

# <sup>PS</sup> Nature and Origin of Dry Natural Gas in the Middle Indus Basin, Pakistan\*

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## Abstract

We show how different processes impact the molecular and C isotopic composition of natural gas in the Middle Indus Basin (MIB), Pakistan where Lower Cretaceous (Sembar) shale beds in the Sulaiman Foredeep that contain Type III/II kerogen generated thermogenic gas. These very dry thermogenic gas samples were generated at high maturity, but post-generation processes also have influenced the composition of natural gas: e.g., the admixture of microbial methane; biodegradation. The C isotopic composition of methane, ethane, and propane in a dry gas sample ( $C_1/C_2 = 74$ ) produced from a Jurassic carbonate reservoir at the Nandpur Field on the Punjab Platform indicates it was generated by isotopically-heavy kerogen ( $\delta^{13}C \approx -23.5\%$  PDB) in the wet gas window ( $VR \approx 1.4\%$ ). A drier ( $C_1/C_2 = 279$ ) gas sample produced from a Paleocene sandstone reservoir at the Pirkoh Field in the Sulaiman Foldbelt was generated at higher maturity ( $VR \approx 1.8\%$ ) by kerogen with the same C isotopic composition. The C isotopic composition of kerogen isolated from the Sembar Formation and from shale beds in the overlying Lower Goru Formation ranges from -23.4 to -25.8‰ PDB, supporting other evidence those Lower Cretaceous source rocks generated the thermogenic gas in the MIB. The presence of isotopically-heavier propane in two other very dry gas samples produced from the Paleocene reservoir and from the underlying Cretaceous reservoir at the Pirkoh Field indicates they are slightly biodegraded.

The C isotopic composition of methane in several “wetter” ( $C_1/C_2 = 82-96$ ) gas samples produced from shallower Lower Eocene limestone reservoirs at the Sui Field in the Sulaiman Foldbelt indicates they contain a small amount ( $\approx 10\%$ ) of microbial methane. Several gas fields also are present on the Mari-Kandhkot High separating the MIB from the Lower Indus Basin. The molecular and C isotopic composition of several natural gas samples produced from Lower Eocene limestone reservoirs at the Kandhkot Field and at the Sui Field are very similar – evidence they have a similar origin. Natural gas samples produced from a shallower Upper Eocene limestone reservoir at the Mari Field are much drier ( $C_1/C_2 = 360-700$ ). But the C isotopic composition of methane ( $\delta^{13}C \approx -48$  to  $-52\%$  PDB) indicates they contain a significant amount ( $\approx 40-50\%$ ) of microbial methane, and the presence of isotopically-heavy ethane ( $\delta^{13}C \approx -14$  to  $-21\%$  PDB) demonstrates microbes have metabolized  $C_{2+}$  compounds. Thus, the very high methane/ethane ratios in the Mari gas samples are not evidence they were generated at very high maturity. Finally, most of the MIB gas samples contain 3.2-8.8 mol%  $CO_2$ , whose C isotopic composition ( $-6.8$  to  $+0.5\%$  PDB) indicates most of the

CO<sub>2</sub> formed during high-temperature diagenetic reactions that involved marine carbonate minerals: i.e. it was not generated by low-maturity kerogen.

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## ABSTRACT

We show how different processes impact the molecular and C isotopic composition of natural gas in the Middle Indus Basin (MIB), Pakistan where Lower Cretaceous (Sembar) shale beds in the Sulaiman Foredeep that contain Type III/II kerogen generated thermogenic gas. These very dry thermogenic gas samples were generated at high maturity, but post-generation processes also have influenced the composition of natural gas: e.g., the admixture of microbial methane; biodegradation. The C isotopic composition of methane, ethane, and propane in a dry gas sample ( $C_1/C_2 = 74$ ) produced from a Jurassic carbonate reservoir at the Nandpur Field on the Punjab Platform indicates it was generated by isotopically-heavy kerogen ( $\delta^{13}C \approx -23.5\%$  PDB) in the wet gas window ( $VR \approx 1.4\%$ ). A drier ( $C_1/C_2 = 279$ ) gas sample produced from a Paleocene sandstone reservoir at the Pirkoh Field in the Sulaiman Foldbelt was generated at higher maturity ( $VR \approx 1.8\%$ ) by kerogen with the same C isotopic composition. The presence of isotopically-heavier propane in two other very dry gas samples produced from that reservoir and from the underlying Cretaceous reservoir at the Pirkoh Field indicates they are slightly biodegraded. The C isotopic composition of methane in several “wetter” ( $C_1/C_2 = 82-96$ ) gas samples produced from shallower Lower Eocene limestone reservoirs at the Sui Field in the Sulaiman Foldbelt indicates they contain a small amount ( $\approx 10\%$ ) of microbial methane. Several gas fields also are present on the Mari-Kandhkot High separating the MIB from the Lower Indus Basin. The molecular and C isotopic composition of several natural gas samples produced from Lower Eocene limestone reservoirs at the Kandhkot Field and at the Sui Field are very similar – evidence they have a similar origin. Natural gas samples produced from a shallower Upper Eocene limestone reservoir at the Mari Field are much drier ( $C_1/C_2 = 360-700$ ). But the C isotopic composition of methane ( $\delta^{13}C \approx -48$  to  $-52\%$  PDB) indicates they contain a significant amount ( $\approx 40-50\%$ ) of microbial methane, and the presence of isotopically-heavy ethane ( $\delta^{13}C \approx -14$  to  $-21\%$  PDB) demonstrates microbes have metabolized  $C_2+$  compounds. Thus, the very high methane/ethane ratios in the Mari gas samples are not evidence they were generated at very high maturity. Finally, most of the MIB gas samples contain 3.2-8.8 mol%  $CO_2$ , whose C isotopic composition (+0.5 to -6.8‰ PDB) indicates most of the  $CO_2$  formed during high-temperature diagenetic reactions involving marine carbonate minerals.

