# Origin of Biogenic Gases in East Coast Basins of India*

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Search and Discovery Article #40731 (2011)
Posted April 29, 2011

*Adapted from extended abstract presented at GEO-India, Greater Noida, New Delhi, India, January 12-14, 2011.

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## Abstract

Natural gas, which represents more than one fifth of total energy consumption in the world, is emerging as a potential clean fuel due to environmental concerns the world over. It has been the fastest growing fossil fuel since the seventies. Knowing whether a natural gas show is biogenic or thermogenic can have critical implications for the presence of hydrocarbons in a basin. Geochemical analyses can reveal the origin of a gas show or seep, and can divulge the presence of an effective petroleum system in a basin. The maturity of a natural gas is derived from its correlation from its source, relative percentage of gas components and their isotopic values ($\delta^{13}C$) and ($\delta D$). The evolution of methane gas by methanogens follows two metabolic pathways: $CO_2$ reduction and acetate fermentation. Acetate fermentation is regarded as major source of methane in fresh water environments:

$*CH3COOH \rightarrow *CH_4 + CO_2$ (*) indicates the intact transfer of the methyl position to $CH_4$.

Reduction of $CO_2$ by hydrogen in anoxic and sulphate deficient environment is the dominant pathway for microbial methane generation. All hydrogen incorporated into methane by this process comes from formation water. Almost all species of methanogens have the ability to form methane via reduction of $CO_2$, which can be represented in the following general equations:

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2\,H_2O$$

Carbon isotopic studies in isolation has its limitation in explaining these metabolic pathways, hence hydrogen isotopic studies serve as a supplementary value addition tool for proper understanding the formation of natural gases. The accumulation of biogenic gas

depends not only on the generation of significant quantities of gas but also on its entrapment. The other factors for commercial accumulations are the marine settings, early structural and stratigraphic traps, formation of adequate seals, rapid rates of sedimentation and deep water clastic habitat.

India’s east coast is emerging as one of the hotspots in the world with huge reserves of natural gas. Two main basins in this area – Krishna Godavari and Mahanadi have shown the potential of vast gas reserves.

## Krishna-Godavari Basin

The Krishna-Godavari Basin lies along the east coast of India, covers the deltaic and inter-deltaic areas of Krishna and Godavari rivers, and extends into the offshore. The basin has significant hydrocarbon potential both in the Tertiary delta as well as in the channel-levee-over bank play types in the deepwater. The structural trend of the basin is NE-SW and has sedimentary fill from Paleozoic to Cenozoic. Two major rivers, Krishna and Godavari and their deltas dominate a major part of the basin. The end of the Mesozoic was marked by volcanic activity. A number of basalt flows belonging to the Deccan Traps are found in the sub-surface as well as in the outcrops. The oldest sediment resting over the basement is of Permian age in Gondwana Graben, confined to the northeastern part of the basin (Mandapeta trough). In the west, close to the basin margin, synrift sediments of Jurassic overlie the basement. In rest of the area, Cretaceous forms the earliest deposited sediments. In the coastal and offshore areas, Cretaceous sediments are deep seated and overlain by thick Tertiary sediments of deltaic origin.

## Mahanadi Basin

Mahanadi Basin is located along northeastern part of east coast of India and covers an area of ~1,400,000 $km^2$ in both on land and offshore up to 2,500m isobath in the Bay of Bengal. The Gondwana sediments (Permo-Triassic) are the oldest sediments in the basin deposited in the continental grabens. The Basin was partly superposed with next phase of basin development in the end Jurassic leading to development of horst graben features along pre-existing weak zones and deposition of non-marine sediments. It was followed by development of delta system and subsequent main transgression. The rift phase ended with the flow of Rajmahal lavas. Subsequent to rifting and volcanism during Early Cretaceous, Mahanadi shelf received continental-deltaic sediments in Late Cretaceous-Paleocene times.

