to be done.

An obviously promising approach is offered by isotope geochemistry. Measurements of the $^{13}C/^{12}C$ stable carbon isotope ratios of CO_2 occurrencies

* RNDr. I. Cornides, CSc., RNDr. Á. Kecskés, CSc., Department of Physics, Pedagogical Faculty, Lomonosova 1., 949 74 Nitra.

Table 1

Data of CO_2-rich mineral waters, neogene volcanic area

Serial No.	Code	Sampling site	$\delta^{13}C$ (PDB)	Free CO_2 mg/litre	Temp. °C	HCO_3^- mg/litre
1	LE-34	Santovka, B-6	— 3.8	2524	14.7	2082
2	LE-35	Santovka, B-9	— 3.8	1370	13.5	1847
3		Santovka, new bore	— 3.8			
4	ZV-70	Dudince, S-3	— 2.5	1560	28.5	3059
5	LE-39	Slatina, BB-1	— 6.5	1886	16.5	2150
6	LC-61	Želovce	— 4.7	1865	11.0	4014
7	LC-45	Sklabina	— 5.7	1900	12.0	1672
8	LC-32	Malý Krtíš	— 4.5	2043	10.5	459
9	LC-34	Muľa	— 4.6	1850	6.0	2663
10	LC-4	Bušince	— 4.2	1502	16.0	6084
11	LC-9	Fiľakovo, Adam	— 6.1	1969	10.0	1322
12	LC-50	Šíd, Tőrey	— 4.4	2600	10.8	970
13	RS-25	Konrádovce	— 5.3	1743	10.0	889
14	RS-19	Hodejov	— 4.6	1938	11.0	1011
15	ZR-3	Bukovina	— 3.0	1431	11.5	2351
16	ZV-17*	Zvolen	— 4.2	1930	16.2	1961
17	ZV-5	Sliač „Štefánka"	— 5.7	2160	12.0	303
18	ZV-7	Sliač „Lenkey"	— 5.2	1652	23.2	1052
19	ZV-8	Sliač „Adam"	— 5.7	1475	22.7	1077
20	ZV-25	Lukavica	— 5.3	924	12.7	1330
21	BB-27	Čerín „Medokýš"	— 3.4	1300	10.5	2538
22	BB-33	Čerín „Kráter"	— 2.6	1710	13.5	3344
23	BB-10	B. Bystrica	— 4.3	1880	17.4	1562
24	BB-21	Brusno „Ondrej"	— 4.3	1210	20.5	1267
25	PV-23	Kokošovce „Taňa"	— 4.6	2300	9.3	1104
26	PV-90	Zlatá Baňa	— 4.8	2000	10.0	415
27	PV-10	Kvašná voda	— 4.9	2170	9.8	580
28	PV-97	Cemjata	— 5.8	2131	10.0	1078

In this and all other Tables:
Code: as given in „Minerálne vody Slovenska" by P. Krahulec, et al., Osveta, Martin 1977.
* : the spring was not quite reliably identified.

have been carried out in many parts of the world (I. Barnes — W. P. Irwin — D. E. White, 1978). As for Slovakia, several data have been measured and published by Barnes and O'Neil (I. Barnes — J. R. O'Neil, 1976). In the early seventies an extensive collection and carbon isotope analysis of CO_2 samples has been carried out throughout Slovakia (I. Cornides — Á. Kecskés, 1973; Á. Kecskés, 1974), the results of which were summarized along with the data measured in Hungary, and a preliminary interpretation was also attempted (I. Cornides — Á. Kecskés, 1974).

