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Stable Carbon and Deuterium Isotope Composition of Natural Gases in Pakistan

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ABSTRACT

The isotopic determination was carried out on gas samples collected from various producing oil and gas fields of Indus basin and also on seepage samples collected from Makran coastal area of Balochistan basin. The analyses were carried out at Federal Institute of Geosciences and Natural Resources (BGR), Germany. The study was undertaken to correlate various associated gases of Potwar and gases of Sulaiman area. The results indicate that most of gases from the producing fields of Potwar are thermogenic gases and exhibit typical properties of associated gases. The gas samples from Sulaiman area are of thermogenic origin with the exception of Mari gas field which contains admixture of bacterial gas. The gas samples from Badin fields are associated thermogenic gases. The seepage samples from Makran coastal area reveal mixed origin.

INTRODUCTION

Gases from various oil and gas producing wells of Indus basin and seepage samples from Makran coastal area were characterised by stable carbon and hydrogen ratios. On the basis of these ratios it is possible to classify gases as biogenic or thermogenic. The samples from producing fields were collected at the well head under atmospheric pressure.

The samples were analysed at the isotope laboratory of Federal Institute of Geosciences and Natural Resources (BGR), Hannover, Germany. The interpretation of data was carried out as per procedure of Faber (1986, 1987) and Schoell (1983). The values are reported in the notation against the PDB and SMOW standard for carbon and hydrogen respectively.

RESULTS AND DISCUSSION

The relevant chemical and isotope data is presented in Tables 1 to 8. The results of various sedimentary areas are summarised as follows.

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Potwar Area

The gas samples were collected from producing fields of Potwar. The chemical and isotope data is presented in Tables 1 and 2. The isotope values are plotted in Figure 1.

It can be seen from Table 2, that high carbon dioxide was met in samples from Toot and some wells of Meyal. In Meyal CO_2-enriched samples came from stratigraphically deep formations. Since there is an increase of maturity from southeast to the west in Potwar, carbon dioxide could have been partly formed by breakdown of certain carbonates at high temperature further towards west.

Figure 1 shows that the values of Dhurnal, Adhi and Meyal are close to each other. Most of the values are falling within the region of thermogenic gases and exhibit typical properties of associated gases. The samples from Joya Mair and Balkassar fields show decrease in heavier isotope and increase in non-methane hydrocarbons. This trend seems to indicate that Joya Mair and Balkassar gases are early products of gas generation. The plotted points rule out any possibility of biogenic origin or generation as a result of catagenesis.

Samples from Potwar are correlated to each other. The straight alignment of the sample points do not give any indication for admixture of biogenic methane or for catagenic origin or for different source material. The samples from Joya Mair and Balkassar are extremely depleted in Deutrium and the sample points are located close to the border of low range of onset of gas generation. Interestingly samples from Adhi seem to be well within main field, pointing to normal mature samples.

Figure 2 is a cross plot of $d13C_1$ vs the ratio $C_1/sum(C_n)$. The lower the latter value, the more heavier hydrocarbons are present in the samples. Gases of bacterial origin contain mainly methane, which is also the main component in high temperature derived gases. For both gases, the ratio $C_1/sum(C_n)$ is approaching unity. Associated gases have ratio below 0.9; the lowest values are expected at the onset of oil generation.

Sulaiman Area

The samples were collected from producing fields of Sui, Mari, Kandhkot and Pirkoh. All the samples were

Table 1. Isotope ratios of natural gas samples from selected oil producing wells of Potwar area.

