THE STABLE CARBON ISOTOPE COMPOSITION OF THE HYDROCARBON AND CARBON DIOXIDE COMPONENTS OF HUNGARIAN NATURAL GASES

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ABSTRACT

The results of carbon isotope ratio measurements for 79 natural gas occurrence of Hungary were interpreted. On the base of carbon isotope ratios characteristic to methane and its distribution with depth genetic groups were determined which differ from each other in the character of the generation process and the type of organic material. The change of carbon isotope ratio with depth and the degree of transformation can be attributed to the common effect of kinetic isotope effect and vertical migration in the case of the methane component of natural gases of thermogeneous origin arising from the same type of organic material and trapped in Neogene reservoir rocks. Carbon isotope ratios referring to strong vertical migration are in general in connection with the high carbon dioxide content of natural gases. It could have been established from the carbon isotope ratios of carbon dioxide that the bulk of carbon dioxide originated from the deeper zones of the lithosphere as a consequence of regional metamorphism of carbonate rocks.

INTRODUCTION

The Pannonian basin is an intermontaneous sinking between the mountain arches of Alps, Carpathians and Dinaric mountains, which is filled up with continuously formed Neogene sediments of Molassic character [SZALAY, KONCZ, 1981]. The base of Neogene formations is formed from Mezozoic and Paleozoic sedimentary rocks with varied evolution. A sediment mass of 7000 meter thickness accumulated in the Neogene sinkings. The sinking of basin parts started in the middle Miocene and became more intensive in the lower Pliocene. The depth of the boundary of Pliocene/Miocene in a part of the Neogene sinkings is 3400—4500 meters, while in the other part is between 1000—2500 meters (average value: 1500 meters). In this latter case Miocene sediments of great thickness were formed. The velocity of sediment formation was 200—500 meters (in average 300—400 meters), and 100—250 meters (in average 100—150 meters) per million years, respectively. The geothermic gradient varies between 0.036—0.055 °C/meter according to present measurements. The velocity of heating up calculated from the present geothermic gradients and velocity of sedimentation varies between 9—1 8°C/million years. This value in the parts of the basin with different sedimentation conditions is 14—18 and 9—12 °C/million years, respectively.

The vitrinite reflections (R_0) measured from Neogene sedimentary rocks and evaluated by the Dow method gave a linear relationship with depth in the coordinate system lg R_0—m × 10^4 with a slope of 1.7—3.1 [Dow, 1978, MÁFKI, MTA GKL, KBFI Reports]. The slope of the lg R_0 — depth function is 1.7—2.2 (average 2.0) for the parts of the basin where Miocene sediments are thin, while for thick Miocene sediments the slope is 3.1 *(Fig. 1)*. The slope of lg R_0 — present temperature functions – expressed in lg R_0/ °C × 10^3 units – is 3.6—5.2 (average 4.4) and 6.3, respective-
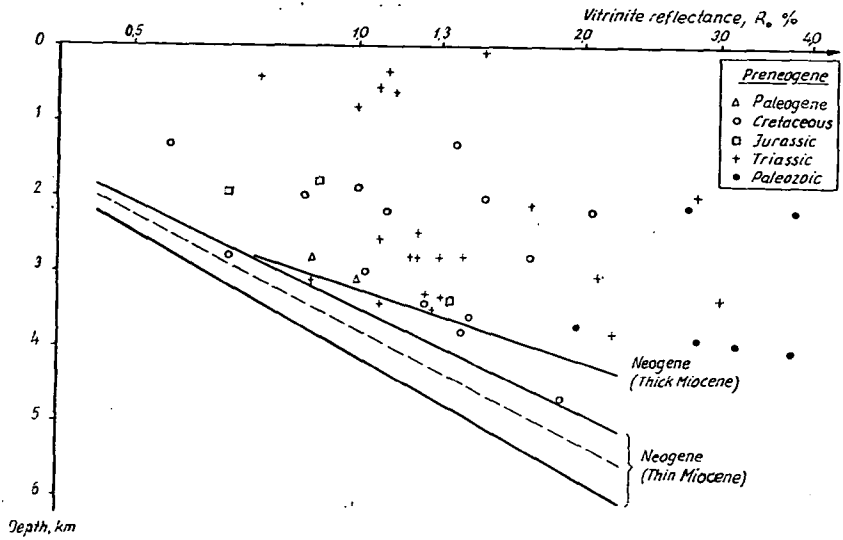
Fig. 1. Relation between the vitrinite reflection and depth in Neogene and older sediments.
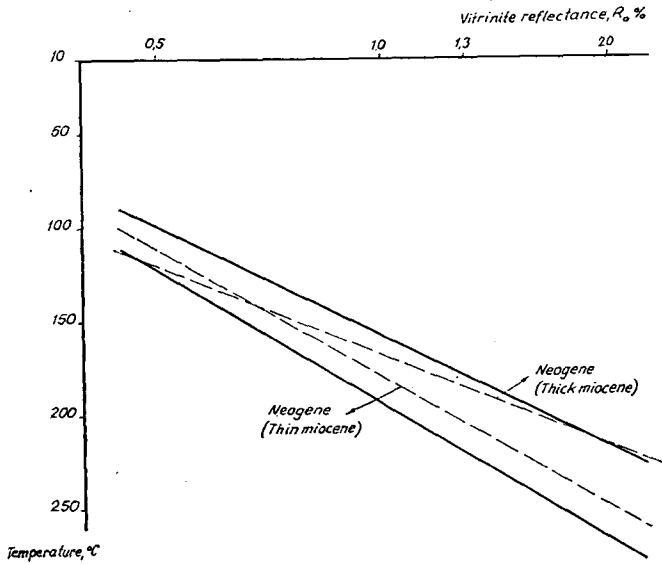

Fig. 2. Relation between the vitrinite reflection and present temperature in the Neogene sediments

ly *(Fig. 2)*. The present temperature of Neogene sediments can be assumed as identical with the maximum temperature reached.