## Samples and Methodology

Carbon and Hydrogen isotopic studies were carried out on more than 30 gas samples from Krishna-Godavari and Mahanadi Basins. The gas samples were analyzed on Varian CP-3800 NGA for molecular composition and stable carbon isotopic studies were carried out on VG IsoPrime Continuous Flow-Isotope Ratio Mass Spectrometer interfaced with Agilent 6890N GC. Hydrogen isotopic measurements were carried out on Thermo Scientific Delta V plus IRMS fitted with trace ultra GC and high temperature conversion (TC-HD) interface, using standard molecular and isotopic composition analytical methods.

## Results and Discussion

The bacterial reduction of $CO^2$ to $CH_4$ give rise to $\delta^{13}C_1$ values as negative as -110 ‰ whereas the corresponding value for fermentation of methylated substrate is lighter by 50 to 60 ‰. The natural gases from Mahanadi Basin characterized based on molecular and carbon isotopic compositions are of bacterial origin whereas in Krishna Godavari Basin the gases are of thermal, mixed and bacterial origin, which are explained in Figure1.

Hydrogen isotope effects during methanogenesis of methylated substrate can lead to deuterium depletion as large as $\delta D_{Methane}$, -500 ‰, whereas bacterial D/H discrimination for the $CO_2$ reduction pathway is significantly less ($\delta D_{Methane}$, -170 to -250 ‰). Mahanadi Offshore gases are typically bacterial generated by $CO_2$ reduction process ($\delta^{13}C_{Methane}$, -59.6 to -69.4 ‰; and $\delta D_{Methane}$, -168 to -197.4 ‰) where as in KG Basin, the distribution of natural gas shows wide variation from thermal, mixed to bacterial. There are condensates and past oil window gases in some part of KG basin in Early Cretaceous Formations ($\delta^{13}C_1$ values, -29 to -31.1‰), oil window gases ($\delta^{13}C_1$ values, -40 to -45‰) and mixed to bacterial gases ($\delta^{13}C_1$ values, -47 to -63‰) the $\delta D_{Methane}$ value, -136 to -224‰), mostly distributed in younger (Pliocene to Miocene) sediments. Geographically bacterial gases are generally prevalent in coastal to offshore areas. The hydrogen and carbon isotopic study of KG and Mahanadi Basin has also been interpreted within the frame work of the above two models; Schoell's $\delta^{13}C_1$ v/s gas wetness and $\delta^{13}C_1$ v/s $\delta D_{Methane}$ plots in the following two diagrams (Figure 2 and Figure 3).

The carbon and hydrogen isotopic data were further used to elucidate the metabolic pathways responsible for formation of Mahanadi and KG Basin gases. It is inferred from these studies that the bacterial gases in both the basins are generated through carbon dioxide reduction pathway (Figure 4).

## Conclusions

The C and H isotopic measurement of methane are reliable tools to characterize bacterial or thermogenic natural gas types. Situations, such as mixing of different natural gases or where extreme substrate depletion and consumption occur, could produce ambiguous methane isotope signals. In these cases, the C and H isotopes of methane are excellent tools for processes of bacterial methane formation. The gases generated in Miocene-Pliocene reservoirs of Mahanadi and KG Offshore basins are of bacterial origin. Combination of carbon and hydrogen isotope studies has proved that the bacterial gas formation is a result of predominantly bacterial carbonate reduction. This is a favored condition of large quantity of microbial gas production in marine environments. Thermally immature sediments in the vast area of east coast basins of India with favorable gas generation settings can also prove to encompass large hydrocarbon pools where structural traps are available.

## Acknowledgements

Authors are grateful to ONGC management for granting permission to present this paper in the Geo-India conference. The authors are highly indebted to Shri P.K. Bhowmick, ED-HOI KDMIPE for his constant inspiration and keen interest in this work.

