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ISTVÁN CORNIDES* — ÁRPÁD KECSKÉS*

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

(Tabs. 2)

Abstract: In a previous paper we presented carbon isotope data of 89 CO_2-rich Slovakian water samples and — based on a statistical analysis of these data — we have found that the upper mantle can be accepted as the source of the deep-seated carbon dioxide in Slovakia with the least amount of difficulties. Recently it has been proven by a helium isotope research that mantle-derived gas is ascending to the surface of the crust in the Carpathian Basin. Furthermore, recalculation of several of the $\delta\,^{13}C$ data measured for the total dissolved carbonate (TDC) has shown that they have become less negative than the value of the original CO_2 gas, due to dissolution of carbonate rocks and significant isotope fractionation, especially in the case of the $\delta\,^{13}C(TDC) > -3$ ‰ values.
These new findings provide additional support for the mantle origin concept.

Резюме: В предыдущей статье были предложены данные об изотопах углерода 89 образцов двуокиси углерода из словацких минеральных вод. На основании статистического анализа этих данных можно с наименьшими затруднениями принять, что источником глубинной CO_2 в Словакии является верхняя мантия.
Последние исследования изотопов гелия указывают, что существуют такие газа выступающие на поверхность через кору в Карпатском бассейне, которые содержат и газ из верхней мантии.
Кроме того переоценка некоторых измеренных значений δ(13C) для совершенно растворенного карбоната (TDC) показала, что эти значения стали менее отрицательными, чем значения исходного CO_2 вследствии растворения карбонатных горных пород и изотопной фракционации особенно в случае $\delta^{13}c$ (TDS) > —3 ‰.
Эти результаты подтверждают наше предложение о генезисе глубинной CO_2 из верхней мантии.

Introduction

In a previous paper we have presented carbon isotope data of 89 carbon dioxide occurences (Cornides — Kecskés, 1982). The samples were taken from CO_2-rich mineral water springs and wells (with free CO_2 over, in the case of 4 springs near to 1000 mg litre) throughout Slovakia, and the $\delta^{13}C$ values of the total dissolved carbonate were measured.

It has been pointed out that the $\delta^{13}C$ values of the samples collected in the neogen volcanic areas and in the adjoining regions of Western Slovakia and of the northern part of Central Slovakia (61 samples) are found in the range from −7 to−3 ‰, except only 3 samples with $\delta^{13}C > -3$ ‰ (all values relative to PDB). Furthermore, the frequency distribution of the carbon isotope data of this group is almost normal (with just a quite small skewness on the positive side) suggesting homogenous origin for these CO_2 occurences.

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* RNDr. I. Cornides, CSc., RNDr. Á. Kecskés, CSc., Department of Physics, Pedagogical Faculty, Lomonosova 1, 949 01 Nitra.

On the other hand, 14 of the 28 samples from North-Eastern Slovakia have $\delta^{13}C$ values higher than -3 ‰, making the frequency distribution of all Slovakian samples more discernibly skewed. The two samples from Cigeľka, close to the Polish border, with $\delta^{13}C > +4$ ‰ values are widely separated even from this overall distribution curve and require special consideration.

Nevertheless, the high majority of the Slovakian CO_2 occurences (72 from 89) are characterized by the -7 to -3 ‰ range of the carbon isotope ratio which is usually considered to indicate mantle origin. (This same kind of carbon dioxide was found dominant also in other CO_2-rich parts of the Carpathian Basin: in Hungary and in Transylvania.)

In the case of the minority (17 samples) of the Slovak CO_2 occurences we suggested that the"original" $\delta^{13}C$ value of the dominant deep-seated carbon dioxide has been changed to higher values due to near-surface dissolution of carbonate rocks by the CO_2-rich mineral waters, that is indicated also by the water chemistry and travertine deposits. And since small scale dissolution of carbonates cannot be excluded even in the case of the majority of the sampled mineral waters with $\delta^{13}C > -3.0$ ‰, this might be the reason for the slight deviation in their frequency distribution curve from the normal. Accordingly, the $\delta^{13}C$ range of the deep-seated Slovak (in general: Carpathian) carbon dioxide we estimated to be about from -7.5 to -4.5 ‰.