Lab-#	Locality/Well	Depth (m)	Formation	d13C$_1$	dDC$_1$	d13C$_2$ (ppm)	d13C$_3$	d13CO$_2$
260	Adhi 5	2654-2680	Khewra	-36.4	-207	-25.2	-23.2	-13.2
261	Adhi 7	2334-2342	Sakesar	-38.9	-227	-26.7	-24.5	-18.3
262	Adhi 9	2671-2674	Tobra	--	--	--	--	--
257	Balkassar A5	2504-2531	Bahdrar	-41.5	-294	-31.7	-27.2	-10.4
258	Balkassar A7	2507-2523	Sakessar	-41.5	-292	-31.4	-27.1	-13.3
259	Balkassar P2	2473-2504	Sakessar	-41.5	-285	-31.3	-26.8	-9.8
236	Bulbuli/Surghar	Surface	Sakessar	-64.3	-198	--	--	-14.0
270	Dhulian 43	2377-2438	Ranikot	-40.2	-249	--	-25.1-	-7.1
234	Dhurnal 1	3755-4000	Chorgali/Sakessar	-38.7	-211	-26.4	-23.0	-15.1
235	Dhurnal 2	3830-3983	Chorgali/Sakessar	-38.7	-208	-26.3	-24.1	-7.00
256	Joya Mair 1	2070-2531	Bahdrar	-41.9	-311	-33.7	-28.1	-12.0
239	Meyal 6	3865-4050	Ranikot/Kairabad	-38.3	-193	-26.0	-23.5	-4.6
240	Meyal 7	3840-3897	Chorgali/Sakessar	-38.7	-215	-26.7	-23.8	-5.7
241	Meyal 9	3734-3842	Sakessar	-38.6	-213	-26.8	-24.0	-6.5
242	Meyal 12	4078-4139	Variegated beds	-38.2	-188	-25.8	-23.3	-6.5
225	Toot 11	4427-4392	Jurassic	-37.1	-188	-29.2	-25.0	-3.9
226	Toot 15	4530-4490	Jurassic	-37.2	-199	-27.7	-25.4	-2.4
227	Toot 16	4466-4383	Jurassic	-36.7	-178	-26.7	-25.1	-3.7

Table 2. Chemical composition of natural gas samples from selected oil producing wells of Potwar area.

Lab-#	Locality/Well	C$_1$	C$_2$	C$_3$	i-C$_4$	n-C$_4$	i-C$_5$	n-C$_5$	N$_2$	C0$_2$	C$_1$/ sumC$_n$
		(Mol%)									
260	Adhi 5	47.4	4.6	2.2	0.6	0.9	0.4	0.5	43.1	0.3	0.837
261	Adhi 7	66.2	7.2	2.9	0.6	0.8	0.3	0.3	21.6	0.1	0.845
262	Adhi 9	1.8	0.2	0.1	0.0	0.0	0.0	0.0	97.8	0.1	0.857
257	Balkassar A 5	56.2	20.0	14.0	2.1	4.0	1.0	1.1	1.0	0.6	0.571
258	Balkassar A 7	52.0	20.1	16.0	2.6	5.1	1.4	1.4	1.0	0.4	0.527
259	Balkassar P 2	65.9	16.3	9.5	1.6	3.0	1.0	1.0	1.2	0.5	0.670
236	Bulbuli/Surghar	29.8	0.0	0.0	0.0	0.0	0.0	0.0	66.6	3.5	1.000
270	Dhulian 43	80.2	10.4	4.4	0.7	1.3	0.5	0.5	1.5	0.6	0.818
234	Dhurnal 1	81.1	10.2	4.4	0.8	1.2	0.4	0.3	1.0	0.5	0.824
235	Dhurnal 2	80.6	10.2	4.6	0.9	1.4	0.5	0.4	0.7	0.5	0.817
256	Joya Mair 1	38.6	22.5	22.2	3.5	7.6	2.0	2.2	1.2	0.3	0.391
239	Meyal 6	81.4	8.4	3.7	0.8	1.2	0.5	0.4	0.8	2.7	0.844
240	Meyal 7	74.4	9.6	4.0	0.7	1.1	0.3	0.3	8.8	0.8	0.823
241	Meyal 9	80.4	10.4	4.6	0.9	1.5	0.5	0.5	0.5	0.7	0.814
242	Meyal 12	72.9	6.4	2.5	0.5	0.7	0.3	0.2	13.7	2.8	0.873
225	Toot 11	62.7	5.0	2.3	0.4	0.8	0.3	0.3	23.1	5.2	0.873
226	Toot 15	72.5	8.9	5.7	1.2	2.5	0.9	0.9	0.6	6.7	0.783
227	Toot 16	79.9	5.9	2.9	0.7	1.4	0.5	0.4	1.4	6.6	0.871

