Origin of Methane in Edge Oil-field Mineral Waters of the Iwonicz Zdrój Spa, Central Carpathian Synclinorium, SE Poland

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N°abstract

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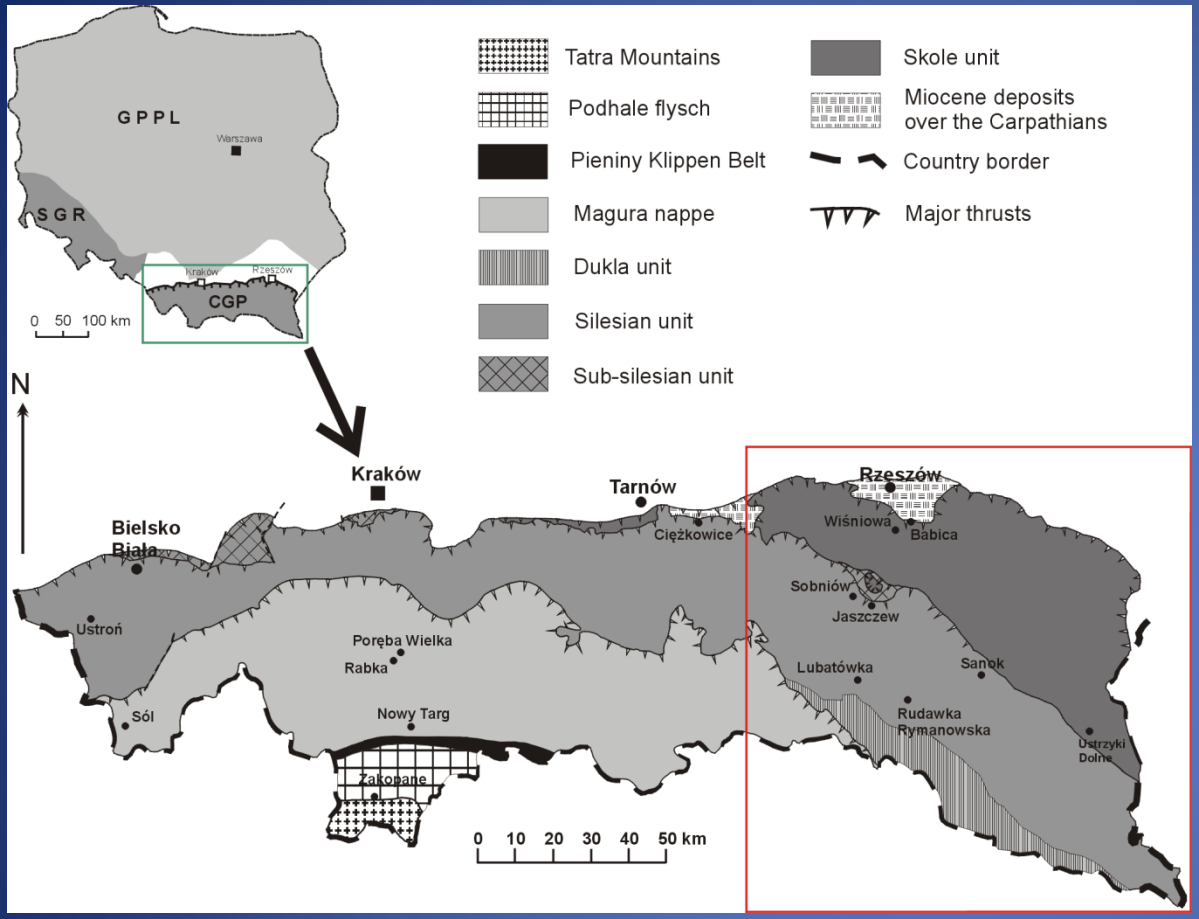
Study area