Some new results

Recently some new findings have again widened the basis for suggesting mantle origin in the case of the deep-seated CO_2 in Slovakia, and in the Carpathian Basin in general.

1. In the early eighties sampling was started in some gas fields in Hungary to obtain data on the elemental and isotopic concentrations of the noble gas content in the earth gases in question. The detailed evaluation of the results has now been completed (Cornides et al., 1986).

As the most interesting result, we point out the high ^3He content of the high yield dry CO_2 gases near the villages Répcelak and Mihályi in the Little Hungarian Plain, 70 kilometers to the south from Bratislava. In Tab. 1. the helium concentration, the $^3He/^4He$ helium isotope ratio and the $^4He/^{20}Ne$ elemental ratio data are presented for three active carbon dioxide wells of this region.

As shown by the $^3He/^4He$ values, the ^3He content is significantly higher in these samples, than that of the atmospheric helium, indicating a considerable amount of mantle helium in the CO_2 gases in question. By the use of the $^3He/^4He$ and the $^4He/^{20}Ne$ data the relative contributions of atmospheric, crustal and mantle helium can be calculated (Sano et al., 1982). The results obtained for the three samples of Tab. 1. are presented in Tab. 2.

Since the $^4He/^{20}Ne$ ratio (which is much higher in these gases, than in the atmosphere — see Tab. 1.) cannot be measured very accurately, the percentage data of Tab. 2. should be regarded only as reasonably estimated values. Nevertheless, the contribution of mantle helium to these gases is definitely established and is quite significant, especially if contrasted to that obtained for earth gas samples of two other regions in Hungary (Debrecen—Hajduszoboszló

Table 1

Helium content, isotope and elemental ratio data obtained for three CO_2 gas wells

Sampling locality, code of the well		^4He ppm	$^3He/^4He$ x 10^6	$^4He/^{20}Ne$
Répcelak,	M-5b	1010	2.9 ± 0.2	1230
Répcelak,	M-24	430	2.6 ± 0.3	88
Mihályi,	M-25	199	5.5 ± 0.3	614

Table 2

Calculated atmospheric, crustal and mantle component of the helium gas contained in the gas of three Co_2 wells

Sampling locality, code of the well		atmospheric (%)	crustal (%)	mantle (%)
Répcelak,	M-5b	0.03	78.3	21.7
Répcelak,	M-24	0.36	80.3	19.3
Mihályi,	M-25	0.05	58.1	41.9

and the Mecsek Mountain), where the mantle helium content was found negligible, i.e. being within the limits of error. In these latter gases the CO_2 content is very low, the main component being methane.

The reasons why this preliminary helium isotope research is considered important are as follows:

a) mantle-derived gas (helium) was found to ascend to the crust's surface in the Carpathian Basin;

b) and this mantle helium seems to be characteristic for the high yield carbon dioxide discharges.

It is also to be mentioned that for the carbon dioxide occurences with high mantle helium content we have received values in the narrow range from —6.5 to 5.2 ‰, i.e. values within the range of mantle CO_2.

As a most recent development, a group of English and Hungarian geophysists and geologists have sampled 60 thermal water reservoirs throughout Hungary, and by reason of $^3He/^4He$ isotope ratios measured for the helium gas they contain it was suggested that an appreciable amount of mantle helium is present in some groups of these waters, particularly in those associated with major faults (Deák et al., 1985).

2. As mentioned in the introduction, in the course of the investigation of CO_2-rich mineral waters we have determined the carbon isotope ratio of the total dissolved carbon. This $\delta^{13}C$(TDC) value can be very reliably measured: we have experienced ± 0.1 ‰ reproducibility when the TDC of the same spring was several times sampled and measured within a period of one year.

On the other hand, the isotope ratio of the total dissolved carbon may be more or less different from that of the "original" deep-seated carbon dioxide gas: the isotope fractionation in the water — carbonate system may result in a significant shift of the $\delta^{13}C(TDC)$ to higher values, especially if a considerable amount of carbonate rock is dissolved by the CO_2-rich water. This is the reason why we estimated a somewhat narrower range for the deep-seated carbon dioxide in Slovakia with a maximum of the frequency distribution curve at about -6 ‰.

