

# PS Models of Natural Gas Origin - A Short History\*

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## Abstract

Since the 1960s, investigators have observed that trends in the molecular and isotopic compositions of natural gases are very similar throughout the world. These natural gas compositions are generally explained by the transition with increasing depth from biogenic gas origin to mixtures of increasing thermogenic component. This transition concept has evolved from a series of models developed over the past 40+ years. One or more of these models is used to determine the origins of natural gas in current natural samples. **Galimov** (1969) graphically distinguished several zones of methane generation in the sediment, while modelling the theoretical curve corresponding to isotopic equilibrium of the methane-carbon dioxide system at the given temperature. The defined zones were: I. Biochemical zone, II. Catalytic zone, and III. Thermal zone. **Stahl** (1974) developed a graphic model explaining the isotopic and molecular compositions of natural gases. The model demonstrated trends in  $\delta^{13}\text{C}$  values and  $\text{C}_1/\Sigma\text{C}_n$  ratios with increasing age and maturity. Light isotopic ratios and very high  $\text{C}_1/\Sigma\text{C}_n$  ratios are indicative of a biogenic gas origin. Zones of higher temperature where chemical processes such as hydrolysis, cracking, and hydrogen disproportion become increasingly important cause isotope ratios of methane to increase and gases to become wetter. Finally, with extreme maturity an overcooked stage of is described, where virtually all the available carbon has been converted to dry methane gas. **Bernard** (1978) studied the origins and concentrations of light hydrocarbon gases in marine sediments and marine seeps. The two parameters that he used to characterize the origins of natural gases in a graphic model, which came to be known as a “*Bernard Plot*,” were  $\delta^{13}\text{C}$  values of methane and  $\text{C}_1/(\text{C}_2+\text{C}_3)$  molar ratios. Molar ratios of the light hydrocarbons expressed in this manner yielded values which varied over 4 orders of magnitude and were deemed to be more distinctive than Stahl's  $\text{C}_1/\Sigma\text{C}_n$  values. Biogenic gases consist almost exclusively of methane, having  $\text{C}_1/(\text{C}_2+\text{C}_3)$  ratios greater than 1,000 and  $\delta^{13}\text{C}$  values of methane more negative than  $-60\text{‰}$ . Thermogenic hydrocarbon gases generally have  $\text{C}_1/(\text{C}_2+\text{C}_3)$  ratios smaller than 50 and  $\delta^{13}\text{C}$  