Based on vitrinite reflections, those depth- and temperature boundaries can be determined in Neiogene sediments, which correspond to the stages of catagenic transformation of organic matter [Dow, 1978], (Table 1). The vitrinite reflections for

TABLE 1

*Depth and temperature boundaries of the stages of catagenic transformations
in the Neogene sediments*

Stage	$R_o\%$	Depth, km	Temperature, °C
Beginning of crude oil formation	0.5	2.1—2.5	100—123
Beginning of wet gas formation	1.0	3.3—4.2	160—190
End of crude oil formation			
Beginning of dry gas formation	1.3	3.6—4.8	180—220
End of wet gas formation	2.0	4.2—5.8	220—270

sediments older than Neogene are of course greater, than for Neogene sediments, or at least approximate those of the Neogene *(Fig. 1)*. This indicates, that a part of pre-Neogene sediments reached only in the Neogene those conditions under which they could generate hydrocarbons. This fact increases the hydrocarbon perspectives of pre-Neogene sediments.

The known Hungarian natural gas accumulations are in the depth interval of surface — 5.5 kilometers. The composition of natural gases varies in a wide range. One of their characteristics is the occurrence of carbon dioxide in a wide concentration range (0—0.98 cu.m/cu.m). This variety of composition which probably indicates a genetic heterogenity, justifies the study of their origin by means of the stable carbon isotope composition of carbonaceous components (hydrocarbons, carbon dioxide).

PREVIOUS WORKS

HOLCZHACKER *et al.* [1981] published the carbon isotope distribution of hydrocarbon components of Hungarian natural gases as well, as its change with depth and carbon dioxide concentration. The maximum depth of biogenetic methane occurrence was determined as 950 meters, while the minimum depth of thermogeneous methane arising from catagenic transformations was determined in 800 meters. The tendentious change of carbon isotope ratio of methane, the enrichment of ^{13}C with depth was attributed to the kinetic isotope effect.

NAMESTNIKOV has pointed out by means of the hydrocarbon composition of the natural gases in the Pannonian basin that the main zone of crude oil formation is in a depth interval of 1.6—3.2 kilometers.

KERTAI attempted first to clear the origin of carbon dioxide based on the carbon isotope composition of carbon dioxide of Hungarian natural gases and on their geologic environment [KERTAI, 1972]. He supposed that the significant carbon dioxide reserves are in connection with the metamorphic base and are the product of the regional metamorphism of carbonates.

TÖRÖK studied the composition distribution in natural gas reservoirs containing carbonated and nitrogeneous natural gases. His gravitational — migration model explained the distribution and distribution types of carbon dioxide within one reservoir and reservoirs located above each other. The depth of „source"can also be determined but the origin of carbon dioxide has not been treated [TÖRÖK, 1979].

CORNIDES and KECSKÉS [1982] and KECSKÉS *et al.* [1981] studied the carbon isotope ratio of Slovakian mineral waters rich in carbon dioxide and came to the conclusion that the problem of carbon dioxide origin in the Carpathian basin can be solved only taking into account the carbon dioxide of juvenile origin, too.

HOLCZHACKER *et al.* [1981] came to the conclusion from the low negative carbon isotope ratio of the methane of highly carbonated natural gases that the methane associated with carbon dioxide was formed at high temperature and in a great depth.

ANALYTICAL PROCEDURES

The carbon dioxide was extracted from the samples by barium-hydroxide. The barium carbonate was prepared with filtration, washing and drying for mass spectrometric measurements. The gas for measurement was made in vacuum with ortophosphoric acid.

The hydrocarbons of carbon dioxide-free gas samples were transformed to carbon dioxide in ampoules containing catalisator and copper oxide (CuO) previously heated in vacuum.

The measurements of isotope ratios were performed on a VARIAN—MAT86 mass spectrometer. Carbon dioxide made of the Stringocephalenkalk von Rübenland carbonate with ortophosphoric acid was used as a standard. The results are converted into PDB standard. The standard deviation of measured data is $\pm 0.25\%$.

The methane was not preparatively separated from the hydrocarbons of natural gases, so the carbon isotope ratios relate to the total amount of hydrocarbons of the given gas. It is known that the carbon isotope ratio of hydrocarbons heavier than methane is a lower negative value [FUEX, 1977]. To prevent greater deviations only the carbon isotope ratio of such gases was evaluated in which the share of hydrocarbons heavier than methane was not higher than 10 per cent. Assuming the highest carbon isotope ratio, -25%, for the C_2 components the maximum deviation is $+2\%$. This little deviation can be neglected near the wide carbon isotope ratio range of the methane, so it was assumed that the carbon isotope ratio measured for the hydrocarbon constituents of a natural gas approximately represents the carbon isotope ratio of the methane.

The preparation of the samples and the mass spectrometric measurements were performed in the Central Research and Development Institute of Mining by K. HOLCZHACKER, P. A. PETIK, É. MEDGYES.

SAMPLE LOCATIONS

The gas samples give information from 79 natural gas accumulations of Hungary. The areal arrangement of gas reservoirs is shown on *Fig. 3*. 67 per cent of the gas samples originated from Neogene reservoirs, 22 per cent from Mezozoic reservoirs covered with Neogene sediments and 11 per cent from Paleozoic reservoirs. The depth interval of the Neogene reservoirs extends from the surface till 5.3 kilometers. The Mezozoic and Paleozoic gas samples originated from a depth interval of 1.8—4.4 and 1.5—3.9 kilometers, respectively.