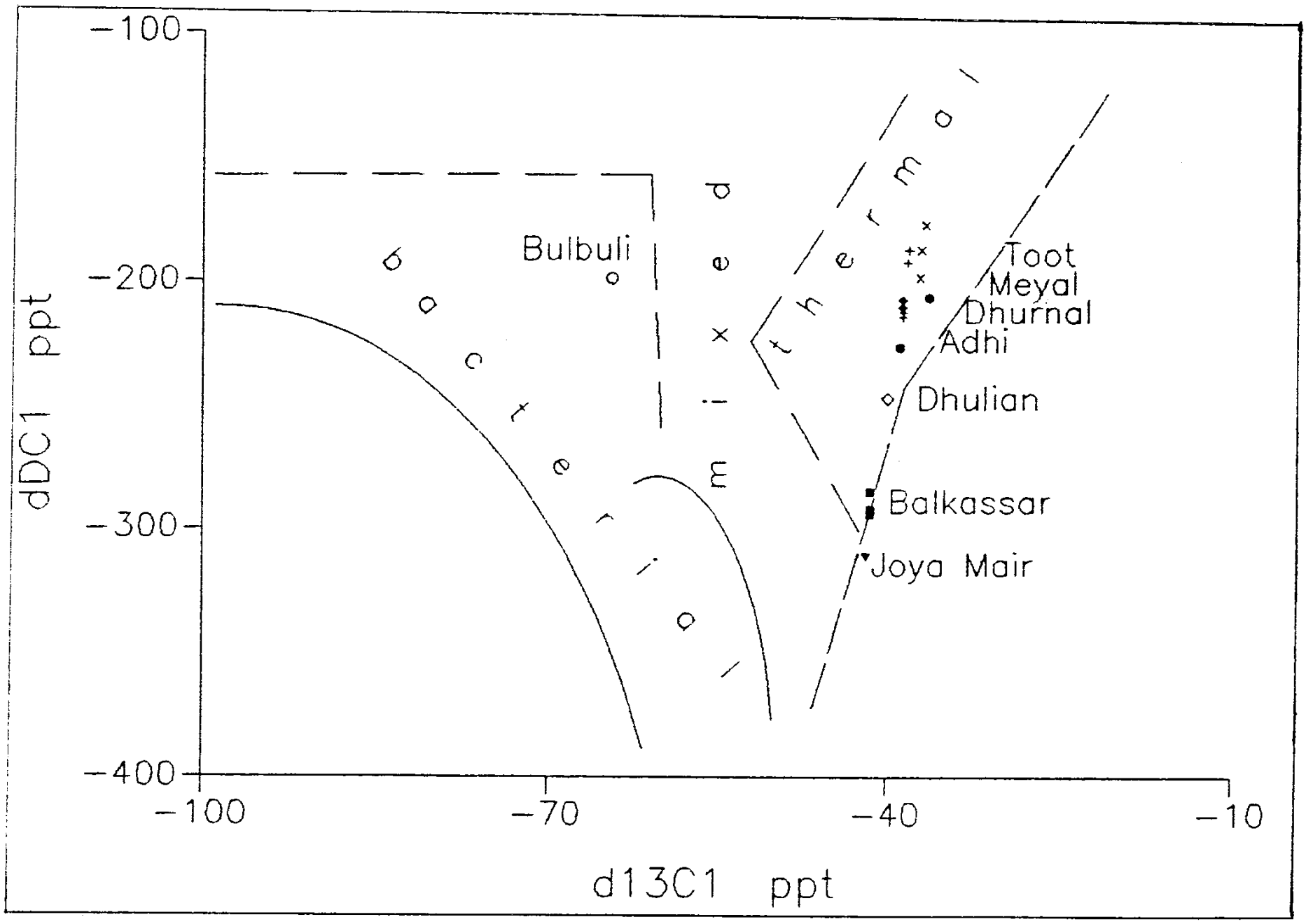

Figure 1— Natural gas samples from producing wells of Potwar area.