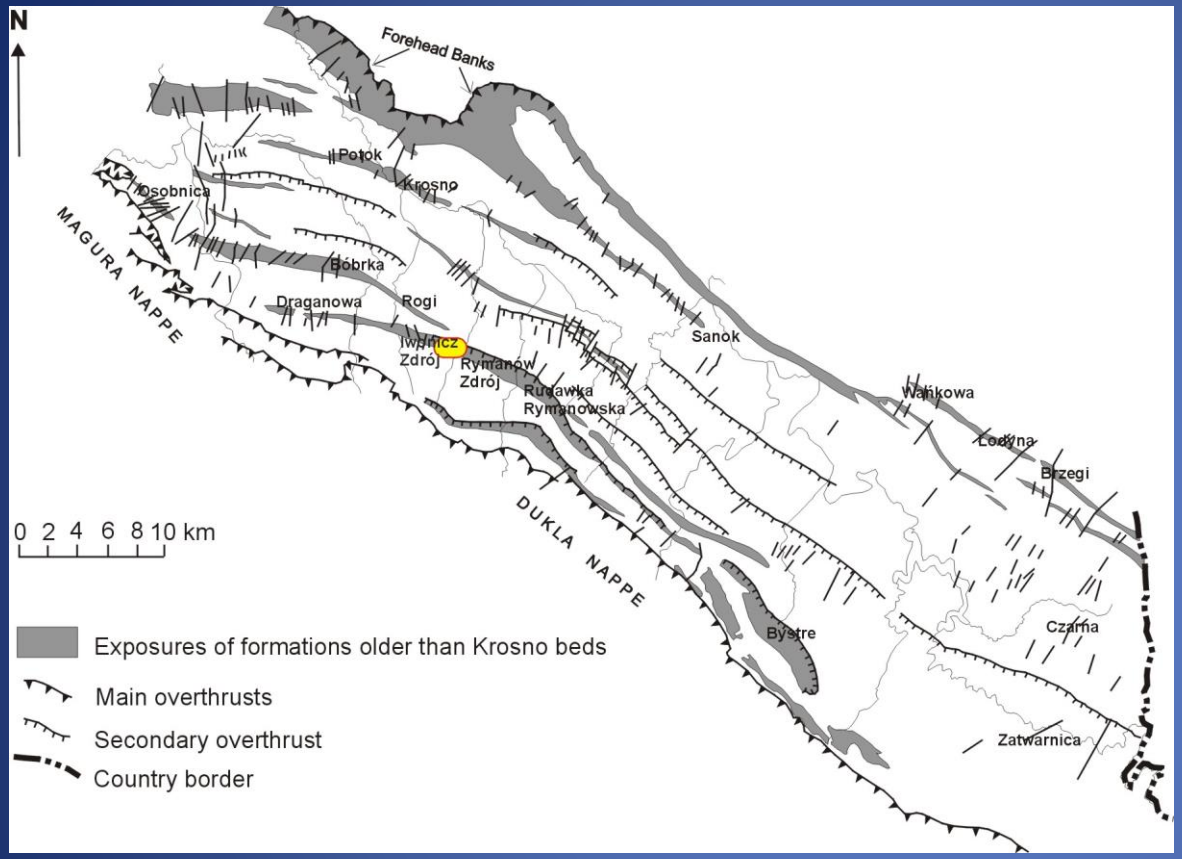
The Polish part of the Carpathian Mts consists of two geologically distinct parts:
(1) the Inner Carpathians – the southern part
(2) the Outer Carpathians (Flysch Carpathians) – the northern part, built of Cretaceous and Paleogene sedimentary formations.

Outer Carpathians are composed of several nappes that were thrusted over one another approximately from the south.

The Outer Carpathians are built entirely of flysch-type sedimentary rocks deposited in a deep sea.