## 1. INTRODUCTION: PETROLEUM GEOLOGY OF THE MIDDLE INDUS BASIN (MIB).

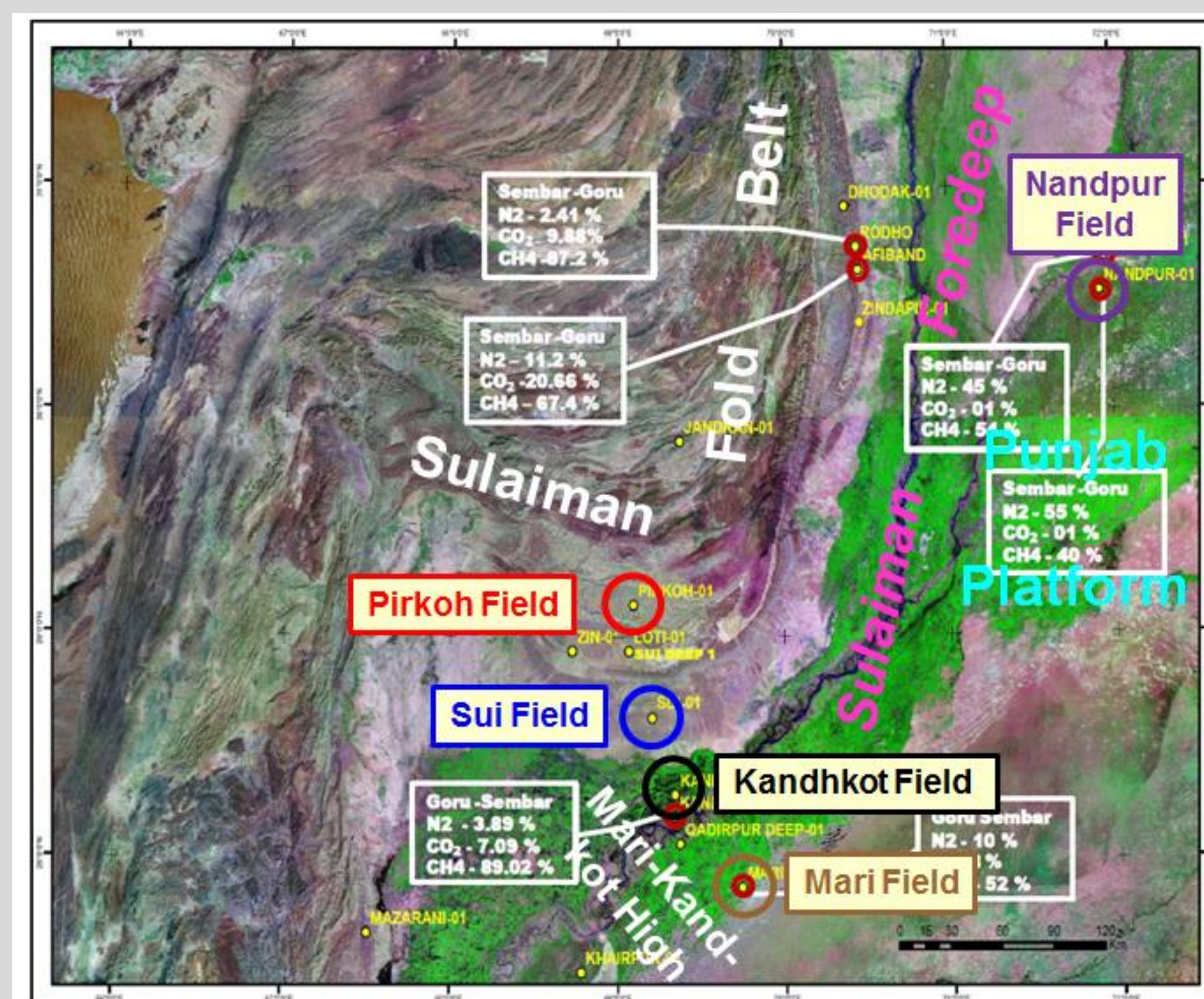


Figure 1. Map of the Middle Indus Basin, showing the location of gas fields discussed in this poster and major structural elements in the basin (adapted from Nazeer et al., 2013).

A large number of commercial gas accumulations have been discovered in the MIB (Mujtaba, 1997). The first large gas discovery was made in the Sulaiman Fold Belt at the Sui Field, where  $\approx 8.5$  Tcf of reserves were discovered. The Mari gas field (containing  $\approx 6.3$  Tcf of reserves) was discovered southwest of the Sui Field. Most discoveries in the Sulaiman Fold Belt are dry gas that also contains a significant amount of  $CO_2$  and nitrogen (Figure 1).

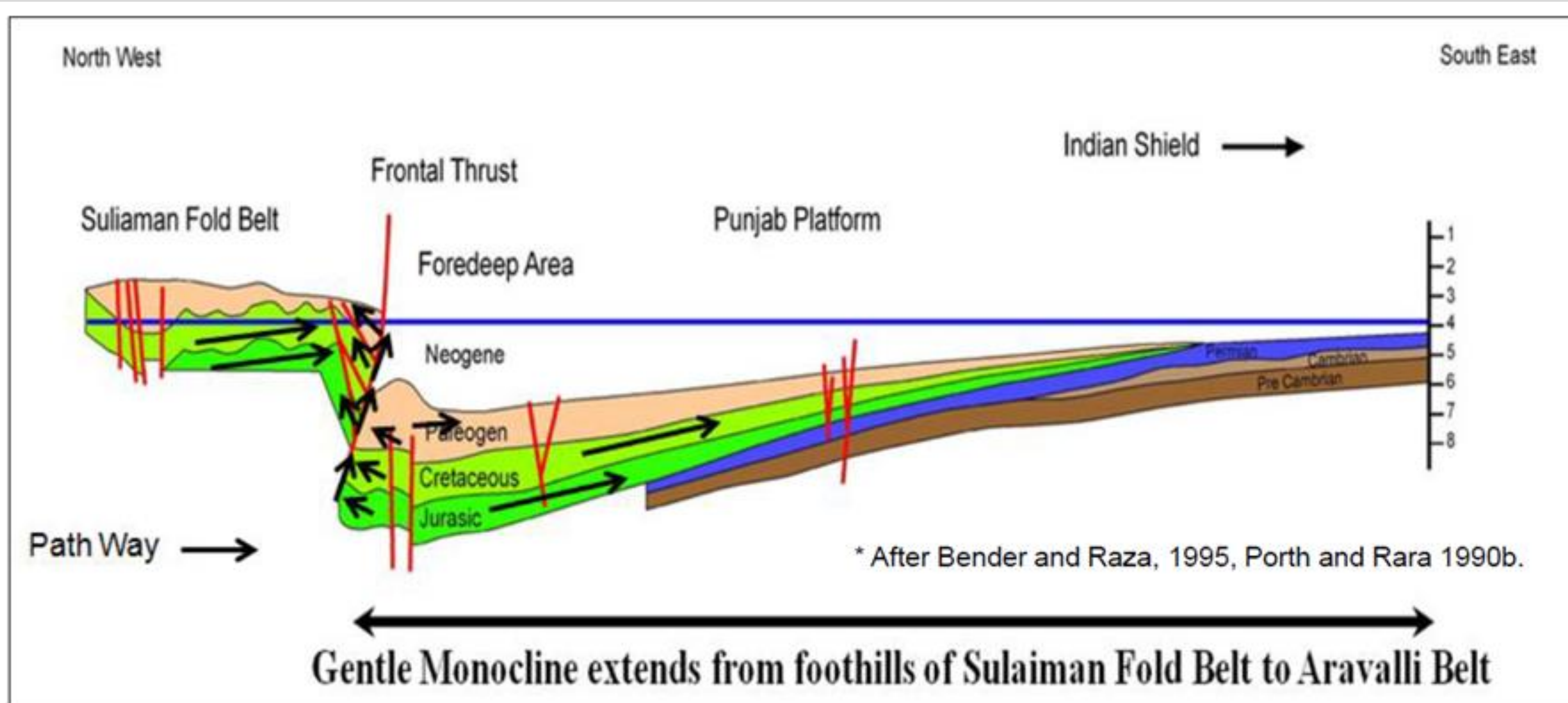


Figure 2. Schematic structural cross section through the Middle Indus Basin (Nazeer et al., 2013). The architecture of the MIB and the Western Canadian Sedimentary Basin are similar.