RESULTS AND DISCUSSION

The carbon isotope ratios of the hydrocarbons

It is known from the literature that the carbon isotope ratio of the methane shows marked differences depending upon the character of the generation process. The thermogenic methane which is the results of catagenic transformation of the organic matter is much more richer in ^{13}C, than the biogenic methane of bacterial

origin. The boundary between biogenic and thermogenic methane is determined empirically based upon the distribution of carbon isotope ratios. The carbon isotope ratio range of the biogenic methane was determined by FUEX [1977] between $-50\%_0$ and $-90\%_0$, while ALEKSEEV [1977] established a range of $-55\%_0$ and $-95\%_0$; the same range for thermogenic methane is, according to FUEX, $-20\%_0$ $--60\%_0$, while
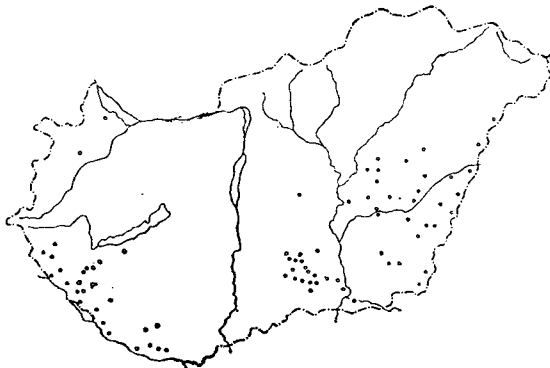

Fig. 3. The natural gas reservoirs studied in Hungary

ALEKSEEV has put it between $-36\%_0$ and $-58\%_0$, The isotope ratio range in the simultaneous presence of thermogenic and biogenic methane is $-50\%_0$ $-60\%_0$ (FUEX] and $-55\%_0--65\%_0$ [ALEKSEEV].

These empirical boundaries in Hungarian natural gases are (*Figs. 4* and *5a*):
— biogenic: $-65\%_0$ and $-81\%_0$ (group „C")
— biogenic+thermogenic: $-59\%_0$ and $-65\%_0$ (group „D"),
— thermogenic: $-22\%_0$ and $-59\%_0$ (groups „A" and „B").

The maximum depth of occurrence of natural gases containing methane of biogenic origin (groups „C" and „D") is 1 kilometer. Maximum reservoir temperatures are 45—60 °C.
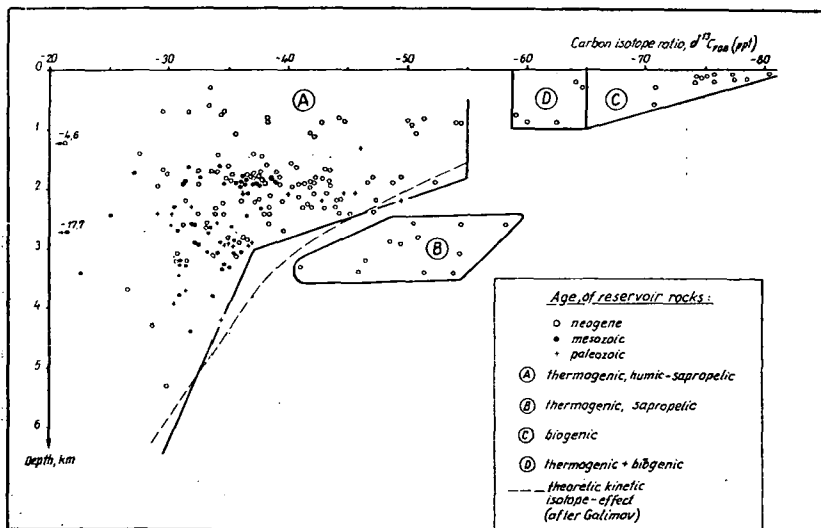

Fig. 4. The carbon isotope ratios of the hydrocarbons of natural gases as a function of depth.

The isotope ratios of thermogenic methanes are determined mainly by the type of the organic matter and the kinetic isotope effect. The methane arising from humic type organic matter is richer in ^{13}C than the methane of sapropelic origin [SCHOELL, 1980]. At the same degree of transformation this difference is 10—15‰. It can be concluded from the carbon isotope ratio distribution of thermogenic methane of the Hungarian natural gases that the high negative values at depths greater than 2.5 kilometers are the consequence of the presence of methane originated from sapropelic type of organic matter (*Figs. 4* and *6.* group „B").
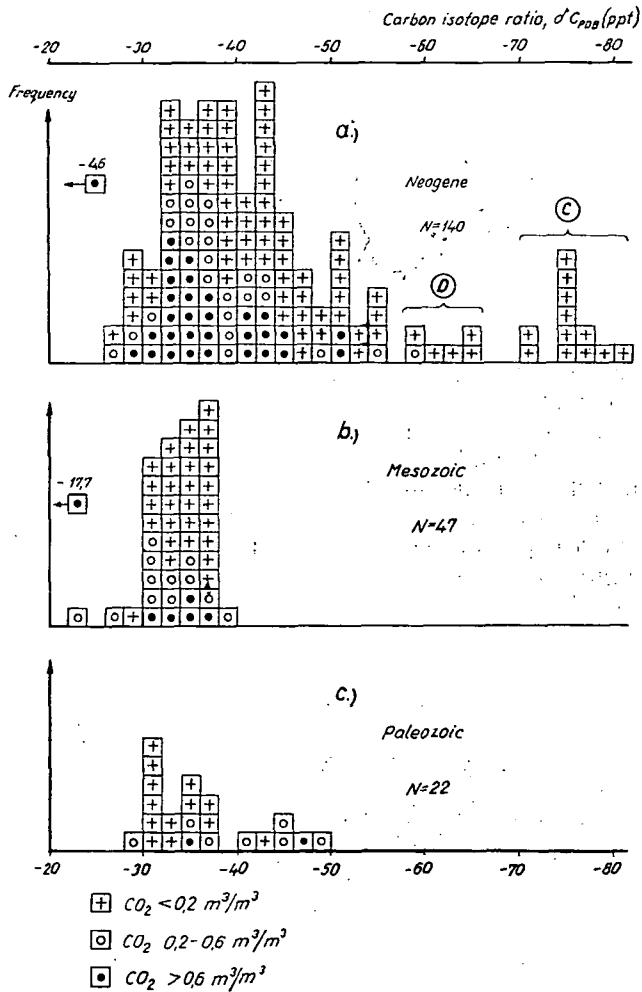