N°abstract

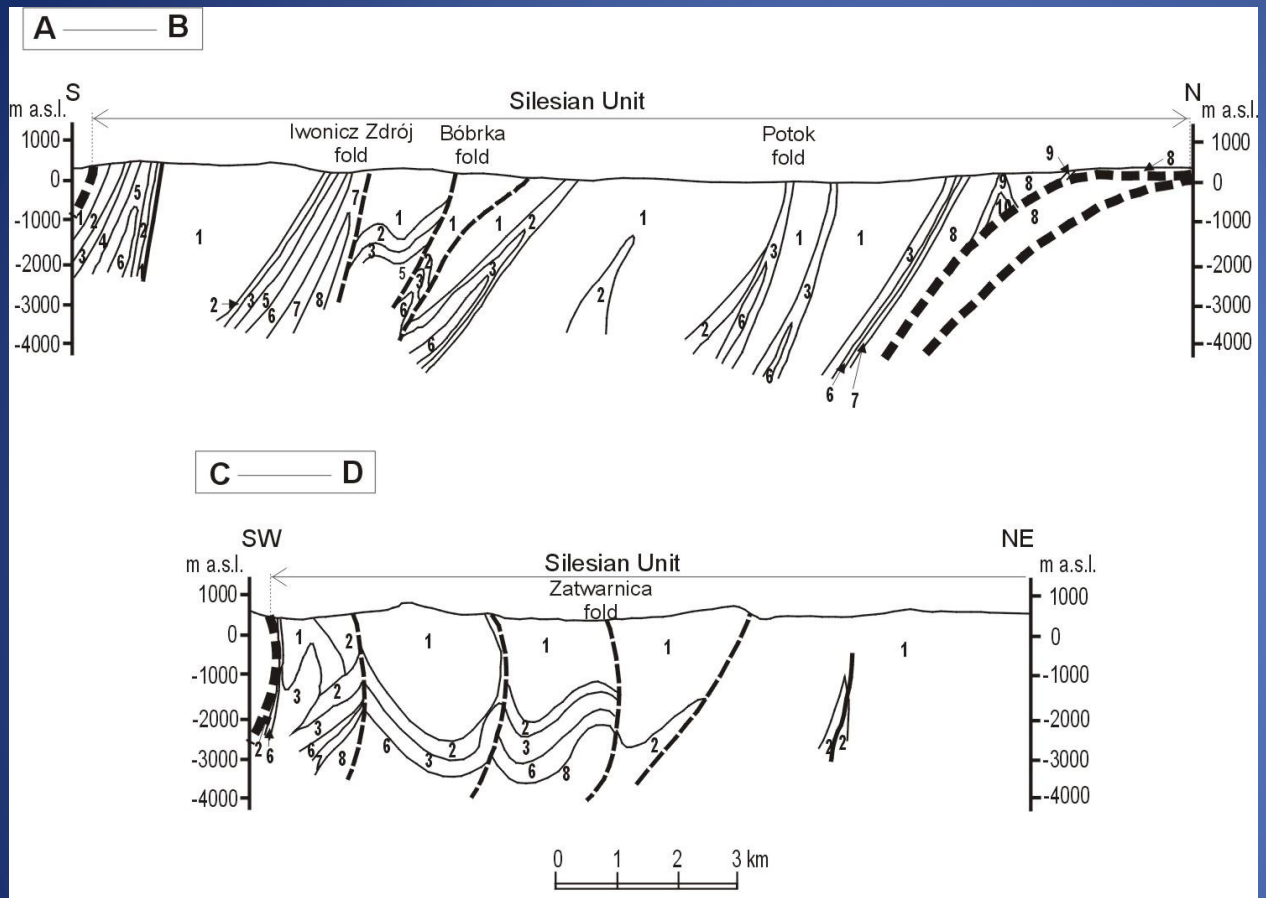
Geology



One of the largest is the Silesian Nappe, encompassing the thickest sequence dominated by coarse-grained sediments.

The Central Carpathian Synclinorium (CCS) is a structure located in the eastern part of the Silesian Nappe. The Upper Cretaceous and Tertiary flysch sediments are major constituents of the CCS.