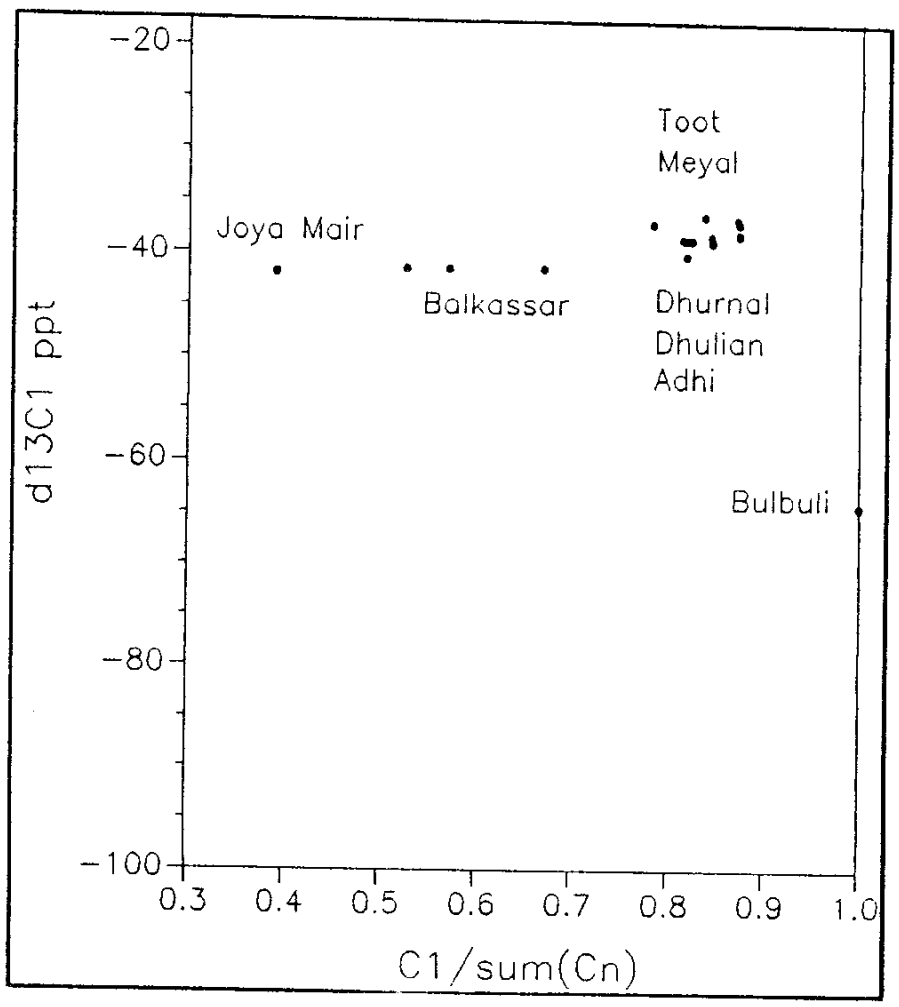

Figure 2— Isotope ratios of d13C_1 ppt Vs C_1/sum(C_n) from oil fields of Potowar area.

analysed for isotopic determination. The results are presented in Tables 3 and 4 and the values are plotted in Figure 3. All the samples contain nitrogen (5 to 27 %), oxygen (0.3-3.8 %) and carbon dioxide (0.8-8.8 %). The samples from Pirkoh and the Sui Main Limestone units contain ten times more carbon dioxide than the samples from Sui Upper Limestone. The cross plot of isotope values indicate that the samples from Mari gas field are homogeneous and can be classified as thermogenic gases containing a small admixture of bacterial derived methane. Methane from carbon dioxide rich zone is isotopically lighter and possibly contain more bacterial derived methane.

Isotopic data, indicate that natural gas of Kandhkot and Sui gas field is identical. For methane, the carbon and deutrium isotope ratios of 12 samples from different horizons are more or less similar. However, there are significant variations in the chemical composition of these gases. Kandhkot gas contain two times more nitrogen than Sui.

From the data, it can be inferred that gases of Kandhkot, Sui and Pirkoh are thermogenic. The concentration of the

Table 3. Isotope ratios of natural gas samples from selected gas producing wells of Sulaiman area.

Lab-#	Locality/Well	Depth (m)	Formation	d13C$_1$	dDC$_1$	d13C$_2$	d13C$_3$	d13CO$_2$
				(ppt)				
3149	Kandhkot10	1220-1253	Sui Upper Limestone	-36.3	-144	-25.7	-24.3	-3.5
3150	Kandhkot 10	1332	Sui Main Limestone	-36.3	-144	-25.7	-25.4	-4.0
3151	Kandhkot 11	1206-1230	Sui Upper Limestone	-36.2	-143	-25.7	-25.9	-4.8
3152	Kandhkot 11	1286	Sui Main Limestone	-36.2	-143	-26.0	-25.8	-6.1
3153	Mari 4	600-670	Habib Rahi Limestone	-47.5	-190	-21.5	--	0.4
3155	Mari 24	600-670	Habib Rahi Limestone	-47.2	-192	-13.8		0.5
3157	Mari 39	600-670	Habib Rahi Limestone	-52.2	-197	-17.3	--	-
3159	Mari 50	600-670	Habib Rahi Limestone	-47.8	-190	-20.3	--	-2.1
937	Nandpur 4	1842	Samana Suk Limestone	-33.1	-143	-28.3	-27.8	-6.8
938	Pirkoh 6	2281-2382	Pab	-33.3	-145	-26.6	-22.0	-4.2
940	Pirkoh 7	2229-2300	Pab	-31.0	-135	-26.2	-25.4	-5.0
941	Pirkoh 7	2070-2193	Ranikot	-31.0	-136	-27.0	-25.8	-
939	Pirkoh 10	2177-2217	Ranikot	-31.4	-136	-27.4	-24.1	-4.0
1060	Sui 16	1200	Sui Upper Limestone	-36.2	-144	-24.5	-25.2	-4.4
1061	Sui 16	1250	Sui Main Limestone	-36.0	-144	-24.2	-24.9	-3.1
1063	Sui 21	1350	Sui Main Limestone	-36.0	-142	-24.0	-24.5	-3.1
1064	Sui 31	1250	Sui Upper Limestone	-36.5	-146	-25.7	-26.3	-6.5
1065	Sui 31	1350	Sui Main Limestone	-36.1	-145	-24.5	-25.1	-2.7
1066	Sui 43	1300	Sui Main Limestone	-36.1	-143	-24.7	-24.9	-3.0
1067	Sui 69	1300	Sui Upper Limestone	-36.3	-144	-24.6	-25.7	-6.5