Table 2

Data of CO_2-rich mineral waters, the Trenčín area

Serial No.	Code	Sampling site	$\delta^{13}C$ (PDB)	Free CO_2 mg/litre	Temp. °C	HCO_3^- mg/litre
1	TO-3	Norovce, JRD	—4.7	1050	6.5	1172
2		Norovce, well	—5.0			
3	TO-17	Norovce, forest	—5.2	1036	8.0	1170
4	TO-5*	Šišov	—4.2	1250	8.0	1025
5	TE-12	Dubodiel	—3.8	1974	9.0	378
6	TE-48	Trenčianske Jastrabie 1.	—3.0	2288	9.0	1318
7	TE-83	Trenčianske Jastrabie 2.	—3.9	2060	9.0	1117
8	TE-27	Mníchova Lehota	—5.5	1024	8.0	895
9	TE-25	Kubrá	—4.3	2085	9.8	1625
10	TE-43*	Soblahov	—6.4	1600	10.0	612
11	TE-17*	Hrabovka	—3.2	1590	14.0	1281
12	TE-23	Záriečie	—6.2	1616	11.0	299
13	TE-21	Chocholná	—4.7	1750	7.0	1202
14	TE-71*	Velčice	—5.2	1276	11.0	409
15	TE-62	Záblatie	—4.7	2050	13.0	1385
16		Koňovce 1 Moravian border	—7.0			
17		Koňovce 2. Moravian border	—6.5			

In the last few years some additional and control measurements were performed, and now the whole set of the available data from Slovakia will be presented, and the problem of origin will be dealt with in some detail.

Experimental

The sampling was carried out by using $Ba(OH)_2$ solution on the spot, i.e. by precipitating the total CO_2 content of 50 ml water as $BaCO_3$. Only springs of higher than 1000 mg/litre free carbon dioxide content were sampled to make sure as far as possible that deep-seated CO_2 is dominant as against dissolved carbonate (inorganic), or soil CO_2 (organic), etc. This way we hope to have fairly well restricted the change of the original carbon isotope ratio of the CO_2 gas migrating to the surface by any other kind of carbon.

Carbon dioxide was recovered for analysis in the laboratory by the usual phosphoric acid treatment. The isotope analyses were carried out by the use of a M 86 type mass spectrometer of Varian MAT, Bremen. The data were corrected according to Craig and converted to values referred to the PDB standard.

The results are presented in several groups (Table 1. to 4.). The classification is inherently arbitrary to some extent: though the most obvious viewpoints were taken into consideration, these were not the same in each case.

Table 3

Data of CO_2-rich mineral waters, northern part of Central Slovakia

Serial No.	Code	Sampling site	$\delta^{13}C$ (PDB)	Free CO_2 mg/litre	Temp. °C	HCO_3^- mg/litre
1	LM-37	Korytnica „Jozef"	— 3.9	3319	6.5	1176
2	LM-41	Korytnica „Žofia"	— 3.9	3170	6.5	1195
3	BB-57	Mýto pod Ďumbierom	— 4.7	2250	10.0	1043
4	BB-47	Jarabá 1.	— 6.1	1810	8.0	244
5	BB-48	Jarabá 2.	— 6.0	2650	2.0	903
6	LM-136	Vyšná Boca 1.	— 5.7	2400	6.8	683
7	LM-148	Vyšná Boca 2.	— 6.4	2650	6.8	592
8	BB-68	Švermovo	— 5.8	2050	13.0	1092
9	LM-93	Lúčky 1.	— 4.8	354	21.5	848
10	LM-91	Lúčky 2.	— 5.0	736	32.0	860
11	LM-92	Lúčky 3.	— 5.1	593	33.0	842
12	LM-10*	Bešeňová 1.	— 3.1	2360	11.0	1946
13	LM-8*	Bešeňová 2.	— 2.4	1360	14.0	2200
14	LM-144	Podtureň	— 4.1	2010	10.0	1739
15	LM-135	Pribylina Račkova dolina	— 4.9	2500	6.0	1989
16	PD-72	Starý Smokovec	— 4.9	1130	6.3	195

The CO_2 occurrencies in the neogene volcanic areas (Štiavnické pohorie, Krupinská vrchovina, Cerová vrchovina in the southern part of Central Slovakia, and Slanské pohorie in Eastern Slovakia) are grouped together on the basis of a reasonable *geological point of view*. The Trenčín group is obviously separated *geographically* (at the feet of and in the mountains Biele Karpaty and Považský Inovec, Western Slovakia).