values more positive than  $-50\text{‰}$ . His geochemical model based on these two parameters was used to show that natural gas compositions can be altered due to mixing of gases from the two sources as well as by microbial action and migration through sediments. **Schoell** (1980) used a genetic diagram in which C and H stable isotopes of various natural methanes were related to each other. This plot has become known as a “*CD Diagram*.” He extended this concept by adding a crossplot of the fraction of  $\text{C}_2^+$  hydrocarbons vs.  $\delta^{13}\text{C}$  values of methane like that of Stahl. These *Schoell Plots* were designed to serve as a guide to interpretation not only of biogenic and thermogenic gases, but also of oil-associated and mixed gases and those of even more complex origins. Schoell differentiated two stages of thermogenic gas: (1) during or immediately following oil formation, which results in gases associated with crude oils

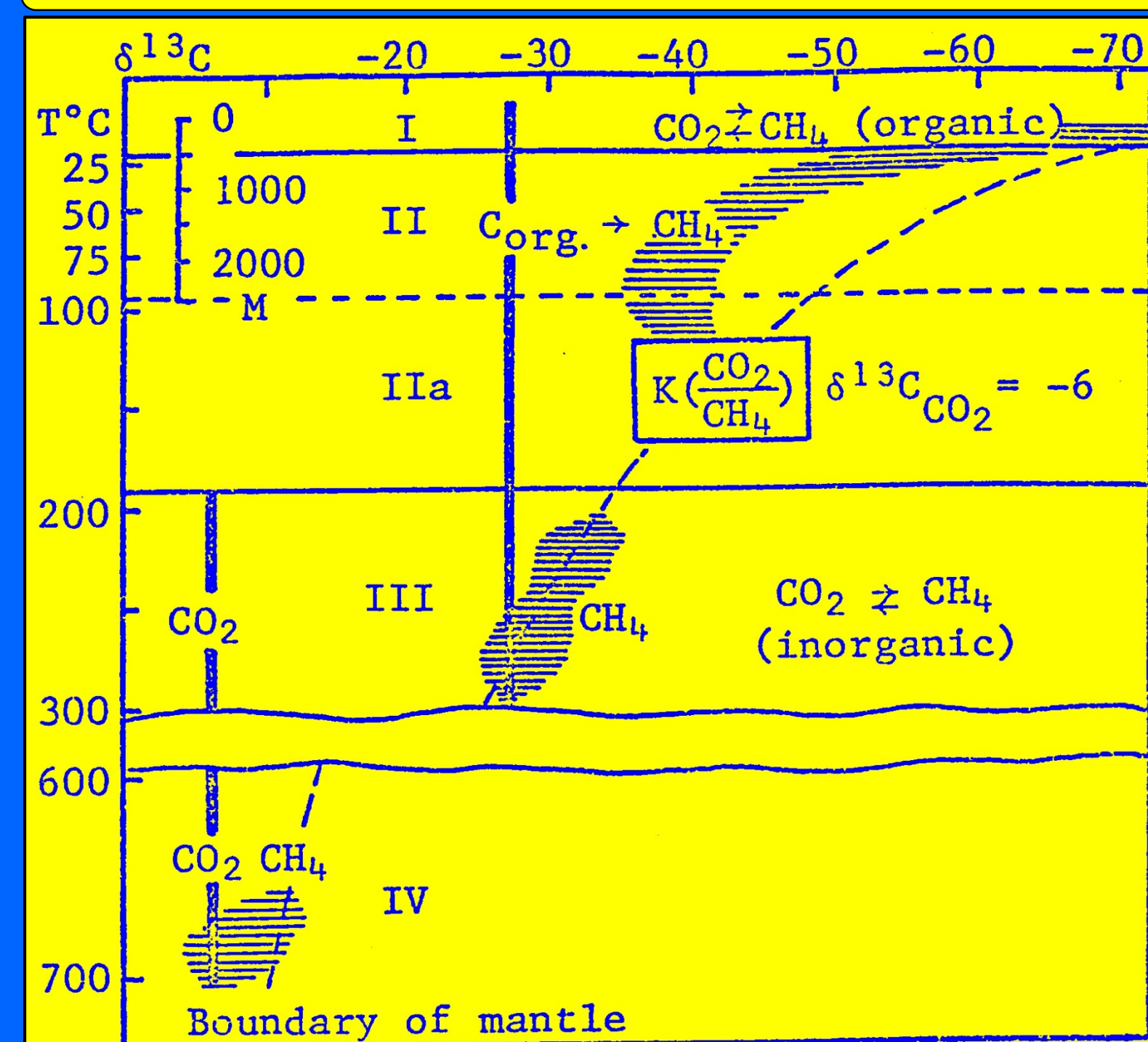
(associated gas), and (2) following the principal stage of oil formation, which results in dry or deep dry gases (non-associated gas). **Faber** (1987) developed a plot illustrating trends in the carbon isotopic compositions of methane, ethane, and propane in natural gases from around the world. In general, the isotopic ratios of carbon in these three components of a thermogenic natural gas trend together, each getting isotopically heavier with increasing maturity of their responsible source material. The graph is commonly called a "*Faber Plot*" and can be used to differentiate natural gases that are derived from a single source from gases that are mixtures derived from two or more sources. A plot of the carbon isotopic ratio of methane vs. ethane, or of propane vs. ethane, that falls on this set of empirical lines supports a singly sourced natural gas, whereas a plot away from the lines suggests that the gas accumulation is a mixture of gases. **Chung** (1988) developed a graphic model to differentiate natural gases that are derived from a single source from gases that are mixtures derived from two or more sources. The method is based on plotting the isotopic composition of methane, ethane, propane, n-butane, and n-pentane as a function of the reciprocal of the carbon number of the gas. A linear trend supports a cogenetic origin, whereas a non-linear fit suggests that the gas accumulation is a mixture of gases, a chemically altered gas, or a gas derived from a structurally heterogeneous carbon source. This plot is commonly known as a "*Natural Gas Plot*" or a "*Chung Plot*."

