APPLICATION OF CARBON ISOTOPES IN PETROLEUM EXPLORATION WITH SPECIAL REFERENCE TO PAKISTAN

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The variation and distribution of stable isotopes of ^{12}C and ^{13}C have been used extensively for oil-source rocks, oil-oil correlation and for differentiating thermogenic gases from biogenic gases. Apart from the carbon isotope ratio the deuterium hydrogen ratio also is occasionally used for oil but it is much more common for gases.

The isotope composition is influenced by the organic source material. Carbon dioxide in atmosphere is richer in ^{12}C *i.e.* "lighter" than the carbon dioxide in sea water. Thus terrestrial plants tend to be richer in ^{12}C than marine plants (such as Algae). Also in sea water there is an isotopic equilibrium between carbon dioxide and bicarbonate. Such reactions lead to changes in the istopic ratios, because carbonate carbon is iostopically significantly heavier than organic carbon.

The carbon isotope technique involves removal of inorganic carbon initially present and then converting the remaining organic carbon to carbon dioxide. The carbon isotope ratios of this carbon dioxide is determined in a sensitive mass spectrometer. The result is expressed as a value which is the derivation (in parts per thousand) from the $^{13}C/^{12}C$ ratio of a standard (PBD) sample. The following equation relates the values of the isopotic ratios of the sample and standard respectively.

$$\Delta\,^{13}C \text{ per mil} = \frac{(^{13}C/^{12}C \text{ (Sample)} - {}^{13}C/^{12}C \text{ (standard)}}{^{13}C/^{12}C \text{ (standard)}} \times 1000$$

A negative value for the Δ indicates that the sample is isotopically lighter and contains less ^{13}C than the standard. A positive value means that it is istopically "heavier" and contains more ^{13}C than the standard.

In petroleum geochemistry carbon istopic analysis provides a useful parameter for correlation studies (oil-oil, oil-source rock, gas-gas) and for the estimation of the maturation.

Genetic Characterization of Natural Gases

Natural gas occurs in a variety of environments. Gases of bacterial origin are found in basins associated with immature sediments. These gases are rich in methane and are not associated with oil. In deeper strata, natural gases are associated with petroleum. Two stages of thermogenic gas formation may be differentiated: (a) during or immediately following oil formation,which results in gases associated with crude oil and (2) after the principal stage of oil formation has passed which results in dry gases.

The specific environments of gas are characterised as under:

Biogeneic gases $\Delta\,^{13}C = -90$ to -60 per thousand
Associated gases $\Delta\,^{13}C = -55$ to -30 per thousand
Deep dry gases $\Delta\,^{13}C = -45$ to -20 per thousand

To characterise and classify gases of Northern Pakistan, samples were collected from selected wells of producing fields and one from gas seepage. The samples were analysed in BGR by stable isotopic mass spectrometry in 1986.

The results of carbon and deuterium isotopic ratio of methane were plotted as shown in Figure 1.

It may be seen from the diagram that most of the samples from producing fields are falling in the region of thermogenic gases while the seepage sample is completely different from the rest of the gases.

Oil-Source Rock Correlation

Application of stable carbon isotope ratios of oil and extract correlations can be useful for exploration. Carbon isotope studies also help in assessing whether two oil types originate from the same or different source rocks.

C-isotope analyses of crude oils, extracts (the soluble organic matter in a rock) and kerogen are informative and play an important role in correlation of source rocks with crude oils. The importance of stable isotope analyses rests upon the fact that it links the oil with kerogen of source rocks. The extract of a source rock represents that portion of an oil, which remains at its place of origin. Therefore, the C-isotope ratio of crude oil found in a reservoir should be similar to the isotopic composition of the extract in the source rock.

Under HDIP-BGR collaborative programme oil and source rocks samples were collected and analysed for isotopic composition in BGR labs.

The stable carbon isotopic ratios of aromatic and saturated fractions of hydrocarbon were used for correlation studies. The results are plotted as shown in Figure 2.