The areas of the third and fourth group (northern part of Central Slovakia and North-Eastern Slovakia, respectively) can also be defined *geographically*, but the dividing line between them was closen by taking into consideration the carbon isotope data too.

Discussion

Evidently, the interpretation of the carbon isotope results has to elucidate the origin (formation) of the deep-seated carbon dioxide and its migration to the surface. The mechanism suggested should equally be in accordance with some global and the local geological evidences, on the one hand, and with the carbon isotope data, including their distribution in the given area, on the other. It is then to be expected that, in addition, the natural clustering of the CO_2 occurrencies will become self-evident as well.

In table 5. the distribution of the carbon isotope data in the four areas (expressed as usually by the $\delta^{13}C$ values in per mil) is concisely characterized by the ranges ($\delta^{13}C_{max}$, $\delta^{13}C_{max}$ and $\Delta\,\delta^{13}C = \delta^{13}C_{max} - \delta^{13}C_{min}$) and the averages ($\bar{\delta}^{13}C$).

Table 4

Data of CO_2-rich mineral waters, North-Eastern Slovakia

Serial No.	Code	Sampling site	$\delta^{13}C$ (PDB)	Free CO_2 mg/litre	Temp. °C	HCO_3^- mg/litre
1	PD-19	Gánovce 2.	— 3.0	1025	19.0	1507
2	PD-20	Gánovce 1.	— 3.1	1570	23.2	1751
3	PD-33	Hôrka	— 3.3	1850	11.5	1342
4	SNV-1	Baldovce	— 3.1	2982	10.0	1549
5	SNV-28	Baldovce, B-4	— 1.8	2626	11.0	2222
6	SNV-24	Baldovce, BV-1	— 4.1	2056	10.0	2150
7	SNV-5	Sivá Brada „U sv. kríža"	— 0.4	1776	13.8	3600
8	SNV-4	Sivá Brada „Sv. Ondrej"	— 0.6	2650	7.0	4125
9	PV-100	Lipovce, S-2	— 2.1	2182	15.5	2432
10	PV-45	Lipovce, S-1 „Salvator"	— 2.4	2214	12.0	1960
11	PV-74	Šindliar	— 2.4	2330	9.0	1770
12	PD-85	Toporec	— 2.2	1750	10.0	1556
13	PD-108	Vyšné Ružbachy	— 2.9	1284	19.0	1299
14	PD-109	Vyšné Ružbachy „Pri kríži"	— 3.4	1306	20.5	1293
15	PD-110	Vyšné Ružbachy 1.	— 3.6	1190	20.5	1037
16	PD-111	Vyšné Ružbachy 2.	— 6.0	1150	20.5	1037
17	PD-106	Vyšné Ružbachy „Kráter"	— 3.0	1008	23.0	1789
18	PD-100	Vyšné Ružbachy „stone pit"	— 4.0	2650	9.0	171
19	PD-7	Forbasy	— 4.0	3200	4.0	329
20	PD-58	Nová Ľubovňa „Alfred"	— 2.9	2200	6.7	836
21	BV-63	Snakov	— 3.0	2060	9.0	647
22	BV-35*	Hrabské	— 1.6	2440	10.0	3220
23	BV-53	Nižný Tvarožec	— 3.3	2300	8.0	1562
24	BV-266	Cigeľka, P-1	+ 4.6	2308	9.0	9484
25	BV-93	Cigeľka P-2	+ 4.4	2850	9.0	16623
26	BV-3	Bardejovské kúpele, „Lekárský prameň"	— 0.7	2095	17.0	3769
27	BV-2	Bardejovské kúpele, „Hlavný prameň"	— 2.5	2493	12.8	2385
28	BV-88	Dlhá Lúka	— 3.0	1725	10.0	4168