The Mesozoic and Cenozoic stratigraphy of the MIB includes a thick sequence of carbonates, shale, siltstones, and sandstones that were deposited on a passive margin before the Indian Plate collided with Asia. The largest gas pools occur in Paleogene carbonate or sandstone reservoirs. Smaller gas pools have been discovered on the Punjab Platform in Jurassic reservoirs.

The Lower Cretaceous Sembar Formation is the most important source rock in the MIB (Figure 3).

Period	Epoch	Formation	Thickness(m)	Lithology	Description
QUATERNARY	Recent	Alluvium	87		Sand with traces of clay and conglomerates.
	Pleistocene	Sivalika	421		Sandstone with streaks of clay/claystone and traces of conglomerates.
TERTIARY	Oligocene	Darginda	70		Marl with thin bands of shale.
		Pirkoh	114		Limestone with traces of shale.
		Siki	60		Clay/claystone with traces marl and shale.
		Habib Rahi	110		Limestone with traces of shale.
		Gharhi	250		Shale with thin bands of limestone.
	Eocene	Sui Up. L. St.	35		Limestone with thin bands of marl and traces of shale.
		Sui Shale Unit	59		Shale with streaks of shale.
		Sui Main L. St.	227		Limestone with thin bands of shale and traces of marl.
CRETACEOUS	Paleocene	Rankot	280		Sandstone with streaks of shale and traces of clay/claystone, siltstone, limestone and conglomerates.
	Eocene	Pali	34		Sandstone with traces of shale.
		Parh	27		Limestone.
	Oligocene	Upper Goru	408		Marl with traces of shale.
	Lower Cretaceous	Lower Goru	679		Marl with intercalations of shale and interbeds of siltstone and minor sandstone in lower parts.
	Lower Cretaceous	Lower Goru "C" Sands	+245		Sandstone with intercalations of shale and interbeds of siltstone.
		Sembar	+250		Source Rock Shale and Siltstone
JURASSIC	Santonian	Santonian	130		Limestone and Sandstone
	Shinarump	Shinarump	75		Sandstone, Clay and Limestone
		Delta	25		Sandstone and Clay

Figure 3. Stratigraphy of Mesozoic and Cenozoic sedimentary rocks in the Sulaiman Fold Belt (Nazir et al., 2012). Red stars = gas reservoirs.

## 2. SOURCE-ROCK BEDS IN THE LOWER CRETACEOUS SEMBAR FORMATION

Marine shale beds in the Sembar Formation probably have generated most of the dry thermogenic gas present in the MIB. Geochemistry data (e.g., RockEval; VKA) indicate those source rocks have only fair-good quality, and principally contain gas-prone (Type III) kerogen with admixtures of oil-prone (Type II) kerogen and inert organic matter (Type IV) (Figure 4). Sembar source rocks have reached the gas window in the Sulaiman Fore Deep (Nazir et al., 2013).

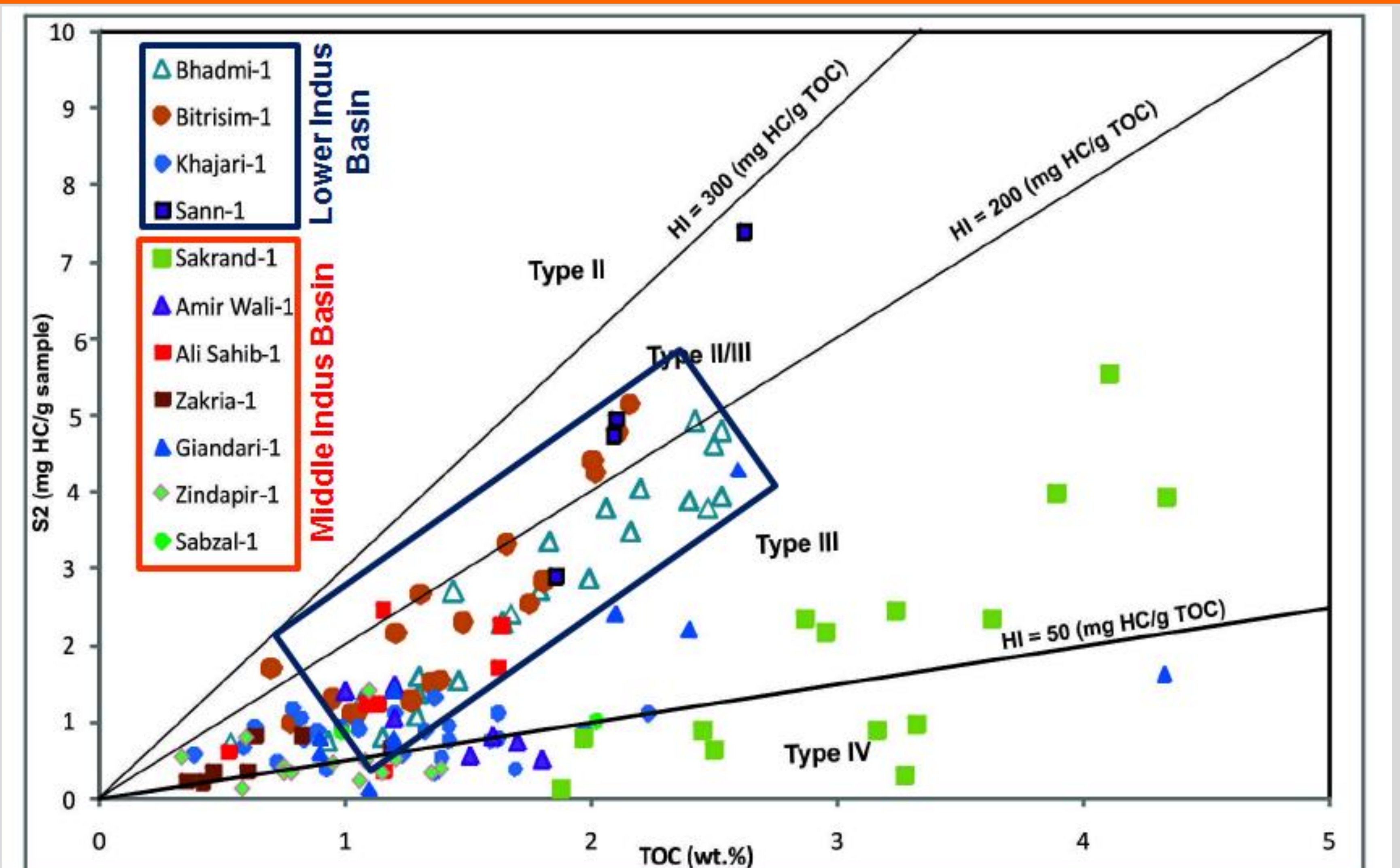


Figure 4. TOC and RockEval data measured on cuttings obtained from the Sembar Formation in the MIB or the Lower Indus Basin (Nazir et al., 2012).