Fig. 5. The carbon isotope ratio distribution of natural gases of reservoir rocks with different age

The change of carbon isotope ratio distribution with depth in the group „A" can be attributed to the kinetic isotope effect. With the increase of depth the ^{13}C enriches in the methane and approximates the carbon isotope ratio range of the generating source, the kerogene [GALIMOV, 1973], PRASOLOV and LOBKOV, 1977], *(Figs.*

4, 6, 7d). Because of the vertical migration, not the autochtonous methane is present in general in the natural gas accumulations, but only a quasi autochtonous methane, which underwent only minor vertical displacement, and syngenetic with the kerogene. That is why the kinetic isotope effect has the form of an envelope curve in the upper region of the carbon isotope ratio distribution at high negative limit values
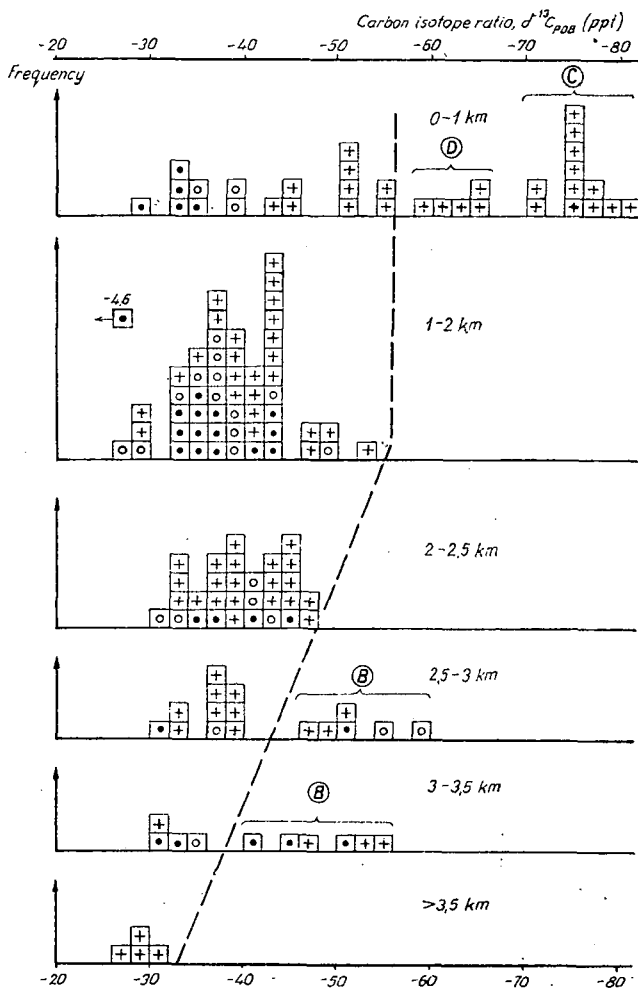

Fig. 6. The carbon isotope ratio distribution of the hydrocarbons in natural gases of Neogene reservoir rocks in different depth intervals

[PRASOLOV and LOBKOV, 1977]. The limiting curve obtained by GALIMOV's theorethical calculations and adapted to the geothermic conditions of the Pannonian basin, representing the effect of the kinetic isotope effect is shown in *Fig. 4*. This is in good agreement with the boundary line plotted by us on the base of upper limit values. It must be mentioned, however, that the correlation of kinetic isotope effect with formation temperature and depth is only a rough approximation, as the effect is determined by such parameters e.g. vitrinite reflection, which reflect the grade of transformation

Carbon isotope ratio, δ^{13}_{PDB} (ppt)

a. Neogene / Mesozoic / Paleozoic

b. Neogene — CO_2 m^3/m^3 — > 0.6 / $0.2 - 0.6$ / < 0.2

c. Mesozoic — CO_2 m^3/m^3 — > 0.6 / $0.2 - 0.6$ / < 0.2

d. Neogene Group (A) — Depth km — < 1 / $1 - 2$ / $2 - 2.5$ / $2.5 - 3$ / > 3

e. Neogene Group (A) — Depth km — $0-1$: $CO_2 > 0.6$ m^3/m^3 / $0.2 - 0.6$ / < 0.2; $1-2$: > 0.6 / $0.2 - 0.6$ / < 0.2
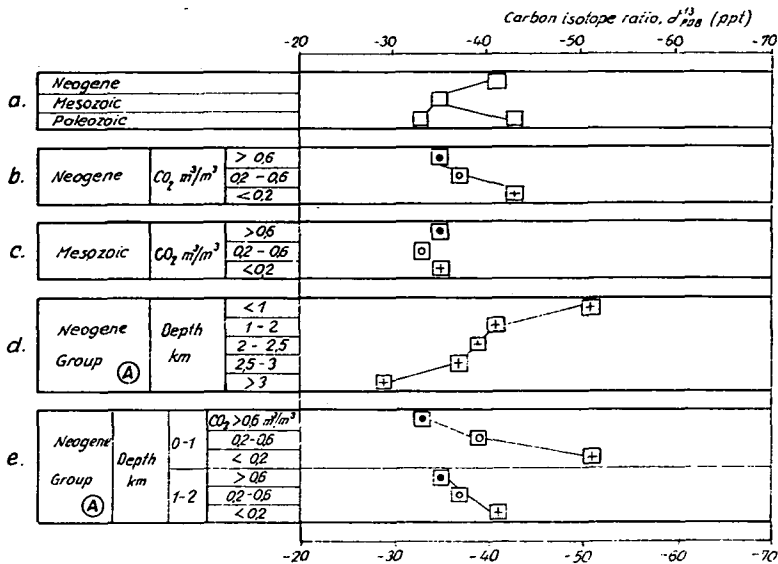
Fig. 7. The median of carbon isotope ratio distributions of the hydrocarbons of Hungarian natural gases