Most of the bitumen from rock samples collected from the sorrounding of Potwar basin are isotopically lighter than the oil samples from Potwar producing fields. Only few of the rock samples can be related to seepage samples. Considering the immaturity of analysed rock samples, it is expected that mature oil would be isotopically heavier than the bitumen from the immature samples.

Stable isotope techniques represent an efficient tool in hydrocarbon exploration work. Especially, it is very useful in source rock-crude oil correlation and genetic characterization of natural gases.

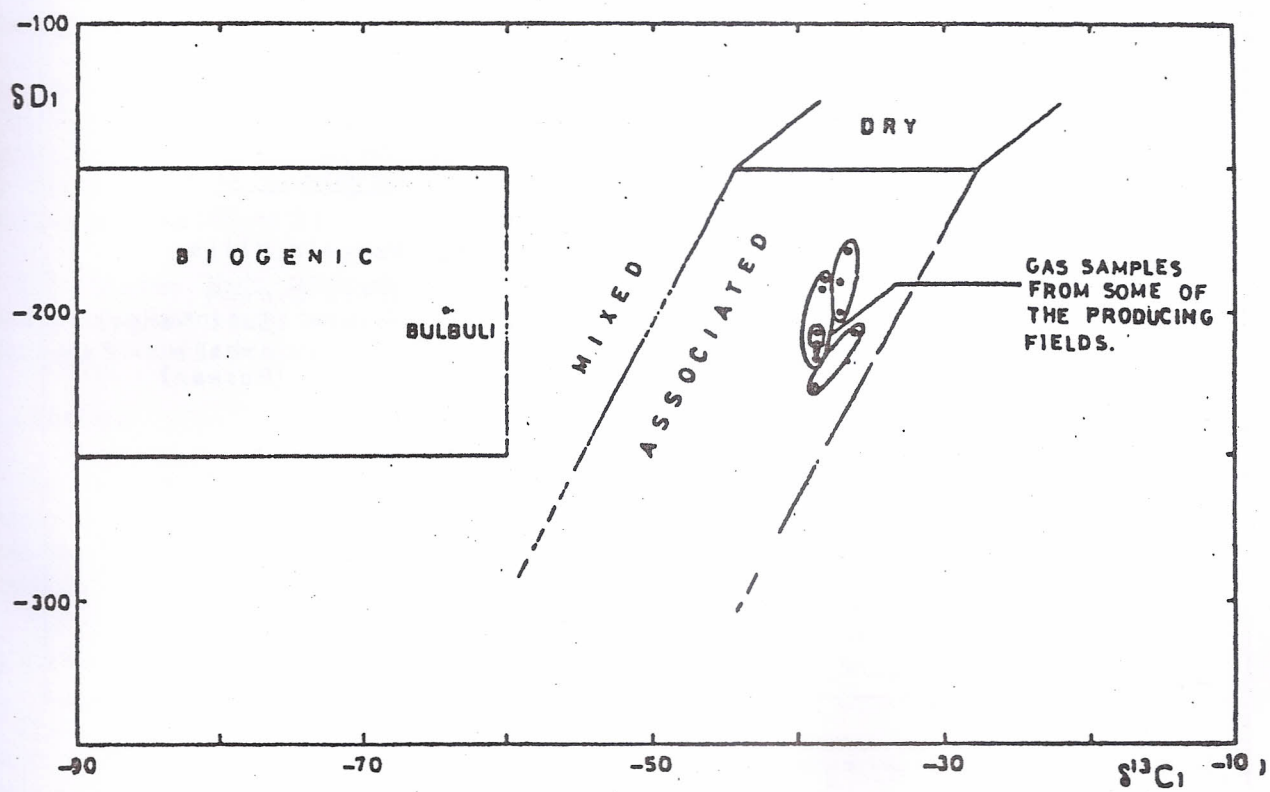

Figure 1: Carbon and Deuterium isotope composition of methane of gas samples from Potwar Basin.