Table 5

Ranges and averages of the carbon isotope data in the four areas

Area	$\delta^{13}C$ ‰		$\Delta\ \delta^{13}C$	$\bar{\delta}^{13}C$
	min.	max.		
Neogene volcanic	— 6.5	— 2.5	4.0	— 4.6
Trenčín	— 7.0	— 3.0	4.0	— 4.9
North Central	— 6.4	— 2.4	4.0	— 4.8
North East	— 6.0	— 0.7	5.3	— 2.8

The close similarity of the groups 1., 2. and 3. is apparent: the ranges and averages are nearly identical. The overall spread of the $\delta^{13}C$ values of these groups is quite small: 93 % of all data is within a range of 3,5 ‰. The frequency distribution is, as shown in Fig. 1., approximately normal.

As a reasonable interpretation of these facts, we may assume common and homogenous origin, and very similar mechanism of formation and migration for these CO_2 occurrencies.

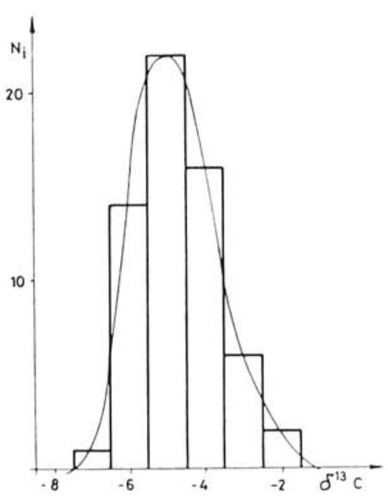

Fig. 1.

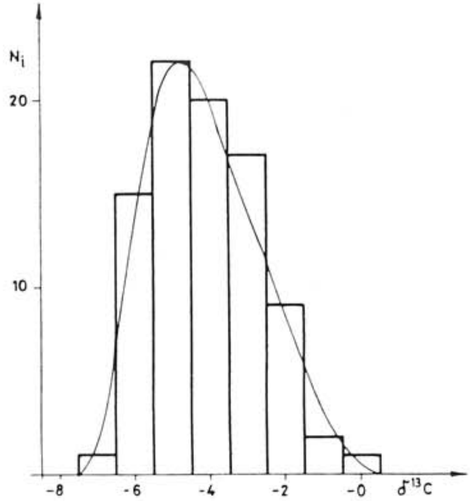

Fig. 2.

On the other hand, the $\delta^{13}C$ data of the fourth group are partly shifted to more positive values, the average is considerably higher (by about 3 ‰), and the spread is considerably wider, even if the two positive values of Cigeľka are ignored.

For this reason the united frequency distribution of all $\delta^{13}C$ data is about doubly as wide as that of the first three groups, and, owing to a considerable positive skewness, it is definitely not normal (Fig. 2). Since a distribution of this type usually indicates a heterogenous population, we think that two different kinds of source (origin) of carbon dioxide is to be postulated in Slovakia to explain satisfactorily the measured isotope data.

According to Barnes and O'Neil the source of the Slovakian CO_2 is calcite of marine origin. However, the eighteen samples they collected and measured do not represent to a desirable extent the deep-seated carbon dioxide of Slovakia. Four of them are mistakenly listed into the Slovakian group, and in the case of other six springs of rather low carbon content the contamination by surface-near organic CO_2 is considerable indeed, making any evaluation useless.

All the remaining samples are, unfortunately, clustering on the positive slope of the frequency distribution curve (Fig. 2). Their average is somewhat higher than - 2 ‰, and is quite far from the $\delta^{13}C$ value - 5 ‰ of the maximum of the frequency distribution, near to which the high majority of the samples is found.