degree of transformation of the organic matter in sediments with different age *(Fig.* and the simultaneous effect of time and temperature [SCHOELL, 1980]. The influence of migration after the formation upon the carbon isotope ratios can be neglected beside the effects of the organic matter type and kinetic isotope effect.

The change of carbon isotope ratio with depth in the natural gases of group „A" is very remarkable. The carbon isotope ratio of methane, in several cases associated with a high concentration of carbon dioxide in relatively shallow formations (depth 0—1 kilometer) corresponds to a depth of formation greater than 3 kilometers. This indicates that in the surrounding of these accumulations there was a significant vertical migration.

There are characteristic differences in the carbon isotope ratio distribution correlated with the age of the reservoir rocks *(Fig. 5)*. The thermogenic methane of the Neogene reservoir rocks has a wider carbon isotope ratio range $(-25\%_0 + -56\%_0)$ than that of the Mezozoic reservoir rocks $(-20\%_0 - -30\%_0)$ where the distribution range is only 10‰. There are two populations in the carbon isotope ratio distribution of the methane originating from Paleozoic reservoir rocks: one of them is in the range of $-28\%_0$ and $-38\%_0$, the other $-40\%_0$ and $-50\%_0$. Although the age of the reservoir rocks is not equal to that of the mother rocks, the differences between the carbon isotope ratio distributions are in connection with the higher degree of transformation of the organic matter in the Mezozoic and Paleozoic sediments, which has been expressed with the vitrinite reflection values *(Fig. 1)*. The population originating from Paleozoic reservoir rocks and characterized with methane enriched in ^{12}C has resulted probably from the migration of the methane which has been generated in Neogene sediments. The population enriched in ^{13}C was taken as characteristic to the methane syngenetic with sediments older than Neogene. The median of carbon isotope distribution ratios indicates a Neogene — Mezozoic — syngenetic Paleozoic sequence in the enrichment of ^{13}C. This seems to show also a relationship with the

40

7a). This relationship, however, can be explained also with the assumption that the type of organic matter shifted towards the humic type. As we have no data about the type of organic matter, the effect of the degree of transformation and the type of organic matter can not be unequivocally separated.

The relatively great number of carbon isotope ratios for methane and the great depth interval of Neogene reservoirs has allowed the correlation of carbon isotope ratio distributions with depth *(Fig. 6).* The carbon isotope ratios can be correlated with the stages of the transformation of organic matter by means of the vitrinite reflections belonging to given depth intervals (Table 2). The width of carbon isotope ratio intervals decreases with the depth: at a depth less than 1 kilometer this range is 54‰, while at depth greater than 3.5 kilometers it decreases to 6‰ parallelly with the enrichment of ^{13}C. In shallow depth (< 1 km) genetically separable gas accumulations has been found which contain methane of biogenic origin (group „C") and both biogenic and thermogenic methane (group „D"). In the depth range of 2.5—3.5 kilometers are found those natural gas accumulations with methane of thermogenic origin which has been formed from sapropelic type of organic matter (group „B"). The carbon isotope ratio distribution of the methane in the natural gases of the group „A" which gives the bulk of the data, reflects the simultaneous effect of the vertical migration and kinetic isotope effect. The width of the range of carbon isotope ratios decreases from 28‰ (depth < 2 kilometers) to 6‰ (depth > 3 kilometers). Parallelly with this phenomenon the median of the carbon isotope ratio distributions according

*Vitrinite reflection ranges and stages corresponding to the depth ranges
in Neogene sediments*

Depth range km	Vitrinite reflection range $R_0 \%$	Stage
0—2	0.2—0.5	Immature
2.0—2.5	0.5—0.6	Beginning of crude oil formation
2.5—3.0	0.6—0.8	The main phase of crude oil formation
3.0—3.5	0.8—1.2	The main phase of crude oil formation and beginning of wet gas formation
$> 3,5$	> 1.2	Formation of wet and dry gas

to the kinetic isotope effect shift towards less negative values with the increase of depth *(Fig. 7a).* In depth greater than 3 kilometers only syngenetic methane exists with carbon isotope ratios corresponding to the carbon isotope ratio of dry gas formed in great depth, and geothermal methane, respectively [FUEX, 1977]. The increase of carbon isotope ratio range with decreasing depth can be attributed to the effect of vertical migration.