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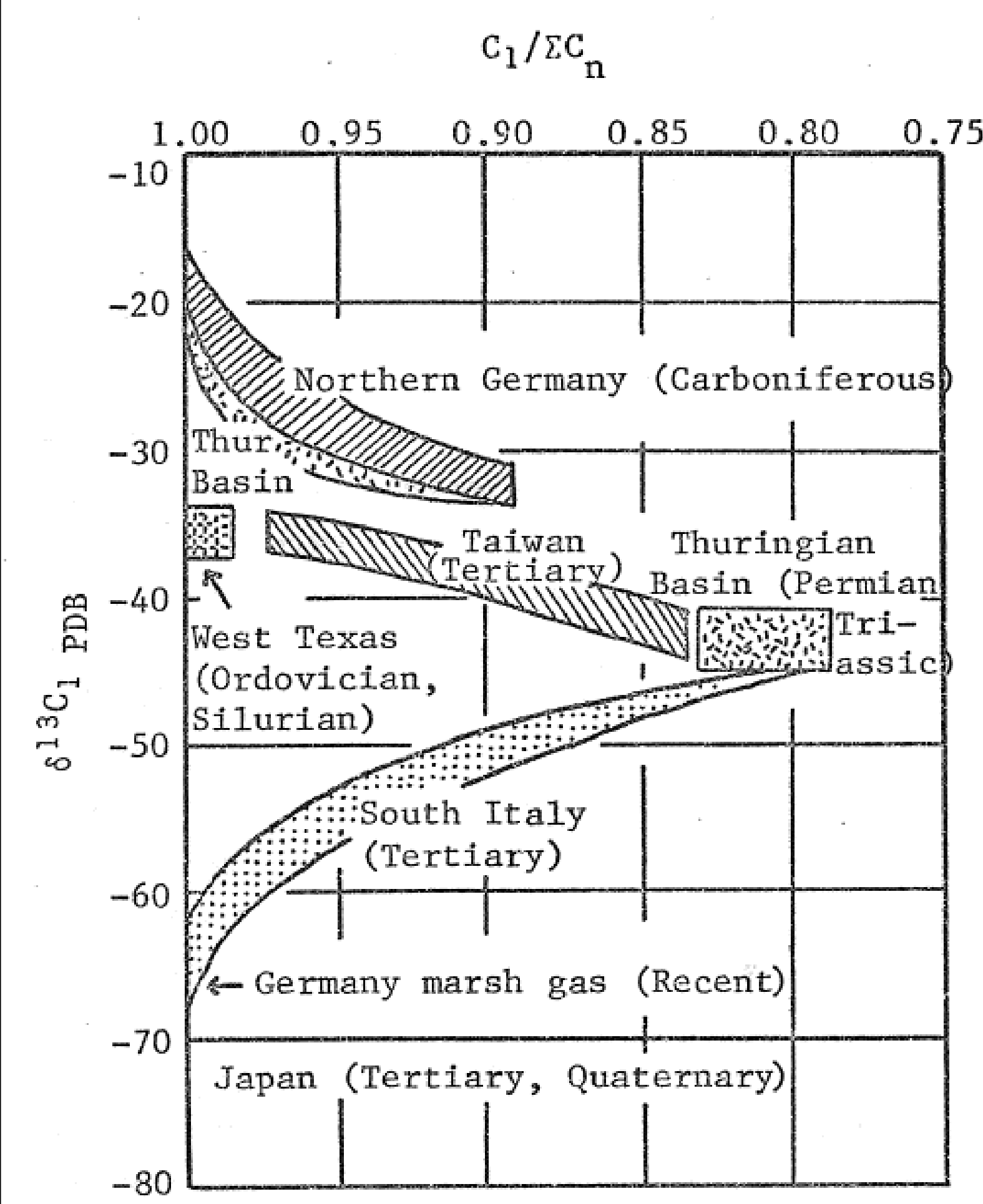
**Bernie B. Bernard**

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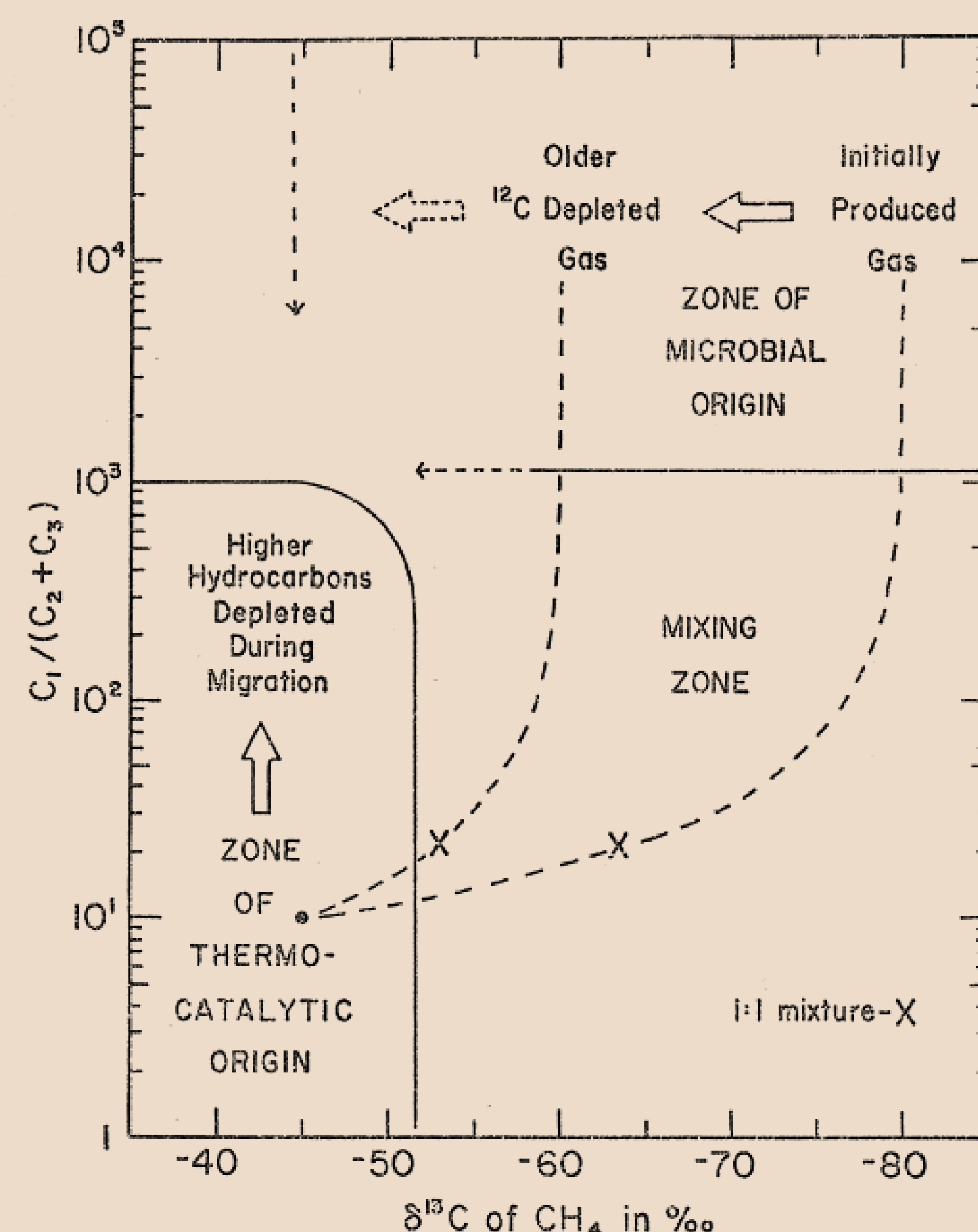


**ZONES:**  
 I - biochemical  