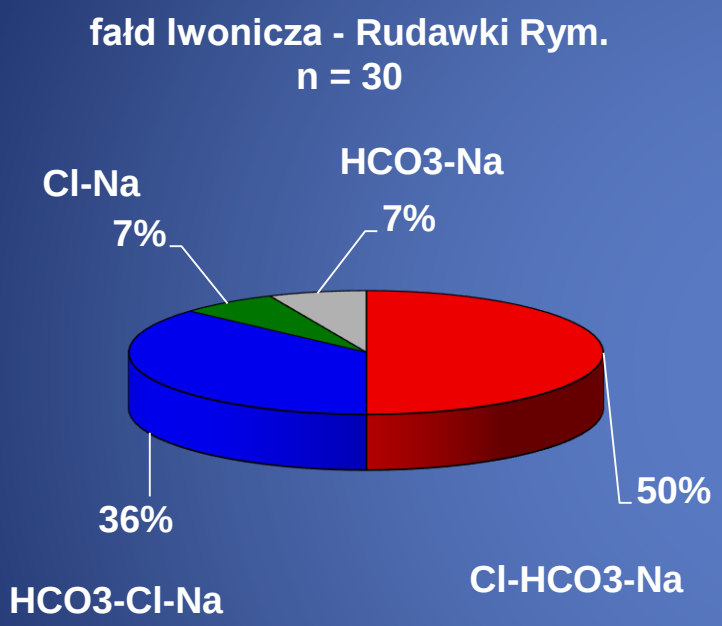
Geology

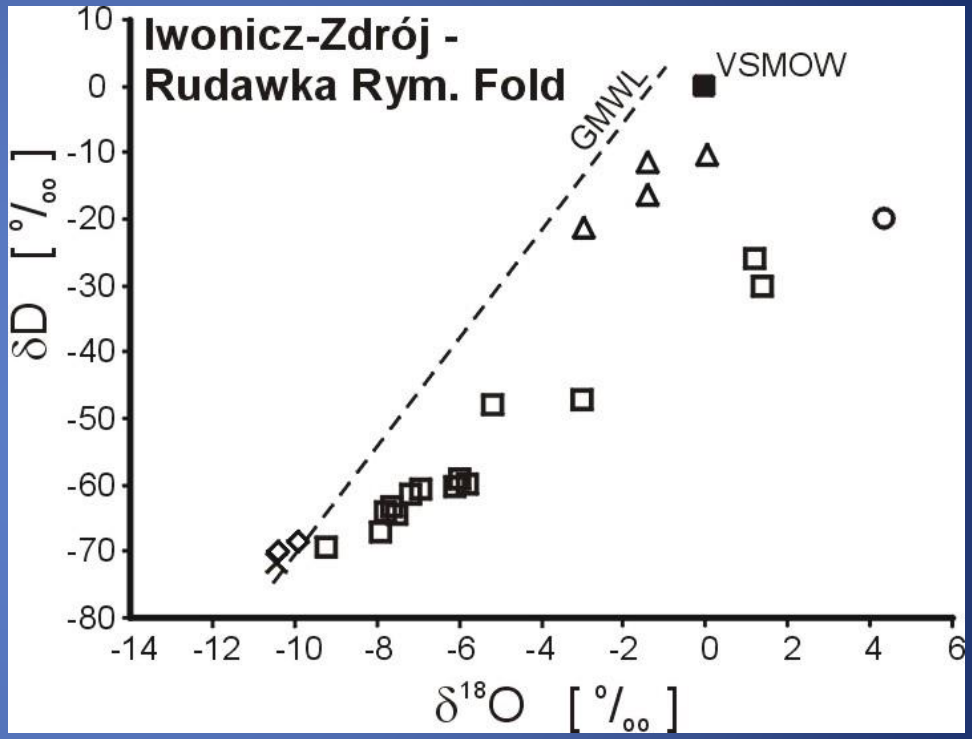


The most important sedimentary formations providing collectors of hydrocarbons and mineralized waters in the CCS are: (i) the Upper Cretaceous – Palaeocene Istebna beds, (ii) the Upper Palaeocene – Lower Eocene Ciężkowice sandstones and variegated shales; and (iii) the Oligocene Krosno beds.

The main reservoirs of oil and mineralized waters in the Iwonicz Zrdój area are found in the Upper Paleocene – Lower Eocene Ciężkowice sandstones that are interbedded by the variegated shales.

Geochemistry of waters





Cl-HCO_3 -Na + CH_4

CH_4 (methan) in groundwater

1. Methane, as a component of carbon biogeochemical cycle, is a crucial element to be followed and investigated, especially in groundwater system where it is one of carbon pool along with DIC (dissolved inorganic carbon).

Determination of sotopic composition of methan in waters of Iwonich Zdrój spa was performed in order to:

- better understand the geochemical processes in flysh sediments of Outer Carpathians,
- explain the origin of edge-oil fields waters extracted in the spa for drinking and curative purpses,
- shed light on the thermal conditions in the geological system.

CH_4 (methan) in groundwater

1. There are three princpal sources of methan in groundwaters which determine its origin (Clark & Fritz, 1997):

   a) biogenic methan – comes frm bacterial reduction of organic mtter:

   $6CH_2O \longrightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$ - fermentation and acetate & fatty acid production

   $CH_3COOH \longrightarrow CH_4 + CO_2$ - methanogenesis: acetate fermentation

   $2CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$ - methanogenesis: CO_2 reduction

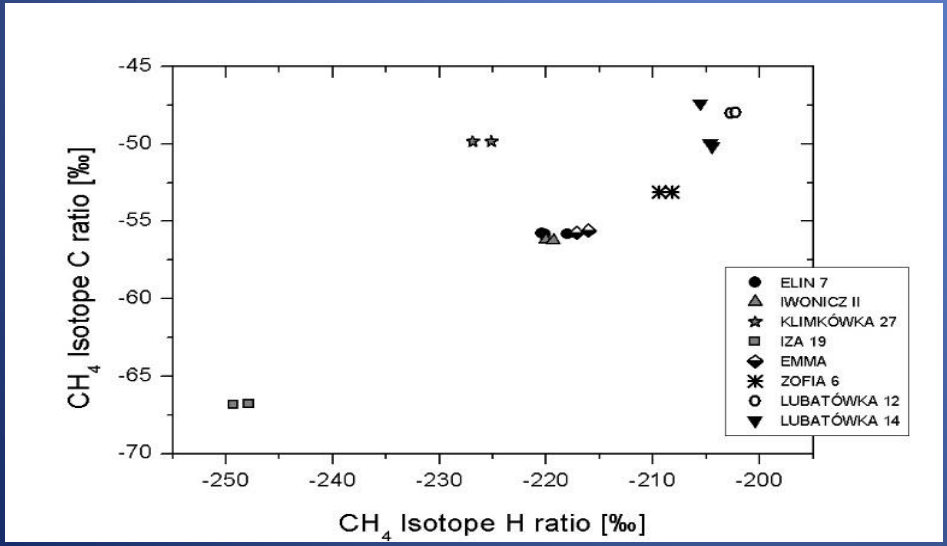
   b) thermocatalytic – comes from high temperature cracking of higher mass hydrocarbons (represents natural gas in sedimentary basins)