One of the characteristics of the Hungarian natural gas accumulations is the frequent occurrence of carbon dioxide in a wide concentration range. It frequently occurs that in the same pool and depth interval the carbon isotope ratio of the methane in natural gases with high carbon dioxide concentration is a significantly less negative value, than that of the methane coexisting with a low carbon dioxide concentration (Table 3). This fact indicated the discrimination of the carbon isotope ratios of the methane depending upon the carbon dioxide concentration of the natural gas *(Figs. 5, 6, 7).* The dependence of the carbon isotope ratio of the methane from the carbon

TABLE 3

The change of the carbon isotope ratio of methane with carbon dioxide concentration

Depth km	CO_2 · m^3/m^3	The carbon isotope ratio of methane $^{13}C_{PDB}$ ‰
3.1—3.4	0.05	− 46.4
	0.51	− 22.6
0.7—0.9	0.11	− 44.9
	0.93	− 29.5

dioxide concentration has occurred only in Neogene gas accumulations; this pheno-menon has not been observed in the gases of Mezozoic reservoirs *(Figs. 7b, 7c)*. The greatest deviations have been found in the natural gases of the shallow (< 1 kilo-meter) Neogene reservoirs *(Fig. 7e)*. The above mentioned deviations decrease with the increase of depth and are not significant under 2.5 kilometers. These facts indicate that the methane of natural gases with high carbon dioxide concentration is not syngenetic with the methane of natural gases with low carbon dioxide concentration and has migrated together with the carbon dioxide to the present accumulation. This statement is not equivalent with that one that the methane of natural gases with high carbon dioxide concentration is syngenetic with the carbon dioxide, because the carbon dioxide during its vertical migration is able to extract the hydrocarbons from the rocks. The anomally low negative carbon isotope ratio of the methane of natural gases with high carbon dioxide concentration in shallow reservoirs proves a marked vertical migration and an open structure. This assumption has been supported by the practical experience that such natural gas accumulations have been formed in the surrounding of structural lines, deep faults [TÖRÖK, 1979].

Two anomalous carbon isotope ratios have to be interpreted in connection with the high carbon dioxide content: −4.6‰ and −17.7‰. It can be supposed in these cases that the methane associated with the high carbon dioxide content was formed from inorganic (carbonate) carbon; the carbon dioxide formed during regional metamorphism or the juvenile carbon dioxide was hydrogenated with water in the hot zones of the lower part of the earth's crust or in the upper part of the earth's mantle [GUCALO, 1980; KRAVCOV, 1980].

THE CARBON ISOTOPE RATIO OF THE CARBON DIOXIDE

The frequent occurrence of carbon dioxide in Hungary and the wide range of carbon dioxide content of natural gases has made possible the study of carbon dioxide origin by means of carbon isotope ratios.

Carbon dioxide can arise from different sources and in different processes in the different zones of the earth. The primary sources of the carbon dioxide are the exogenous (atmospheric) and endogenous (from the material of the earth's mantle) juvenile carbon dioxide. The atmospheric carbon dioxide can be divided into two groups with markedly different carbon isotope ratios: one of it contains inorganic carbon (the bulk of carbonates) independent of the metabolism of living organisms, the other is composed of so called organic carbon as a result of the metabolism of living organisms. Several processes form carbon dioxide from the exogenous carboniferous material containing organic and inorganic carbon (Table 4). The

TABLE 4

The transformation of organic and inorganic carbon of exogene origin into carbon dioxide

Geosphere		The quality of carbon	The process of carbon dioxide formation
Biosphere		Organic carbon	Oxidation (with atmospheric oxygen, microbic)
Lithosphere	Upper part of the earth crust		The microbic oxidation of hydrocarbons
			Oxidation (with atmospheric oxygen)
			Diagenesis, catagenesis
			Contact metamorphism
		Inorganic carbon	Hydrolysis
			Dissolution with CO_2 of different origin
			Contact metamorphism
	Lower part of the earth crust, upper part of the earth mantle	Organic and inorganic carbon	Regional metamorphism

microbial and atmospheric oxidation as well as the diagenetic transformations of the organic matter is going on in shallow depth, and accordingly at low temperatures. Higher temperature and greater depth are necessary for the catagenic processes of organic material and the hydrolysis of carbonates. In the lower part of the earth's crust and in the upper part of the earth's mantle in the pressure- and temperature range corresponding to the greenschist-, epidote- and epidote-amphibolite rock facies, during regional metamorphism carbon dioxide arises both from the organic carbon existing in graphit state and the inorganic carbon of the carbonates. Significant amount of carbon dioxide arises from the impure carbonates simultaneously with the formation of epidote and tremolite [HOEFS and MORTEANI, 1979; KREULEN, 1980]. The hydrogenation of carbon dioxide arising from the decomposition of carbonates during regional metamorphism may result such methane the carbon isotope ratio of which is in the range of inorganic carbon [GUCALO, 1980; KRAVCOV, 1980]. As it was previously shown similar situation has been found in the Hungarian gas accumulations, too. The contact metamorphism and the dissolution of carbonates, on the contrary, can not be adapted to predetermined depth- and temperature ranges.

The lower part of the earth's crust and the upper part of the earth's mantle is able to generate carbon dioxide more than four order of magnitude, the magmatic rocks of anatectic origin generate carbon dioxide more than one order of magnitude, than the sedimentary rocks [SOKOLOV, 1971]. These data indicate that gas accumulations with high carbon dioxide concentration have been formed mainly from carbon dioxide generated in the lower part of the earth's crust and in the upper part of the earth's mantle. This means that the source of the bulk of carbon dioxide is mainly the juvenile carbon dioxide and the carbon dioxide generated by regional meta-

morphism [KERTAI, 1972; HOEFS and MORTEANI, 1979; KREULEN, 1979; PANKINA, 1979; MAXIMOV *et al.*, 1980; PANKINA *et al.*, 1978].