 II - catalytic  
 IIa - transitional  
 III - thermal  
 IV - abyssal

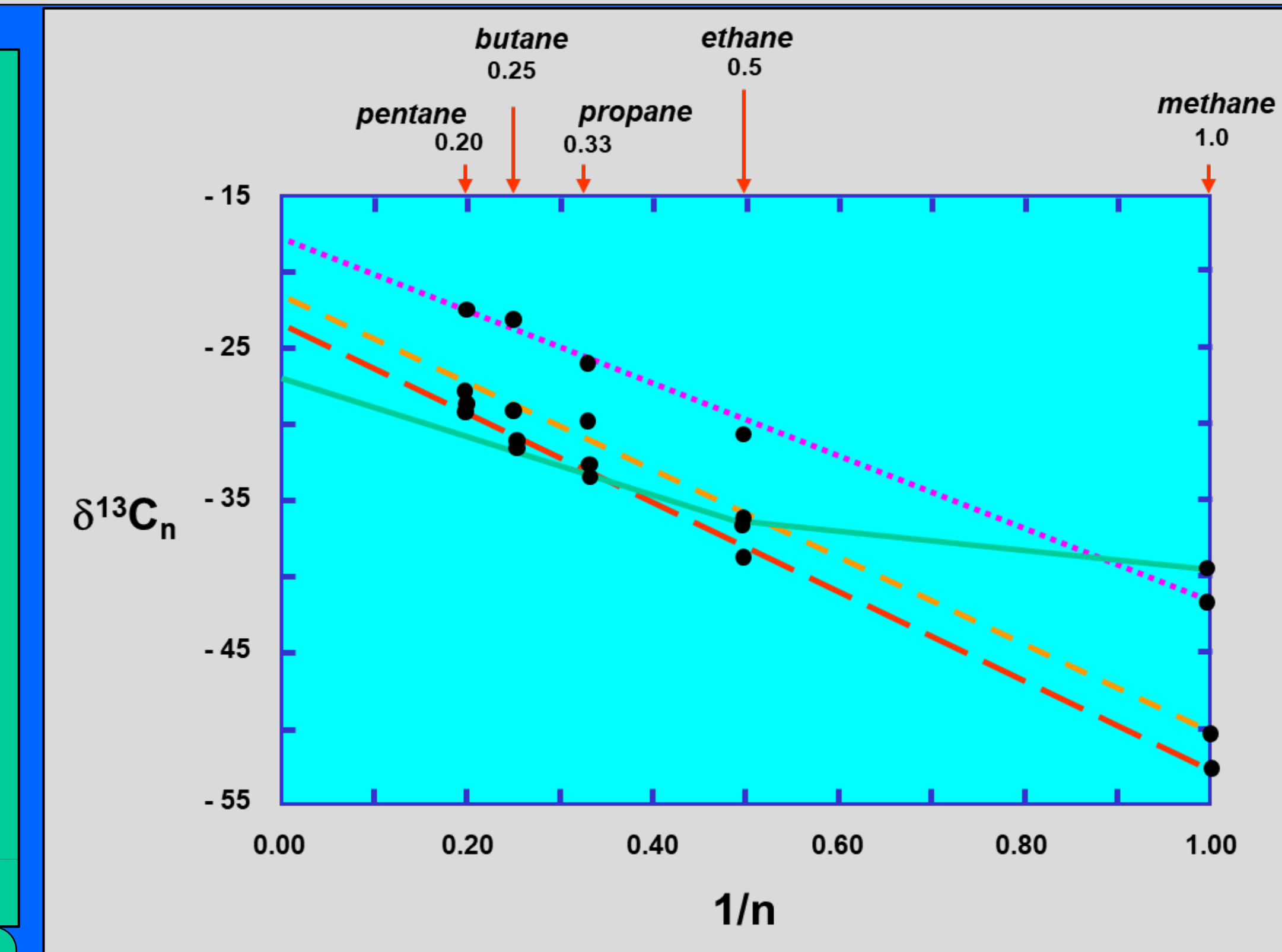
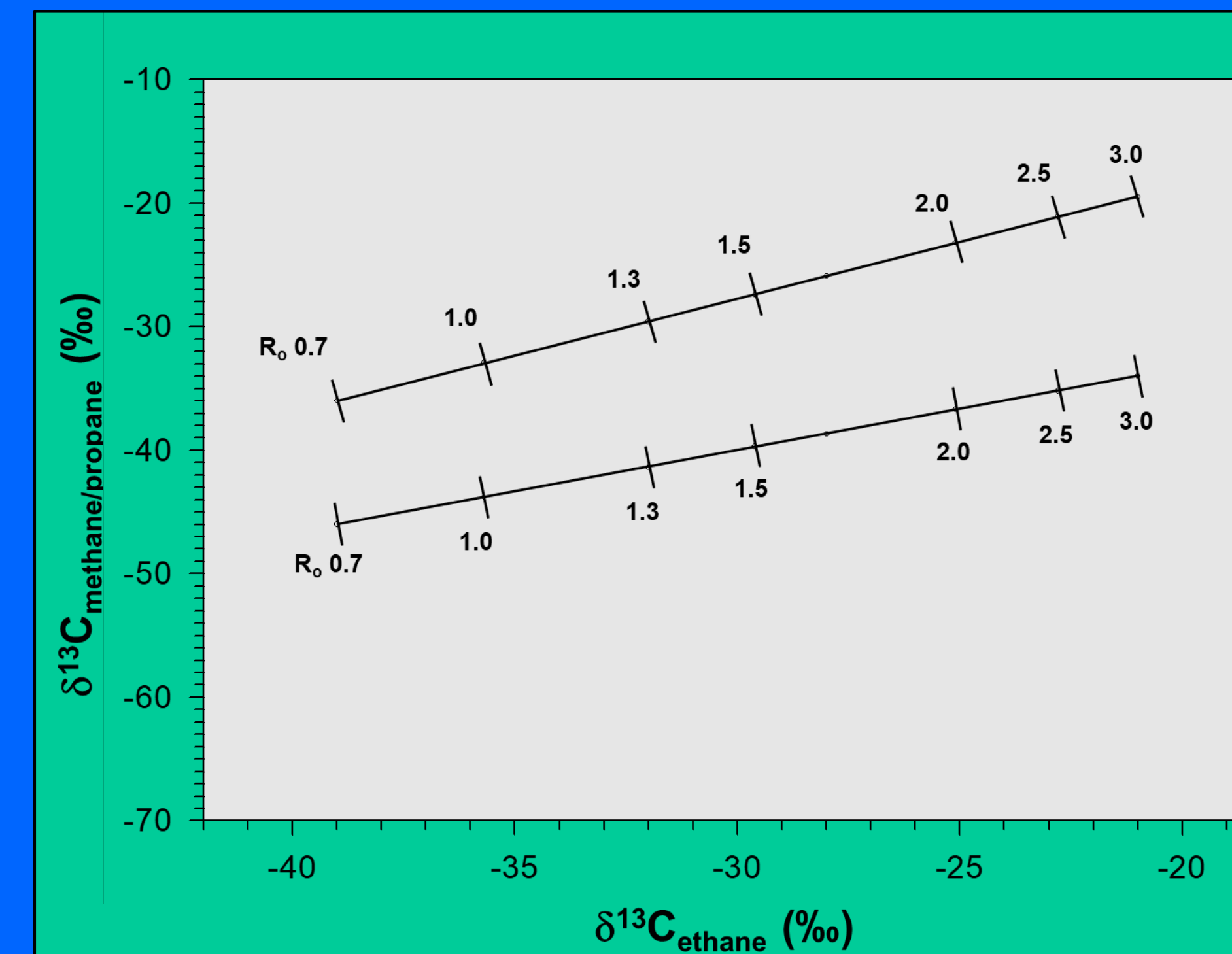


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**Bernard (2019)** uses a screening plot that accounts for complexities of gases found in marine sediments. Competing processes include local gas production, consumption, migration, alteration, fractionation, and especially mixing. This gas-source discernment tool exploits the distinct 3:1 thermogenic ratio between  $C_2+C_3$  and the  $C_4+C_5$  alkane isomers, as contrasted with that of biogenic gases. It is supported and explained by a thermo-catalytic-cracking predictive model for gas compositions as a function of maturity.