   c) abiogenic – comes from abiotic reactions in groundwater with very low redox potential in abesence of organic matter by reduction of CO_2, during alteration of mafic rocks. Such abiotic methan is enriched in $\delta^{13}C$ (values above -40 $^{o}/_{oo}$), and $\delta^{2}H$.

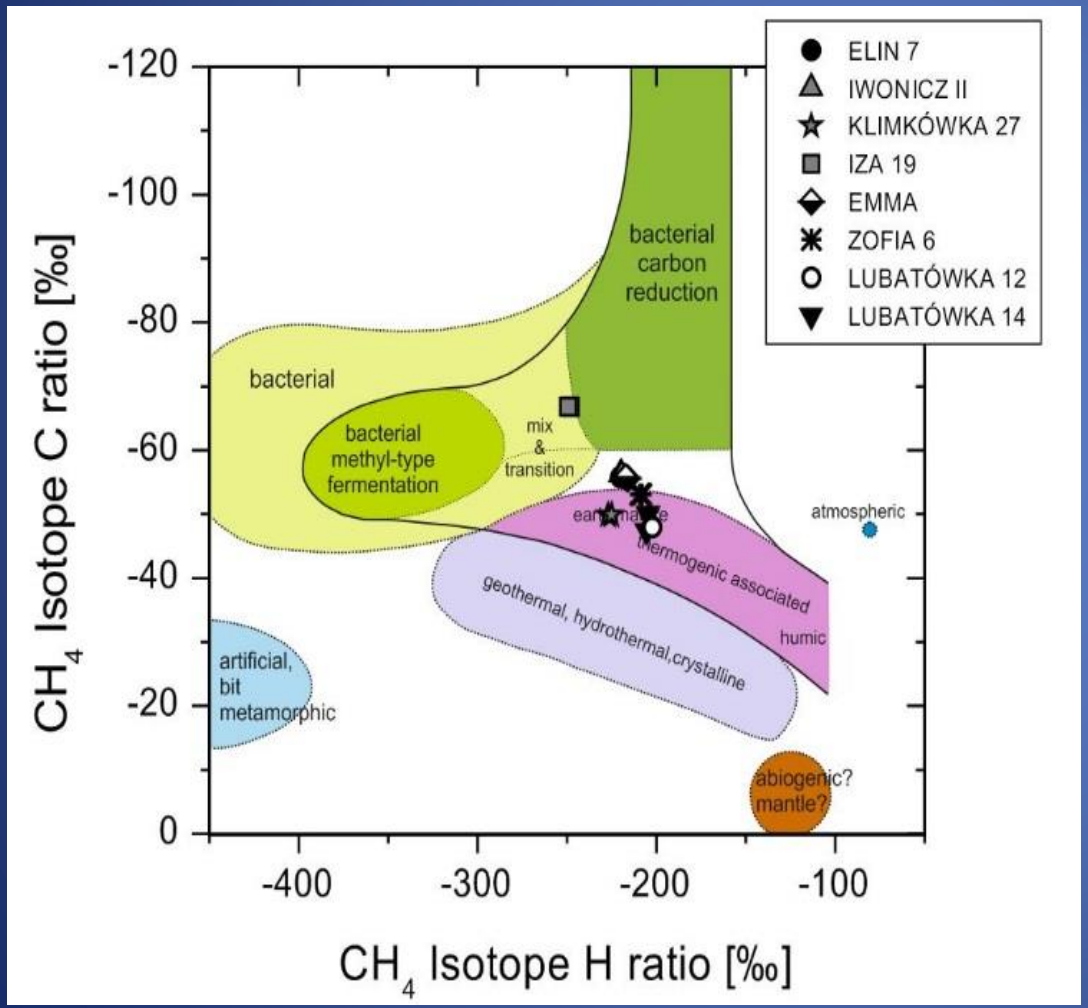
CH_4 isotopic composition

Well	Total depth [m]	pH	T [°C]	SC [mS/cm]	CH_4	
					δD [‰]	$\delta^{13}C$ [‰]
ELIN 7	230	7.66	12.6	8.38	-220.3	-55.81
ZOFIA 6	330	7.66	12.2	15.3	-208.82	-53.10
IWONICZ II	394	7.99	11.1	7	-219.68	-56.22
KLIMKÓWKA 27	485	7.85	10.3	14.24	-226.89	-49.84
IZA 19	120	8.56	9.7	0.983	-248.58	-66.84
EMMA	283	7.88	12.7	7.51	-216.60	-55.67
LUBATÓWKA 12	985	7.55	16.8	25.9	-202.75	-48.04
LUBATÓWKA 14	820	7.7	11.5	23	-204.63	-49.95

The isotopic composition of methane in edge-oil field waters in Iwonicz Zdrój spa range from -67‰ to -48‰ and -249‰ to -203‰, for carbon and hydrogen respectively.



CH_4 origin

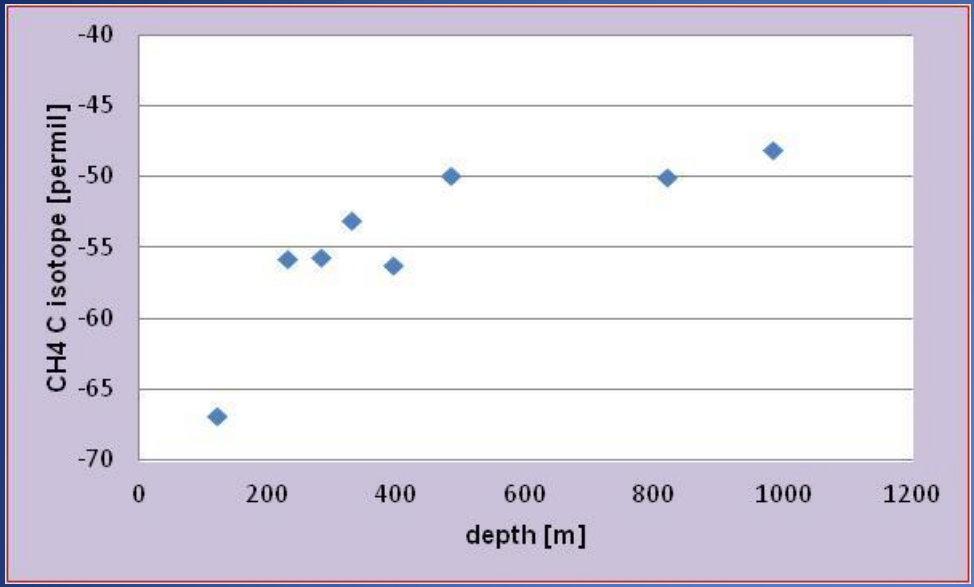


Genetic classification diagram for methane, based on C and H isotopes (after Whiticar, 1996).

According to Whiticar (1999) classification, the origin of methane is connected with

(i) early maturation processes,
(ii) thermogenic processes and/or
(iii) mixed sources.