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## 3. MOLECULAR AND C ISOTOPIC COMPOSITION OF GAS SAMPLES AND SOURCE ROCK SAMPLES COLLECTED FROM SEVERAL FIELDS IN THE MIDDLE INDUS BASIN

We used geochemical data measured on gas samples collected at the Pirkoh and Sui fields in the Sulaiman Fold Belt, two gas fields on the Mari-Kandhkot High, and the Nandpur Field on the Punjab Platform (Table 1).

Well Name	Formation	O <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>1</sub> /C <sub>2</sub>	C <sub>3</sub>	iC <sub>4</sub>	nC <sub>4</sub>	iC <sub>5</sub>	nC <sub>5</sub>	δ <sup>13</sup> C <sub>1</sub>	δDC <sub>1</sub>	δ <sup>13</sup> C <sub>2</sub>	δ <sup>13</sup> C <sub>3</sub>	δ <sup>13</sup> CO <sub>2</sub>
%																	
Nandpur-04	Samanasuk Limestone	0.3	7.0	77.5	14.9	0.2	75	n.d.	n.d.	n.d.	n.d.	n.d.	-33.1	-143	-28.3	n.d.	-6.8
Pirkoh-06	Pab Sandstone	0.5	7.7	7.7	83.7	0.3	280	n.d.	n.d.	n.d.	n.d.	n.d.	-33.3	-145	-26.6	n.d.	-4.2
Pirkoh-07 (Pab)	Pab Sandstone	0.7	6.9	8.3	83.7	0.3	280	0.1	n.d.	n.d.	n.d.	n.d.	-31.0	-135	-26.2	-25.4	-5.0
Pirkoh-07 (Ranikot)	Ranikot Formation	0.6	6.6	7.4	85.1	0.3	280	0.1	n.d.	n.d.	n.d.	n.d.	-31.0	-136	-27.0	-25.8	-4.0
Pirkoh-10	Ranikot Formation	1.1	6.4	9.7	82.5	0.3	280	0.1	n.d.	n.d.	n.d.	n.d.	-31.4	-136	-27.4	-24.1	-4.0
Sui-16 (SML)	Sui Upper Limestone	0.5	1.1	6.0	90.9	1.0	91	0.3	n.d.	0.1	n.d.	n.d.	-36.2	-144	-24.5	-25.2	-4.4
Sui-16 (SUL)	Sui Main Limestone	0.5	7.1	5.2	85.9	0.9	95	0.2	0.1	0.1	n.d.	n.d.	-36.0	-144	-24.2	-24.9	-3.1
Sui-21	Sui Main Limestone	0.6	6.7	14.5	77.1	0.8	96	0.2	0.1	0.1	n.d.	n.d.	-36.0	-142	-24.0	-24.5	-3.1
Sui-31 (SUL)	Sui Upper Limestone	0.5	0.5	7.1	90.3	1.1	82	0.3	0.1	0.1	n.d.	n.d.	-36.5	-146	-25.7	-26.3	-6.5
Sui-31 (SML)	Sui Main Limestone	0.7	5.7	6.4	85.8	1.0	86	0.3	0.1	0.1	n.d.	n.d.	-36.1	-145	-24.5	-25.1	-2.5
Sui-43	Sui Main Limestone	0.7	5.2	6.2	86.5	1.0	87	0.2	0.1	0.1	n.d.	n.d.	-36.1	-143	-24.7	-24.9	-3.0
Sui-69	Sui Upper Limestone												-36.3	-144	-24.6	-25.7	-6.5
Kandhkot-10 (SUL)	Sui Upper Limestone	3.8	4.0	26.9	64.1	0.9	71	0.2	0.1	0.1	0.1	0.1	-36.3	-144	-25.7	-24.3	-3.5
Kandhkot-10 (SML)	Sui Main Limestone	3.6	4.4	27.8	63.0	0.9	70	0.2	0.1	0.1	0.1	0.1	-36.3	-144	-25.7	-25.4	-4.0
Kandhkot-11 (SUL)	Sui Upper Limestone	0.6	5.5	15.0	77.5	1.0	78	0.3	0.1	0.1	0.1	0.1	-36.2	-143	-25.7	-25.9	-4.8
Kandhkot-11 (SML)	Sui Main Limestone	0.6	3.2	13.7	80.9	1.2	67	0.3	0.1	0.1	0.1	0.1	-36.2	-143	-26.0	-25.8	-6.1
Mari-04	Habib Rahi Limestone	1.7	5.6	22.9	69.6	0.1	700	n.d.	n.d.	n.d.	n.d.	n.d.	-47.5	-190	-21.5	n.d.	0.4
Mari-24	Habib Rahi Limestone	0.4	4.0	18.6	76.8	0.2	380	n.d.	n.d.	n.d.	n.d.	n.d.	-47.2	-192	-13.8	n.d.	0.5
Mari-39	Habib Rahi Limestone	0.6		23.1	76.0	0.2	380	n.d.	n.d.	n.d.	n.d.	n.d.	-52.2	-197	-17.3	n.d.	
Mari-50	Habib Rahi Limestone	0.4	8.8	18.7	71.9	0.2	360	n.d.	n.d.	n.d.	n.d.	n.d.	-47.8	-190	-20.3	n.d.	-2.1

Table 1. Molecular and C isotopic composition of gas samples produced from several fields located in the Middle Indus Basin (Ahmad and Alam, 1992).

Methane/ethane ratios demonstrate that gas samples from the Pirkoh Field are drier than gas samples from the Sui Field or the Kandhkot Field. Gas samples from the Mari Field are even drier ( $C_1/C_2 \approx 360-700$ ) (Figure 5).