There are two ways to attempt determining $\delta^{13}C(CO_2,g)$ data, i.e. the original isotope ratio of the deep-seated carbon dioxide gas. Experimentally one may try to sample the gas volatilizing from the water to the atmosphere. In the case of chemical and isotopic equilibrium in an open system the $\delta^{13}C$ value of this sample should be identical with $\delta^{13}C(CO_2,g)$, and Hałas—Lis (1980) have shown that this method of sampling is sufficiently reproducible.

In a theoretical approach we may recalculate $\delta^{13}C(CO_2,g)$ from the $\delta^{13}C(TDC)$ data making use of the equations of chemical and isotopic equilibria. The reliability of this method is limited by the fact that various approximations are inevitably involved.

In a recent paper Leśniak (1985) presented calculations of this kind for the carbon dioxide — underground water system of the Polish Carpathians using 29 carbon isotope data of Lis—Hałas (1980). Since this paper deals also with 12 Slovakian samples the $\delta^{13}C$ data of which we have measured, a chance was given for a limited application of the computational method in our case.

Unfortunately, Leśniak has not calculated the $\delta^{13}C(CO_2,g)$ values for the individual samples, instead he has drawn two curves for $\delta^{13}C(CO_2,g) = -1.0$ ‰ and -3.0 ‰ in the TDC $-$ $\delta^{13}C(TDC)$ and in the pH $-$ $\delta^{13}C(TDC)$ plane (see Fig. 4. and 5., respectively, in his paper). Nevertheless, the dots representing the samples in question in these figures, namely their positions relative to the curves drawn, give information on the respective $\delta^{13}C(CO_2,g)$ values. In particular, it is clearly revealed that 10 samples show $\delta^{13}C(CO_2,g)$ values lower than -3.0 ‰, including 7 which have $\delta^{13}C(TDC) \geqq -3.0$ ‰ data.

To obtain numerical values we have made inter- and extrapolation in Leśniak's Fig. 4. and as a result a $\delta^{13}C(CO_2,g)$ range of -1.8 to -5.7 has been found for the 12 samples, instead of the $+4.6$ to -4.3 range of the $\delta^{13}C(TDC)$ data. It is to be pointed out, that if we neglect the two Cigeľka samples, all values are near to -4.0 ‰ or well over that, in good agreement with our earlier estimation.

Discussion

A statistical analysis of the relatively high number of our data has revealed that the least amount of objections is to be faced if the results are interpreted by assuming mantle origin for the Slovakian deep-seated carbon dioxide.

The new results outlined above eliminate two of the objections against this mantle origin concept.

One of them is based on the reasoning that migration of mantle gases into the crust and to its surface should be considered impossible in such a tectonically-magmatically relatively quiet region like the Carpathian Basin. The detection of significant amounts of mantle helium in earth gases inside the Carpathians obviously rejects any such argument, though it doesn't, of course, provide direct evidence for the mantle origin of the carbon dioxide too.

As already mentioned, it is also objectionable that we used δ^{13}C(TDC) data in the case of CO_2-rich waters when we attempted to elucidate the origin of the deep-seated carbon dioxide by interpreting the carbon isotope composition. Nevertheless, the knowledge of the fractionation coefficients between the carbonate species, and also of their relative quantities in the solution, makes possible a semi-quantitative estimation of the shift from δ^{13}C(CO_2,g) to δ^{13}C(TDC), reducing thereby the uncertainty caused by this problem. This is what we did: we explained the skewness of the frequency distribution curve on the positive side by a considerable amount of dissolved carbonate, i.e. by high relative quantity of the HCO^{-3} species, the carbon of which is much heavier than that of the CO_2 molecules.

Leśniak's results definitely support our estimation. For all the twelve samples the δ^{13}C(CO_2,g) values are lower (by 3.0 ‰ on average) than the respective δ^{13}C(TDC) data, the difference being larger for high, smaller for lower δ^{13}C(TDC) values (positive correlation). It can be inferred from these results data higher than about —4 ‰ disappear from the frequency distribution of the δ^{13}C(CO_2,g) values, i.e. the skewness found in the case of the TDC disappears when the CO_2 gas is investigated.