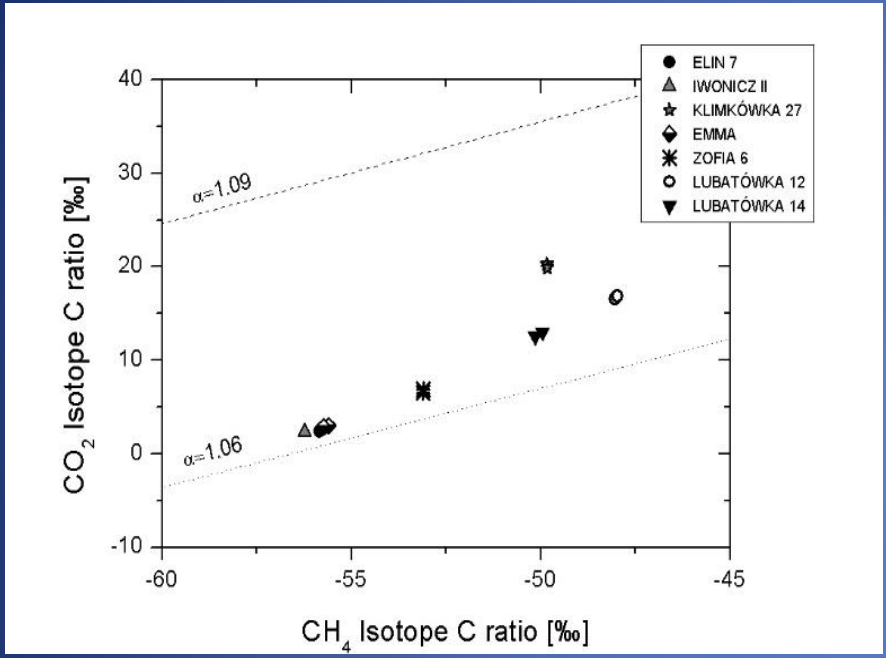
CH_4 origin



The $\delta^{13}C_{CH4}$ is correlated with depth (higher values with depth) it can be assumed that thermogenic associated methane is a major fraction of gas in deep wells and the bacterial contribution may increase in shallower wells, in which bacterial activity may be more robust.

The influence of natural degassing (or other secondary processes) on the isotopic composition of methan during sampling were not considered in details. However, if degasing plays an important role, it can be expected that lighter isotopes generally degas faster and collected methane may be rather depleted in heavier isotopes. If it would be the case, all measured values would be in the range of “early mature, thermogenic associated”.

CH_4 origin: biogenic via CO_2 reduction



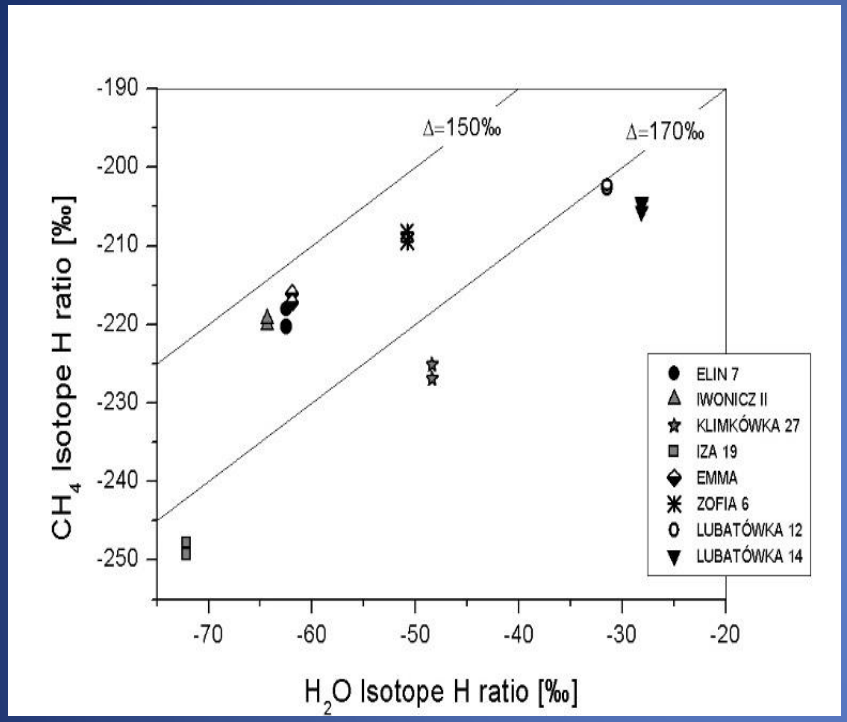
Acetate fermentation or CO_2 reduction are two pathways through which biogenic methan can be generated.

The differentiation of these pathways is possible by estimating the fractionation factor $\alpha^{13}C$ between coexisting CH_4 and CO_2 in the freshwater, calculated as:

$$\alpha^{13}C_{CO2\text{-}CH4} = (\delta^{13}C_{CO2} + 1000) / (\delta^{13}C_{CH4} + 1000).$$

It has been proved that values from 1.06 to 1.09 are characteristic of CO_2 reduction (Whiticar et al., 1986; Whiticar 1999, Lansdown et al., 1992).

CH_4 origin: acetate fermentation admixture?