The determination of the origin of carbon dioxide by means of carbon isotope ratios is difficult, however, because the carbon dioxides of different origin, which can be well distinguished by carbon isotope ratios, may mix within a given geosystem, or may be generated simultaneously from different sources. During the regional metamorphism carbon dioxide with different carbon isotope ratios is generated simultaneously from carbon of graphite state and from carbonates. The mixture of such carbon dioxide is richer in ^{12}C depending upon the concentration of the graphite, than the carbonates are. This effect can be so marked that the carbon dioxide originated from the regional metamorphism can be distinguished from the juvenile carbon dioxide [HOEFS and MORTEANI, 1979]. The alternative origin hypotheses of different authors have been based on these problems. The most frequent origin hypotheses are: a) juvenile, b) regional metamorphism of carbonates and graphite and c) the mixture of the above mentioned. Further complications are caused by the vertical migration, because in this process the carbon dioxide is able to dissolve carbonates, or to blend with the carbon dioxide of organic origin which has been formed in different processes (oxidation, catagenesis). In the former case the carbon dioxide enriches in ^{13}C, in the latter one in ^{12}C. It is evident from these difficulties, that the reliable determination of carbon dioxide origin can not be performed only by means of the carbon isotope ratios, which, although they are extremely useful and necessary, can only be used with limited validity without geologic interpretation.

The carbon isotope ratios of the carbon dioxide of Hungarian natural gases have been in the range -1.1% — -18.1%. The median of the frequency distribution is at -5% and -6%, the boundaries of probable values interval — median $\pm$ standard deviation — are at -4 and -9%, respectively *(Fig. 8a)*. The carbon isotope ratio distribution has shown a dependence upon carbon dioxide concentration. The greatest significant deviation has occurred at natural gases having a carbon dioxide concentration lower and higher than 0,6 cu.m/cu.m. The statistical test used has been the KOLMOGOROV—SMIRNOV's no-parameter-method with a reliability of 95 per cent. The difference between the two distributions depending upon the concentration of carbon dioxide has had a character, that in natural gases with high carbon dioxide concentration (higher than 0.6 cu.m/cu.m) carbon dioxide with an isotope ratio higher than -10% did not occur *(Figs. 8b and 8c)*. Therefore it can be concluded that in natural gases containing carbon dioxide with an isotope ratio higher than -10% the proportion of carbon dioxide formed from organic carbon is higher. The range of the probable carbon isotope ratio distribution of carbon dioxide in natural gases with high carbon dioxide content is between -4% and -7%, which corresponds to the carbon isotope ratio of juvenile carbon dioxide, -4% and -8% [KREULEN, 1980; EGLINTON and MURPHY, 1969; KROPOTOVA, 1979; PUCHELT and HUBBERTEN, 1980]. However, these carbon isotope ratios could be also the result of mixing carbon dioxides formed during the regional metamorphism of carbonates and graphite.

The carbon isotope ratios of the carbonates of Hungarian sedimentary rocks are in the range of $+4\%$ and -4% [HOLCZHACKER *et al.*, 1981]. The proportion of carbon dioxide with a carbon isotope ratio of less than -4% increases, while the proportion of carbon dioxide with a carbon isotope ratio higher than -10% decreases with the depth (Table 5). This trend can be interpreted in such a way that the carbon dioxide rich in ^{13}C blends with the carbon dioxide of organic origin rich in ^{12}C as the

depth decreases; the source of carbon dioxide rich in ¹³C is in greater depth in the litosphere.

There is no significant deviation between carbon isotope ratio distributions of carbon dioxides originating from reservoir rocks of different age (*Figs. 9* and *10*). However, the frequency of high negative carbon isotope ratios ($>-10\%_0$) characteristic of carbon dioxide of organic origin is relatively high at the carbon dioxides
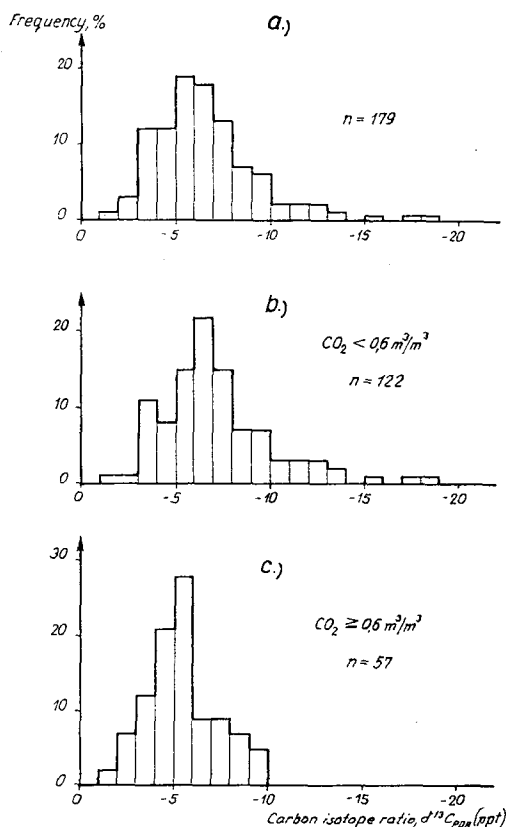

Fig. 8. Carbon isotope ratio distributions of the carbon dioxide of Hungarian natural gases

TABLE 5

The change of the carbon isotope ratio distribution of the carbon dioxide with depth

Depth, km	Frequency, per cent	
	$>-4\%_0$	$<-10\%_0$
< 1.5	4	19
1.5—2.0	12	8
2.0—2.5	12	10
2.5—3.0	19	4
> 3.0	32	6

of Neogene reservoir rocks (13 %). This frequency for the carbon dioxides of Mezozoic and Paleozoic reservoir rocks is only 2—6 per cent.