Of course, it should not be overlooked that recalculated data are available for just over 10 % of the total number of the Slovakian samples, and since even this small number of data have not been "fully" recalculated, their usefullness is somewhat limited by the uncertainties of the extrapolation. Furthermore, Leśniak's treatment of the data involves several arbitrary assumptions that may have introduced errors of various kind and magnitude. For instance, it is obvious that real carbon dioxide — underground water systems are neither ideally open, nor ideally closed to CO_2 gas (see e.g. Deines et al., 1974) and also equilibrium conditions may not always have been established. As for the twelve Slovakian samples, ten of them have δ^{13}C(CO_2,g) values within a range of 2 ‰ width, with an average of 4.6 ‰. Accordingly, these samples really have identical values within ± 1 ‰. On the other hand, the Cigeľka samples have δ^{13}C(CO2,g) values near to -2 ‰, i.e. well outside the above range, though the shift from the measured δ^{13}C(TDC) value is the largest for these samples (6.5 ‰). Therefore, the ideal open system conditions may not be valid in their case, and the δ^{13}C(TDC) value may have become higher due to the heavy carbon of the dissolved carbonate. Another explanation is offered by the unique chemistry of the Cigeľka waters: exceedingly high HCO^{-3} to free CO_2 ratio, low Ca^{2+} content, but unusually high concentration of Na^+ ions.

Still, on the whole, we think that Leśniak's data give approximate but interpretable information on the carbon isotope ratio of the 12 samples of Slovakian deep-seated CO_2. After all, he used the theoretical results and computer program of excellent experts in the field. Unfortunately, however, the way in which Leśniak interpreted the results is devoid of the minimum of any scientific method.

The conclusions he has drawn by the help of isotope data are based on Fig. 4. (p.282) of his paper. As for the interpretation of our Slovakian data, he states:

"...Cornides and Kecskés' belief that CO_2 becomes from the mantle is incompatible with the numerical values $-1\,‰ > {}^{13}C(CO_2,g) > -3\,‰$" (p.284). ("becomes from" is obviously used for "comes from" or "originates from").

However, the author has not presented $\delta^{13}C(CO_2,g)$ "numerical values" at all and for this reason we had to rely on his figures. Strangely enough, it is clearly seen both in Fig. 4. and Fig. 5. that the "closed circles representing Slovakian waters" are not between the two curves derived for $\delta^{13}C(CO_2,g) \doteq -1.0$ and $-3.0\,‰$, respectively, except the two Cigeľka waters. Leśniak himself too used these figures to prove that $\delta^{13}C(CO_2,g)$ is constant: "In general the data points fall (Fig. 4) between two curves, i.e. $-1\,‰ > \delta^{13}C(CO_2,g) > -3\,‰$", but what kind of non-Euclidean geometry helped him to see the data points to be "in general" (i.e. mostly) between the two curves? As a matter of fact, Leśniak's statistics is very poor: 2 Slovakian samples between the two curves (just the exceptional ones from 89 samples) and 10 outside. And even if we look at all samples including also those from Poland — which, of course, didn't concern our considerations — the number of the "inside" and "outside" sample points is almost the same.

Accordingly, Leśniak rejects our suggestion (not "belief"!) that mantle is the most probable source of the deep-seated CO_2 in Slovakia (and in the Carpathian Basin), on the basis of 2 non-representative samples (well outside the frequency distribution curve) against 87 representative samples, and this is really "incompatible" with any correct use of statistics in scientific research.

Finally, we think that Lis and Hałas' (1980) suggesting mantle origin for the CO_2 occurences of Głębokie, Muszyna, Szczawnica and Żegiestów, is reasonable. This is supported also by Leśniak's figures (though not by himself) in which the respective data points are well below the $-3.0\,‰$ curve, similarly as in the case of the 10 Slovak samples. (Curiously enough, this fact was perceived by Leśniak only for 3 Polish samples).

As for the other samples in the Polish Carpathians, we think that further investigation is needed to see whether another source of CO_2 (marine limestone) is to be suggested as well. Unfortunately, in this case the reliability of Leśniak's calculations is additionaly decreased by the "double recalculations" and by the apparent misunderstanding concerning the Hałas group's method of sampling.

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