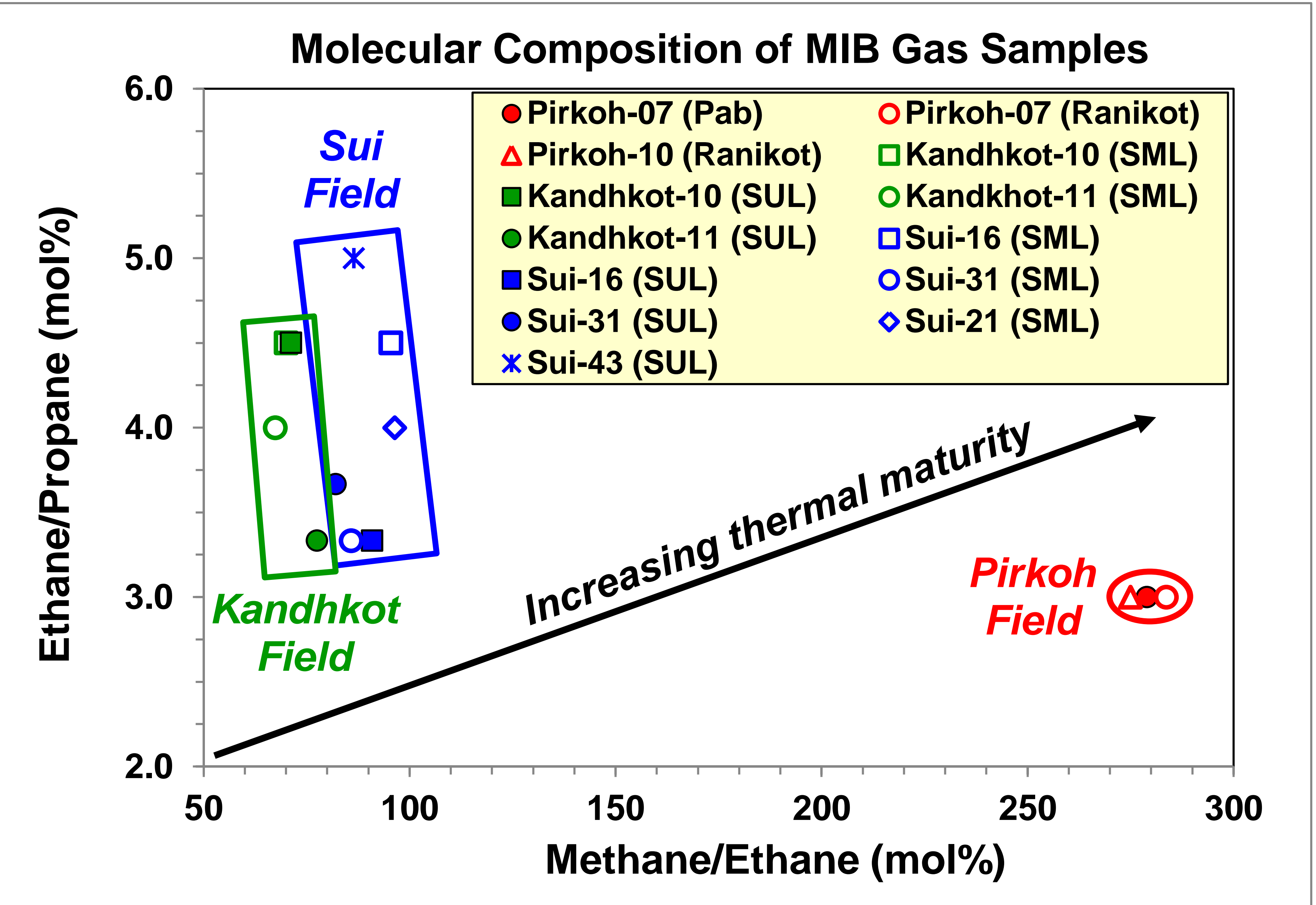


Figure 5. Methane/ethane and ethane/propane ratios in gas samples produced from several fields in the MIB.