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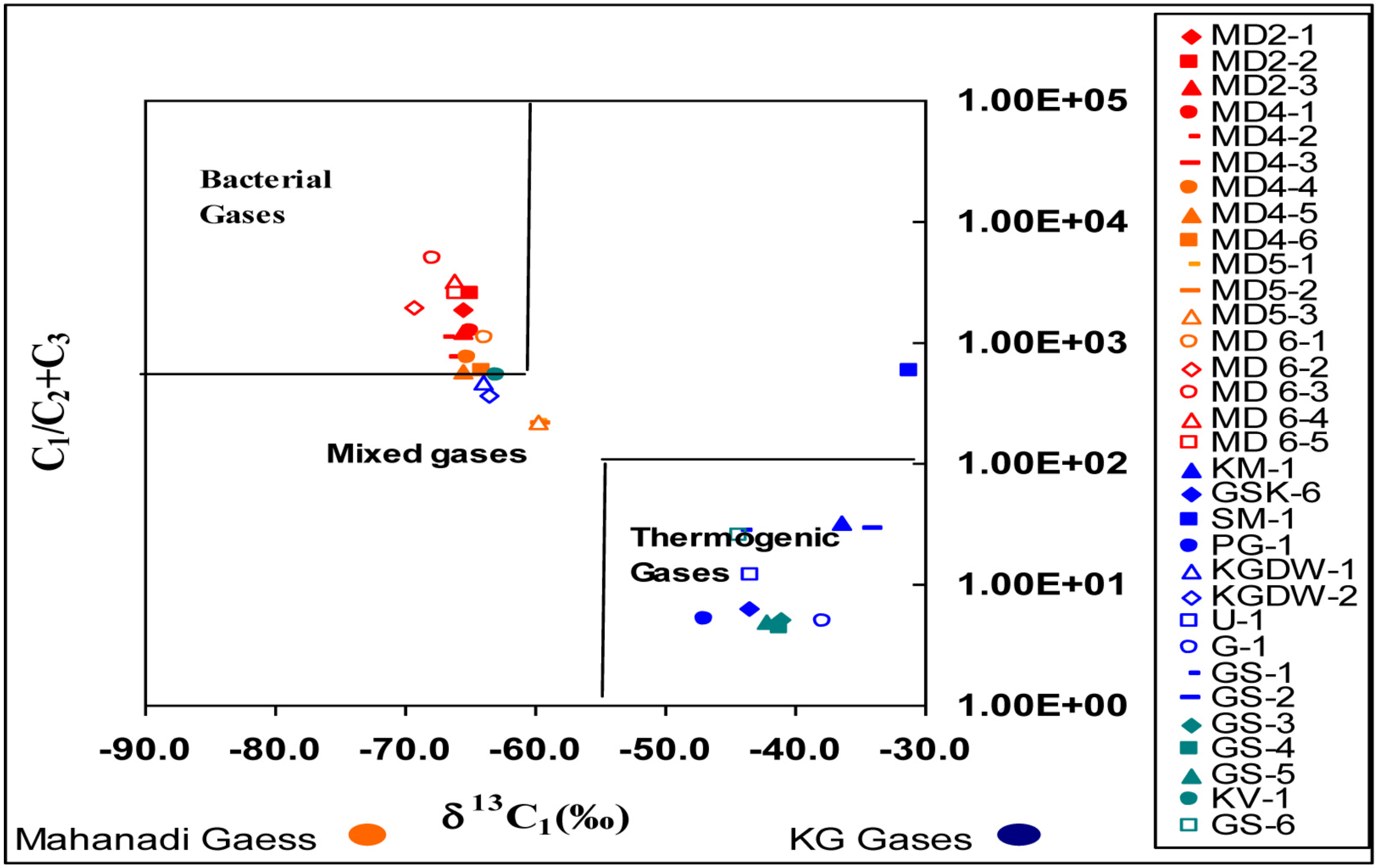


Figure1. Genetic characterization of KG and Mahanadi Basin gases indicating bacterial nature of Mahanadi gases while KG Basin gases showing thermal, mixed and bacterial sources.