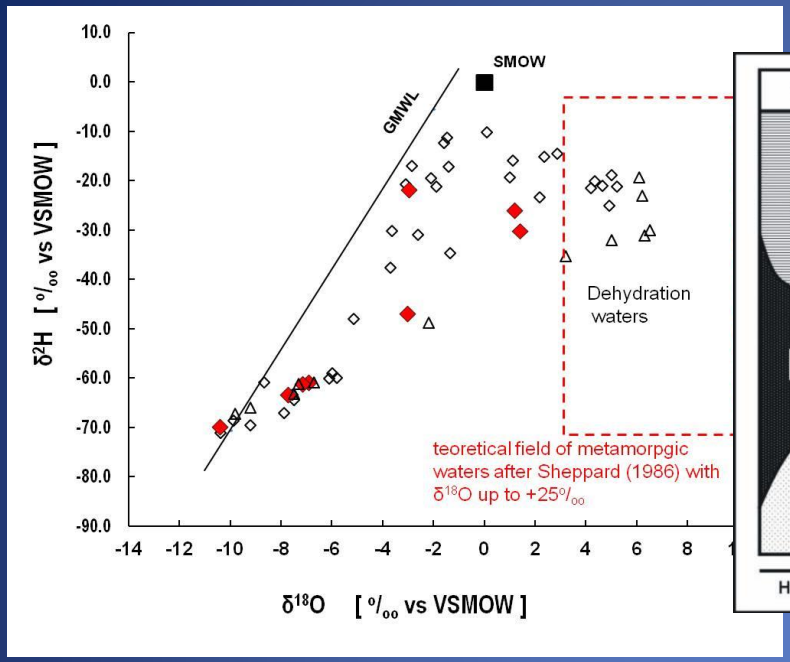
Investigation on methanogenic pathways can be carried out with the CH_4-H_2O coexisting pairs, capitalizing on the relationship between the δ^2H of the formation water and δ^2H_{CH4}.

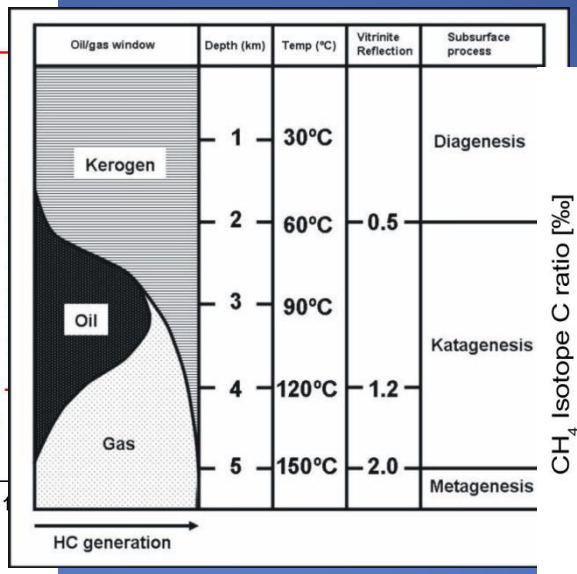
The methanogenic pathway influences methane δ^2H_{CH4} producing through CO_2-reduction values depleted ca. 160‰ (Whiticar, 1999). For this methanogenic pathway the relationship between δ^2H_{CH4} and δ^2H of associated formation water was described by following equation:

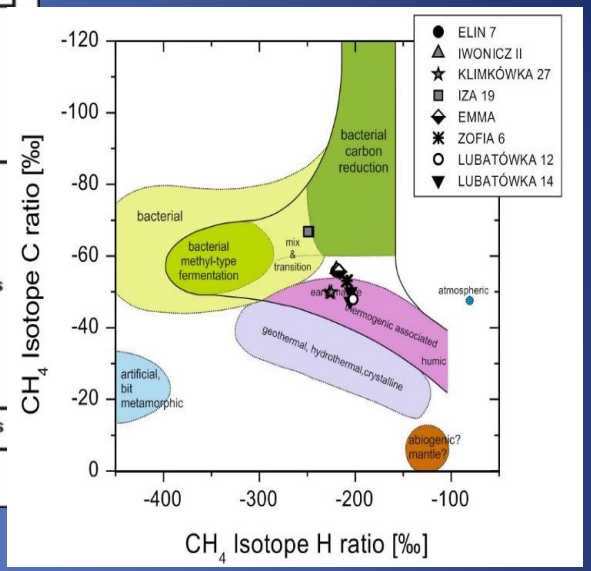
$$\delta^2H_{CH4} = \delta^2H_{H2O} - 160‰ (\pm 10‰)$$

An half of the pairs of δ^2H for coexisting CH_4 and H_2O have values between extremes confirmed the CO2-reduction pathway, however, the rest suggests contribution from acetate and methyl-type fermentation .

Conclusions for CH_4 and water origin







Dehydration of mixed layers smectite/illite Temperature range: 103 – 173°C

Geothermometric studies of Carpathian dehydration waters:
Mg-Li: 88 – 159 °C
Na-K: 32 – 97 °C