## 4. THE PRESENCE OF MICROBIAL METHANE IN MIB GAS SAMPLES

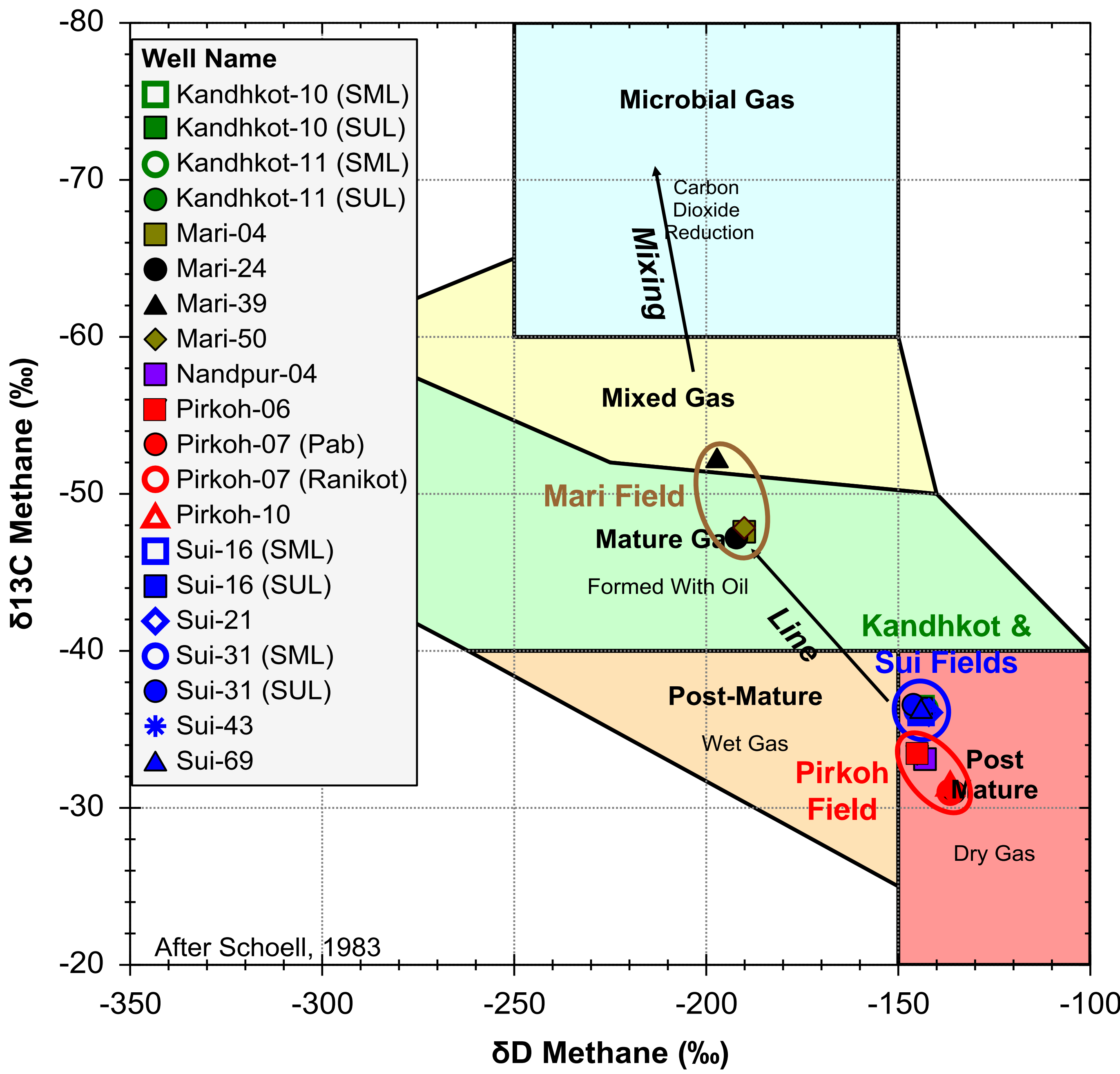


Figure 6. C and H isotopic composition of dry gas samples produced from the MIB.

Nitrogen is associated with dry thermogenic gas in the MIB. Because microbial methane probably contains very little nitrogen, microbial methane dilutes the abundance of nitrogen in a mixed gas sample. We used that principal and geochemical data measured on OGDCL gas samples produced from Mesozoic reservoirs on the Punjab Platform to estimate the C isotopic composition of microbial methane in the MIB ( $\approx -71$  per mil PDB) (Figure 7).

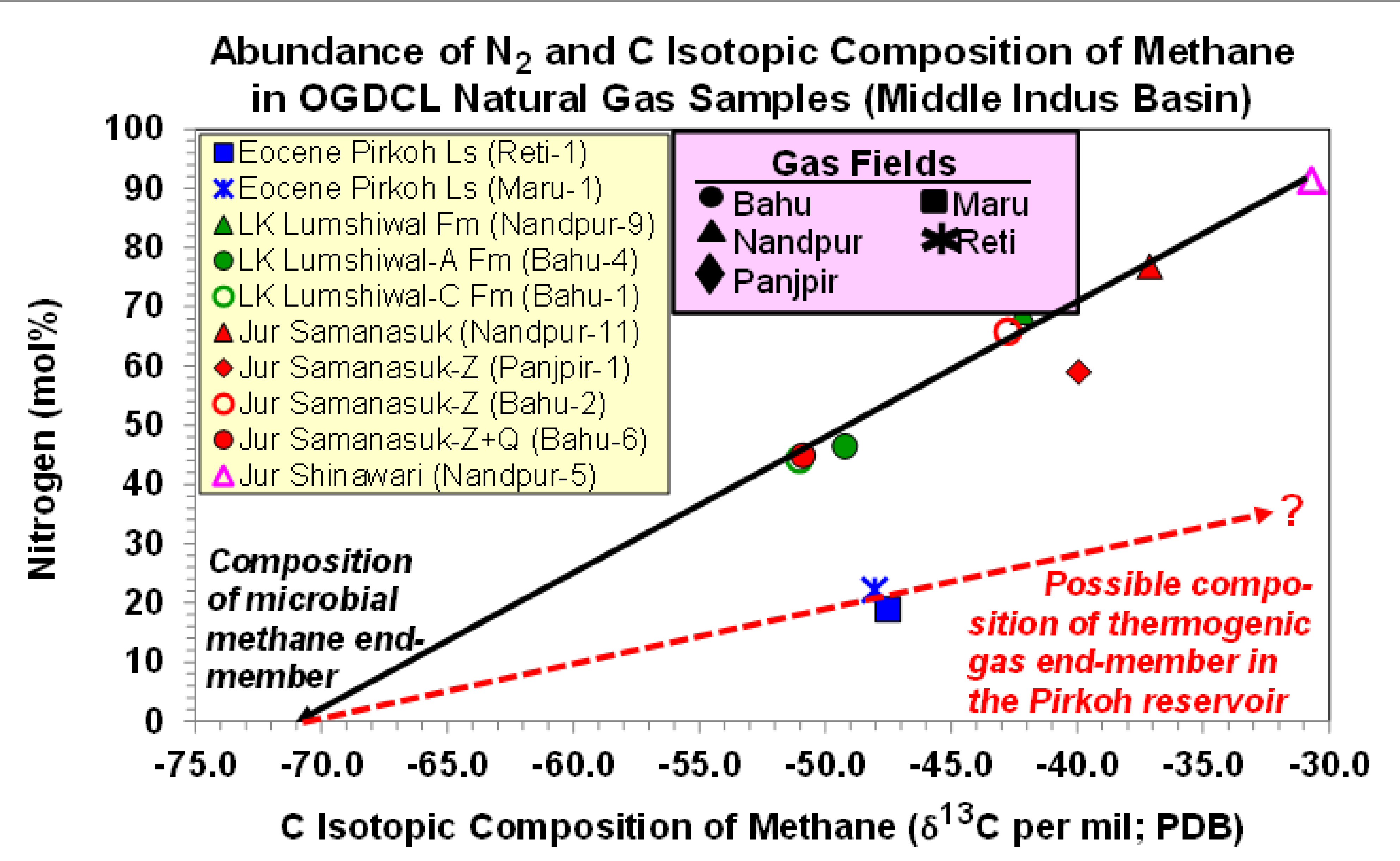
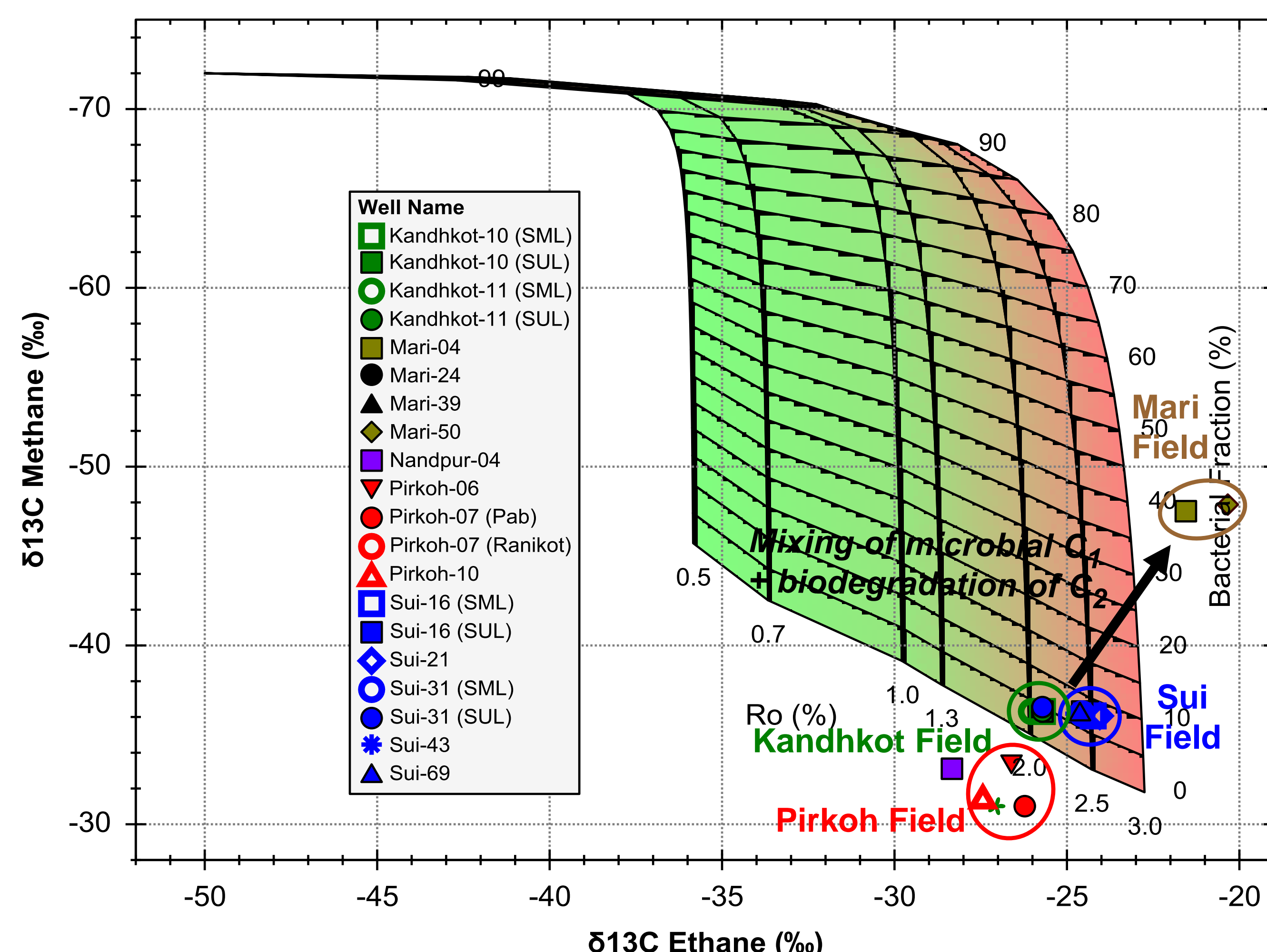