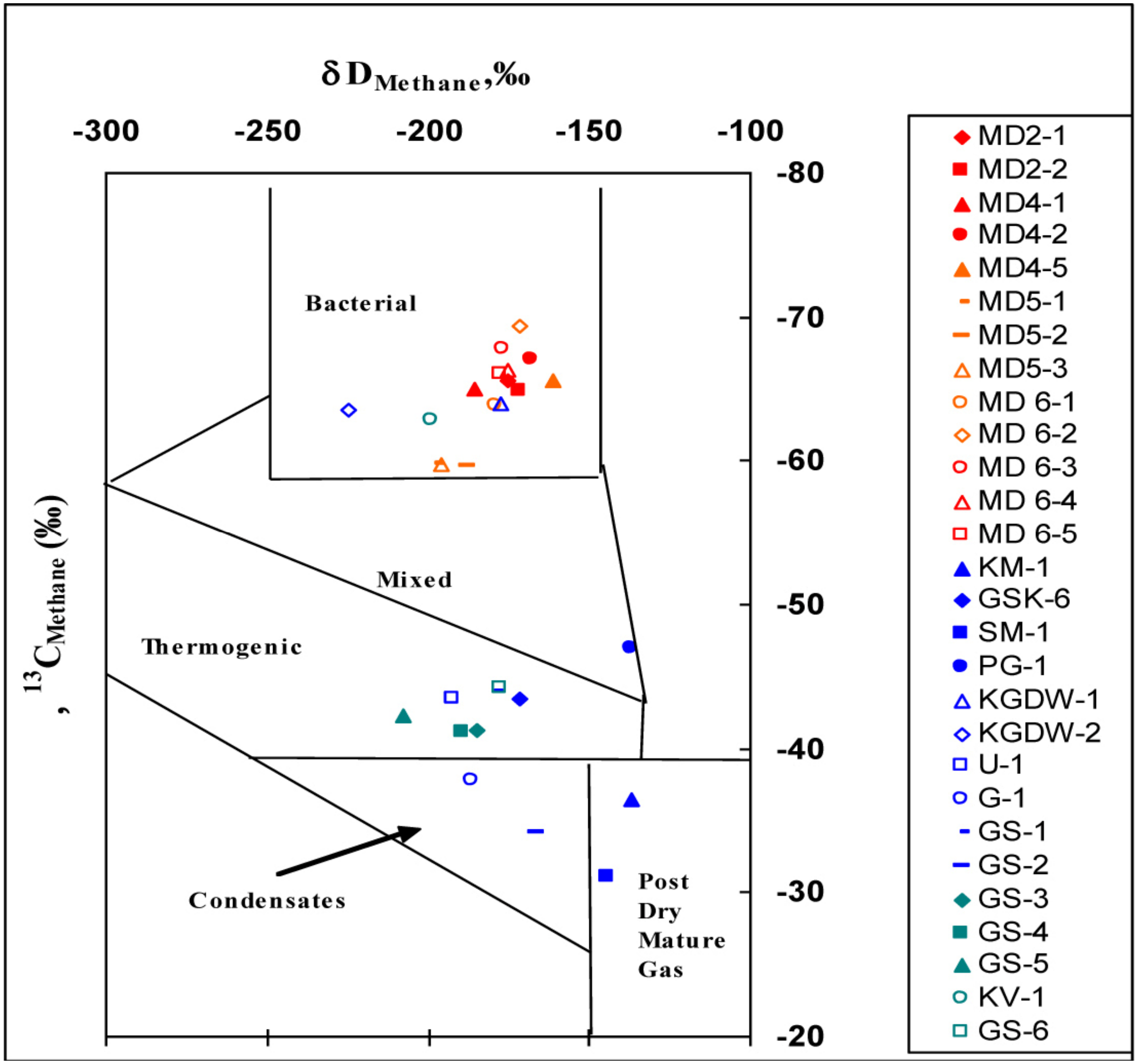


Figure 2. KG gases on Schoell's plots indicating KG Basin gases are post mature, oil associated and bacterial in nature.