An important conclusion can be drawn concerning the origin of carbon dioxide if the carbon isotope ratio distributions are plotted as a function of carbon dioxide
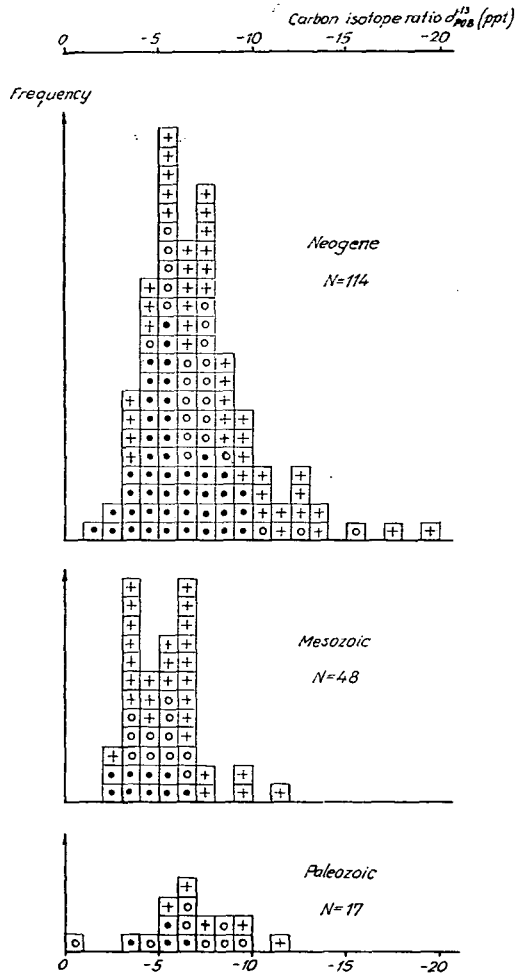

Fig. 9. The carbon isotope ratio distributions of the carbon dioxide of natural gases from reservoir rocks of different ag

concentration for reservoir rocks of different age (*Figs. 10b, c* and *d*). The carbon dioxide enriches in ^{13}C with the increase of carbon dioxide concentration and the carbon isotope ratio approximates the range of carbonates. It can therefore be concluded, that the bulk of carbon dioxide has been formed in the lower part of the earth's crust during the regional metamorphism of carbonates as it has been supposed earlier by KERTAI [1972].
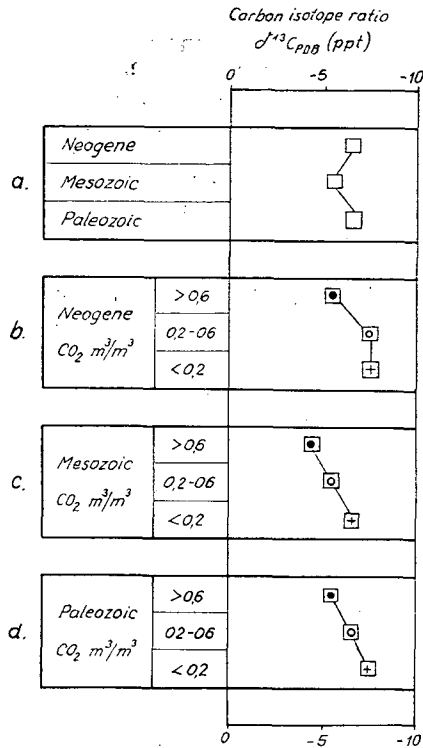
Fig. 10. The median of the carbon isotope ratio distribution of the carbon dioxide

CONCLUSIONS

1. The Hungarian natural gases can be divided into four genetic groups based on the carbon isotope ratio distribution of the methane as a function of depth: biogenic origin (group „C"); mixture of biogenic and thermogenic methane (group „B"); methane of thermogenic origin formed from sapropelic organic matter (group „D"); and the bulk of methane which has also thermogenic origin and has been formed from humic sapropelic organic matter (group „A").

2. The differences in the carbon isotope ratio distributions for reservoir rocks of different age indicate, that the methane of Mezozoic reservoir rocks has either a higher degree of transformation or originates from a more humic organic matter. The origin from an organic matter of higher degree of transformation seems to be proved by the vitrinite reflections of the Mezozoic reservoir rocks. The carbon isotope ratio distribution of the methane of Paleozoic reservoir rocks shows two populations: one of them is in the range of carbon isotope ratio of the methane of Mezozoic reservoir rocks, the other is probably of Neogene origin.

3. The change of carbon isotope ratio distribution with depth for the methane of Neogene reservoir rocks (group „A") indicates a kinetic isotope effect. The consequence of vertical migration is the increase of carbon isotope ratio ranges with decreasing depth. Carbon isotope ratios reflecting the effect of vertical migration occur frequently simultaneously with high carbon dioxide concentrations. The carbon isotope ratio distribution of methane associated with a carbon dioxide content

higher than 0.6 cu.m./cu.m. differs significantly from that of the methane of natural gases with low carbon dioxide concentration in a depth less than 2 kilometers. The methane of natural gases with high carbon dioxide concentration is enriched in [13]C. Such carbon isotope ratios of the methane of natural gases with high carbon dioxide content also occur, which indicate the anorganic carbonate origin of the methane.

4. There are significant differences in the carbon isotope ratio distribution of the carbon dioxide with the concentration. The share of carbon dioxide enriched in ^{12}C, i. e. of organic origin, is greater in natural gases with low carbon dioxide content. With the increase of carbon dioxide concentration the carbon isotope ratio distribution of the carbon dioxide shifts towards the enrichment in [13]C. This indicates that the bulk of carbon dioxide resulted from the regional metamorphism of carbonates.

5. The change of carbon isotope ratio distribution with depth indicates that the bulk of carbon dioxide originates from the deeper zones of the lithosphere. The carbon dioxide enriches in ^{13}C with increasing depth and decreases the frequency of carbon isotope ratios indicating the presence of carbon dioxide of organic origin.

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