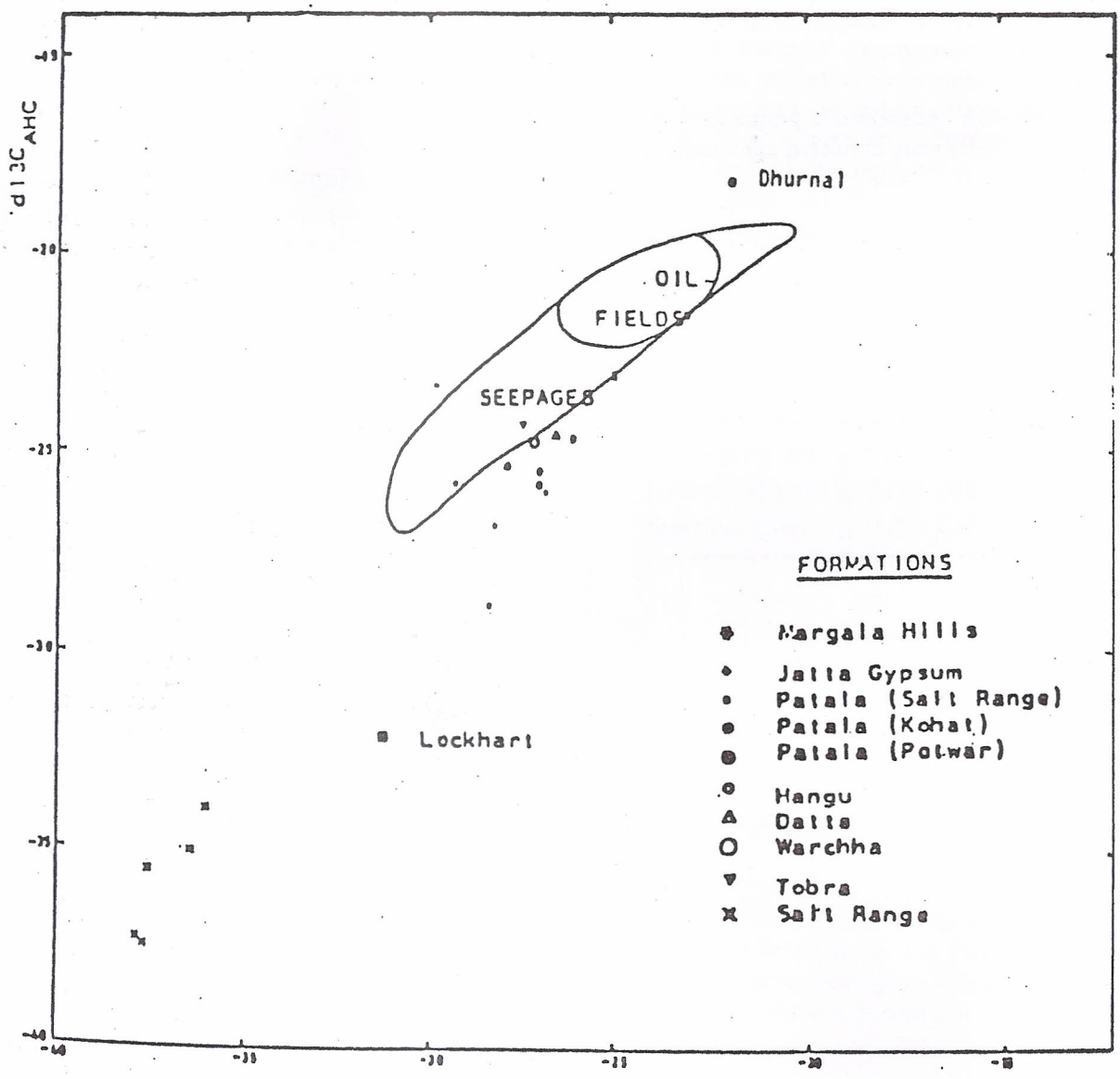

Figure 2. Distribution of carbon istope ratios of saturated and aromatic hydrocarbons of potential source rocks and oils of Potwar Basin.