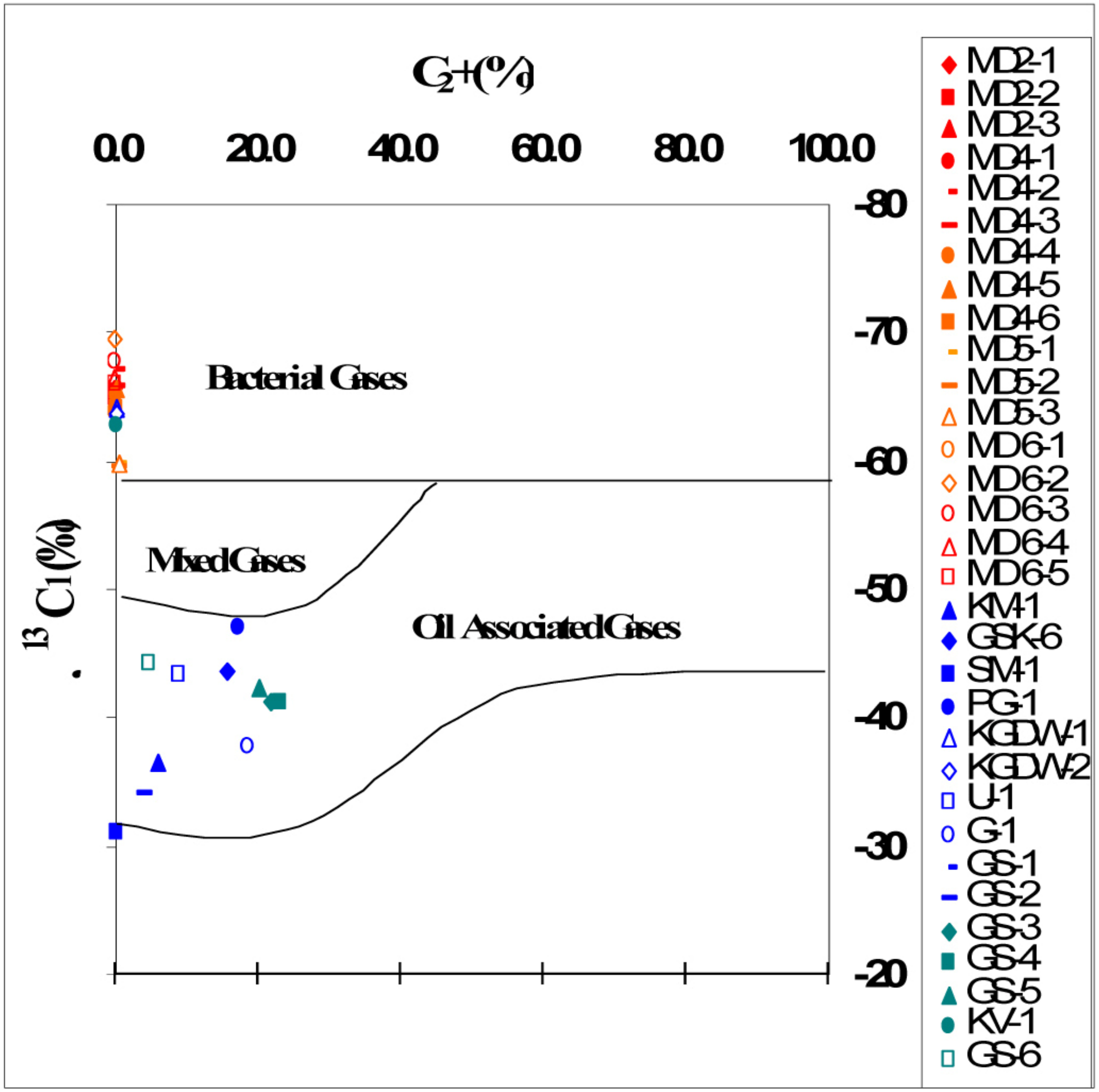


Figure 3. Mahanadi Basin gases on Schoell's plots indicating bacterial nature of Mahanadi Basin.