Figure 7. Estimating the C isotopic composition of microbial methane in the MIB.



## 5. THERMAL MATURITY OF MIB GAS SAMPLES

The C isotopic composition of methane, ethane, and propane can be used to estimate the level of maturity at which thermogenic gas was generated – but only if that sample does not contain microbial methane and it is not biodegraded (a process that alters the C isotopic composition of  $C_{2+}$  compounds (James and Burns, 1984).





## 9. INTERPRETING MICROBIAL METHANE + THERMOGENIC GAS MIXING LINES WHEN SAMPLES HAVE BEEN BIODEGRADED

The gas samples produced from the Mari Field do not lie on the canonical mixing line between high-maturity thermogenic gas and microbial methane even though they are ≈50:50 mixtures of both types of natural gas. The explanation is that the thermogenic gas component is biodegraded – significantly increasing the methane/(ethane + propane) ratio (Figure 12). They incorrectly seem to contain a significant amount of the type of microbial methane that forms in landfills during the fermentation of acetic acid.

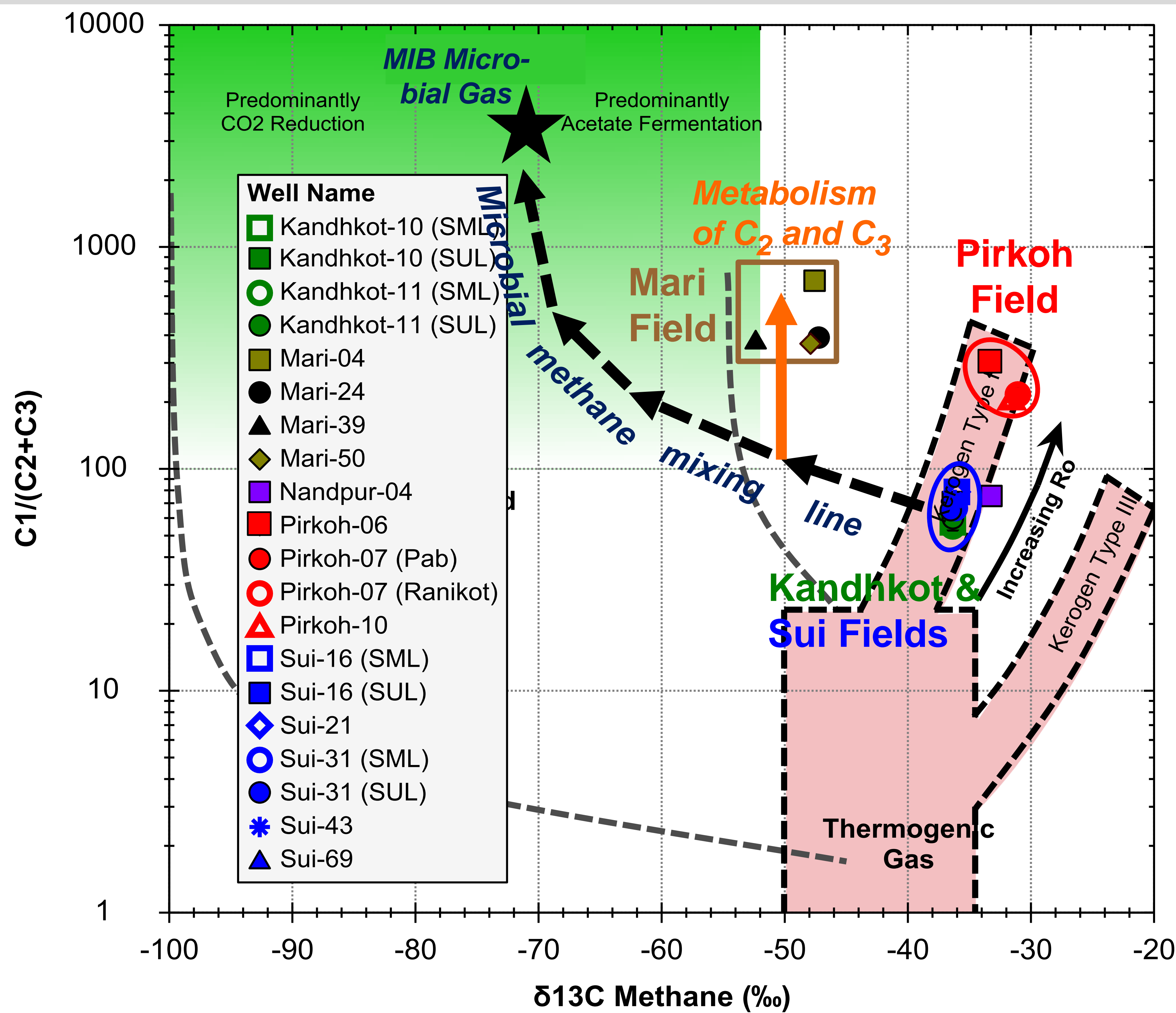


Figure 12. The biodegradation of  $C_{2+}$  compounds in Mari gas samples makes it difficult to interpret the kind of microbial methane they contain using a standard method developed by Whiticar (1994).