The frequency distribution of our 89 samples may be thought to represent more reliably the whole population of the deep-seated carbon dioxide occurrencies in Slovakia. From the distribution observed in the case of the first three groups a rather homogenous population may be inferred, with about $\delta^{13}C = -5$ ‰ as the most frequent carbon isotope datum. The slight positive skewness may be explained by the existence of some two-component CO_2 occurrencies in which a more positive secondary component is admixed to the deep-seated main component with near to -5 ‰, or even more negative $\delta^{13}C$ values. The obvious source of the secondary component is marine limestone, in the Carpathian Basin these carbonate rocks are mostly found in the $\delta^{13}C$ range 0 to +3 (I. Cornides, 1971). The high (e.g. less negative than -3 ‰) $\delta^{13}C$ values, that very rarely occur in the areas of the first three groups, may appear as a result of limestone by the CO_2-rich ground water (low temperature rock—water interaction). As evidences the travertine deposits formed by the water (e.g. in Čerín and Bešeňová), and the very high bicarbonate contents can be mentioned. (For Čerín see Á. Kecskés et al., 1981).

Similar shift to less negative, or even to positive values is more frequently found in North-Eastern Slovakia, where large amounts of calcium carbonate are available in the flysch rocks of that area. The result is the rather high average of -2.8 ‰.

Besides changes to considerably higher ^{13}C contents, small shifts averaging e.g. about 1 ‰ may also occur owing to dissolution of relatively small amounts of carbonate material. These changes, though do not affect perceptibly the normality of the frequency distribution, may result in somewhat less negative $\delta^{13}C$ values even in the range -7 to -4 ‰, and thereby even this main part of the distribution curve, i.e. its "normal component", is probably affected to the extent of a small translation, e. g. of about 1 ‰, in the direction to higher ^{13}C concentration.

Conclusions

Based on the carbon isotope data of 89 properly selected CO_2 occurrencies in Slovakia, the following statements seem to be justified:

1. The carbon isotopic composition of the high majority of the CO_2 occurrencies in Slovakia are found within the range of -7 to -3 ‰: nearly 95 % in the case of the first three groups, and still more than 80 % if the occurrencies in North-Eeastern Slovakia are also taken into account.

2. On the other hand, the share of occurrencies with δ^{13} values in the marine carbonate range is quite low, and nearly negligible outside North-Eastern Slovakia.

3. Though it is, in principle, possible to explain the existence of $\delta^{13}C$ values around -5 ‰ by assuming mixtures of carbonate derived and organic CO_2, strict validity of a well defined mixing ratio for the great majority of the carbon dioxide occurrencies is highly improbable. It would be also quite difficult to give an account of the very low frequency of CO_2 occurrencies with $\delta^{13}C$ values in the limestone range.

4. The frequency distribution of the carbon isotope data suggests a deep-seated carbon dioxide characterized by the ^{13}C range of -7.5 to -4.5 ‰ to be the main component of the CO_2 occurrencies in Slovakia. This range is usually

considered to be indicative for juvenile, i.e. for magmatic ore mantle origin.

5. By the same reasoning the carbon dioxide of marine carbonate origin is to be taken as minor component, except the cases of the rather few occurrencies of relatively high $\delta^{13}C$ values. Both the local geological evidences and the chemistry of the mineral waters in question suggest low temperature rock—water interaction, relatively near to the surface, as the mechanism by which carbonate CO_2 appears in the waters.

6. According to similar investigations carried out in the Hungarian neogen volcanic areas (I. Cornides — Á. Kecskés, 1974) and in the Transylvanian Eastern Carpathians (I. Cornides — M. Cornides, 1981) the origin of the deep-seated carbon dioxide in Slovakia is identical with that recognized also in other CO_2-rich parts of the Carpathian Basin, and is different from that of the carbon dioxide Barnes and O'Neil have investigated in Bohemia, for which the flysch rocks underlying the Bohemian Massif and currently undergoing metamorphism are suggested by them as source material and formation mechanism, respectively (I. Barnes — J. R. O'Neil, 1976).

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