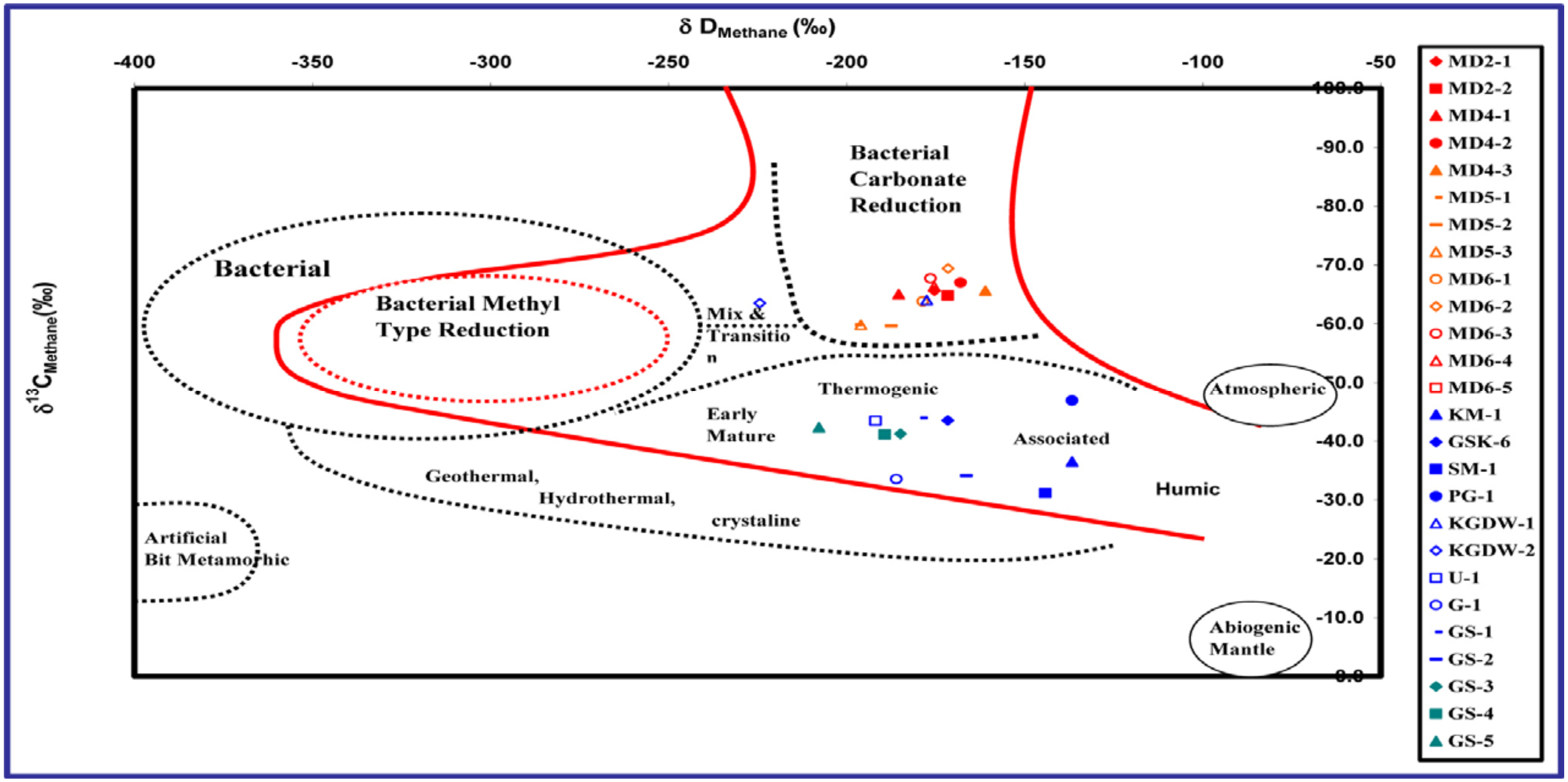


Figure 4. Classification of bacterial and thermogenic gas by the combination of $^{13}C$ $_{Methane}$ and δ D $_{Methane}$ studies, indicating the nature and processes of natural gas generation (Whiticar, 1998)