### Key Observation and Conclusions

Thermogenic gas samples in the Middle Indus Basin also commonly contain some amount of microbial methane that formed during the reduction of  $CO_2$ . The C isotopic composition of the microbial methane is ≈ -70 per mil PDB.

The thermogenic component of dry natural gas in the MIB principally was generated by source-rocks beds in the Lower Cretaceous Sembar Formation in the Sulaiman Foredeep at  $VR \geq 1.4\%$  by gas-prone kerogen that contains isotopically-heavy C ( $\delta^{13}C \approx -23.5$  per mil PDB).

Gas samples produced from the shallow Habib Rahi reservoir at the Mari Field on the Mari-Kandhkot High are moderately to severely biodegraded. Those gas samples are extremely dry because they contain a significant amount of microbial methane, and microbes metabolized  $C_{2+}$  compounds.

Most of the  $CO_2$  in the gas samples we studied was generated during high-temperature diagenetic reactions that involved marine carbonate minerals.

## 10. ORIGIN OF CARBON DIOXIDE IN GAS SAMPLES PRODUCED FROM THE MIB

The C isotopic composition of  $CO_2$  can be used to help understand the origin of that non-HC compound in gas samples: e.g.,  $CO_2$  that forms during the anaerobic biodegradation of oil contains “heavy” C, while  $CO_2$  that forms during the diagenesis of kerogen contains “light” C. The C isotopic composition of  $CO_2$  in MIB gas samples ranges from -6.8 per mil to +0.5 per mil. Because a feasible magmatic source of  $CO_2$  in the MIB has not been identified, the most reasonable interpretation is that compound principally formed during the diagenesis of marine carbonate minerals (Figure 13).

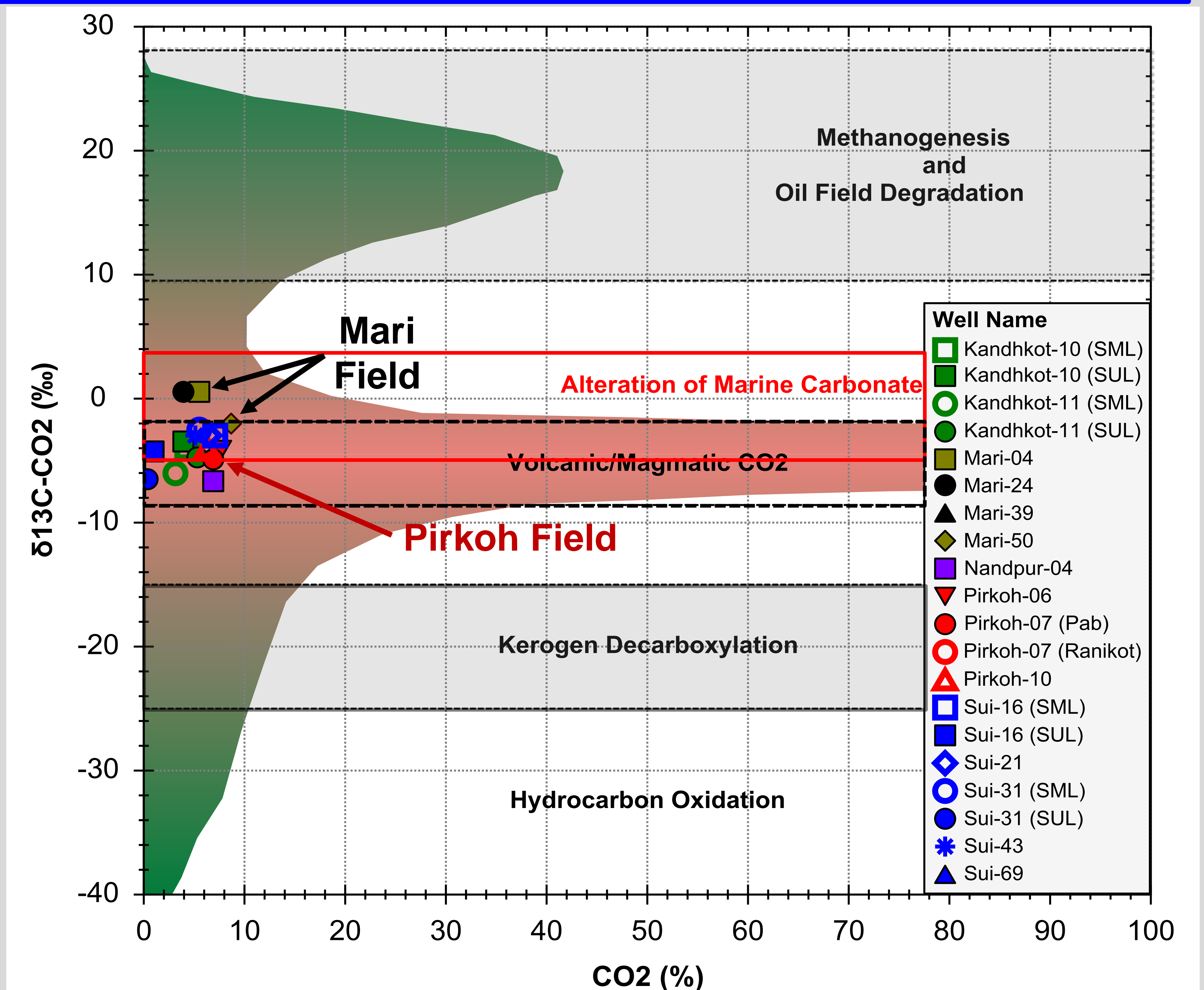


Figure 13. C isotopic composition of carbon dioxide in MIB gas samples.

**Acknowledgments.** We thank OGDCL for permission to publish geochemical data measured on several gas samples collected from the MIB, and on kerogen samples isolated from several MIB source-rock samples. We also thank Weatherford Laboratories Inc. for permission to present these results.

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