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# Stable Isotope Geochemistry

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### 3.10.6 Natural Gas

Natural gases have been found in a wide variety of environments. While methane is always a major constituent of the gas, other components are higher hydrocarbons (ethane, propane, butane), $CO_2$, $H_2S$, $N_2$, $H_2$, and rare gases. Two different processes are responsible for the formation of the major methane occurrences. The most useful parameters in distinguishing the two different types are their $^{13}C/^{12}C$ and D/H ratios.

*Biogenic Gas.* According to Rice and Claypool (1981), over 20% of the world's natural gas accumulations are of biogenic origin. Biogenic methane commonly occurs in recent anoxic sediments and is well documented in freshwater environments, such as lakes and swamps and in marine environments, such as estuaries and shelf regions. Two primary metabolic pathways are generally recognized for methanogenesis: fermentation of acetate and reduction of $CO_2$. Although both pathways may occur in both marine and freshwater environments, $CO_2$ reduction is dominant in the sulfate-free zone of marine sediments, while acetate fermentation is dominant in freshwater sediments.

During the microbial action kinetic isotope fractionations on the organic material by methanogenic bacteria result in methane very much enriched in $^{12}C$, typically with $\delta^{13}C$-values between -110 to -50‰ (Schoell 1980, 1984b; Rice and Claypool 1981; Whiticar et al. 1986). In marine sediments the methane formed by $CO_2$ reduction is often more depleted in $^{13}C$ than methane formed by acetate fermentation in freshwater sediments. Thus, typical ranges for marine sediments are between -110 and -60‰, while methane from freshwater sediments ranges from -65 to -50‰ (Whiticar et al. 1986).

The distribution between methane of freshwater and of marine origin is even more pronounced on the basis of hydrogen isotopes. Marine bacterial methane has $\delta D$-values between -250 to -170‰, while biogenic methane in freshwater sediments is strongly depleted in D with $\delta D$-values between -400 to -250‰ (Whiticar et al. 1986).

Different sources of hydrogen in biogenic methanes can be accounted for these large differences in hydrogen isotope composition. Formation water supplies the hydrogen during $CO_2$ reduction, whereas during fermentation three-quarters of the hydrogen come directly from the methyl group, being extremely depleted in D.



*Thermogenic Gas.* Thermogenic gas is produced when organic matter is buried to greater depths. Increasing temperatures modify the organic matter due to various chemical variations, such as cracking and hydrogen disproportion in the kerogen. $^{12}C-^{12}C$ bonds are preferentially broken during the first stages of organic matter maturation. As this results in an $^{13}C$-enrichment of the residue, more $^{13}C-^{12}C$ bonds are broken with increasing temperatures, producing higher $\delta^{13}C$-values. Thermal cracking experiments carried out by Sackett (1978) have confirmed this view and showed that the resulting methane is 4 to 25‰ lower than the parent material. Thus, thermogenic gas typically has $\delta^{13}C$-values between -50 and -20‰ (Rice 1983; Schoell 1980, 1984b). Gases generated from nonmarine (humic) source rocks are isotopically heavier than those generated from marine (sapropelic) source rocks at equivalent levels of maturity.

In contrast to the $\delta^{13}C$-values, $\delta D$-values are independent of the composition of the precursor material, but solely depend on the maturity of kerogen. The combination of $\delta^{13}C$- and $\delta D$-determinations on natural gases is one of the most promising tools for gas-gas correlations. In a $\delta^{13}C$- versus $\delta D$-diagram (see Fig. 54) not only can a clear distinction of biogenic and thermogenic gases from different environ-

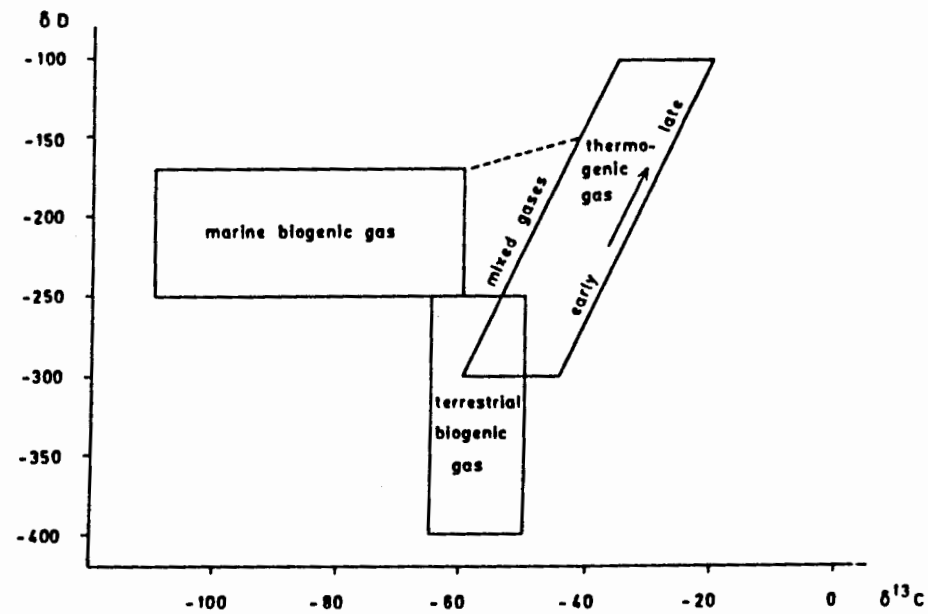


Fig. 54. Natural gas genetic classification diagram using $\delta^{13}C$ and $\delta D$ of methane. (After Whiticar et al. 1986)