Table 4. Chemical composition of natural gas samples from selected gas wells of Sulaiman area.

Lab-#	Locality/Well	C$_1$	C$_2$	C$_3$	i-C$_4$	n-C$_4$	i-C$_5$	n-C$_5$	N$_2$	O$_2$	CO$_2$	H$_2$S	C$_1$/ sum/C$_n$
		(Mol %)											
3149	Kandhkot 10	64.1	0.9	0.2	0.1	0.1	0.1	0.1	26.9	3.8	4.0	0.0	0.981
3150	Kandhkot 10	63.0	0.9	0.2	0.1	0.1	0.1	0.1	27.8	3.6	4.4	0.0	0.981
3151	Kandhkot 11	77.5	1.0	0.3	0.1	0.1	0.1	0.1	15.0	0.6	5.5	0.0	0.982
3152	Kandhkot 11	80.9	1.2	0.3	0.1	0.1	0.1	0.1	13.7	0.6	3.2	0.0	0.981
3153	Mari 4	69.6	0.1	0.0	0.0	0.0	0.0	0.0	22.9	1.7	5.6	0.0	0.998
3155	Mari 24	76.8	0.2	0.0	0.0	0.0	0.0	0.0	18.6	0.4	4.0	0.0	0.998
3157	Mari 39	76.0	0.2	0.0	0.0	0.0	0.0	0.0	23.1	0.6	--	0.0	0.997
3159	Mari 50	71.9	0.2	0.0	0.0	0.0	0.0	0.0	18.7	0.4	8.8	0.0	0.997
937	Nandpur 4	14.9	0.2	0.0	0.0	0.0	0.0	0.0	77.5	0.3	7.0	1.0	0.985
938	Pirkoh 6	83.7	0.3	0.0	0.0	0.0	0.0	0.0	7.7	0.5	7.7	0.0	0.995
940	Pirkoh 7	83.7	0.3	0.1	0.0	0.0	0.0	0.0	8.3	0.7	6.9	0.0	0.996
941	Pirkoh 7	85.1	0.3	0.1	0.0	0.0	0.0	0.0	7.4	0.6	6.6	0.0	0.996
939	Pirkoh 10	82.5	0.3	0.1	0.0	0.0	0.0	0.0	9.7	1.1	6.4	0.0	0.996
1060	Sui 16	90.9	1.0	0.3	0.0	0.1	0.0	0.0	6.0	0.5	1.1	0.0	0.984
1061	Sui 16	85.9	0.9	0.2	0.1	0.1	0.0	0.0	5.2	0.5	7.1	0.0	0.985
1063	Sui 21	77.1	0.8	0.2	0.1	0.1	0.0	0.0	14.5	0.6	6.7	0.0	0.985
1064	Sui 31	90.3	1.1	0.3	0.1	0.1	0.0	0.0	7.1	0.5	0.5	0.0	0.982
1065	Sui 31	85.8	1.0	0.3	0.1	0.1	0.0	0.0	6.4	0.7	5.7	0.0	0.984
1066	Sui 43	86.5	1.0	0.2	0.1	0.1	0.0	0.0	6.2	0.7	5.2	0.0	0.985
1067	Sui 69	89.5	1.0	0.3	0.1	0.1	0.0	0.0	7.4	0.8	0.8	0.0	0.984

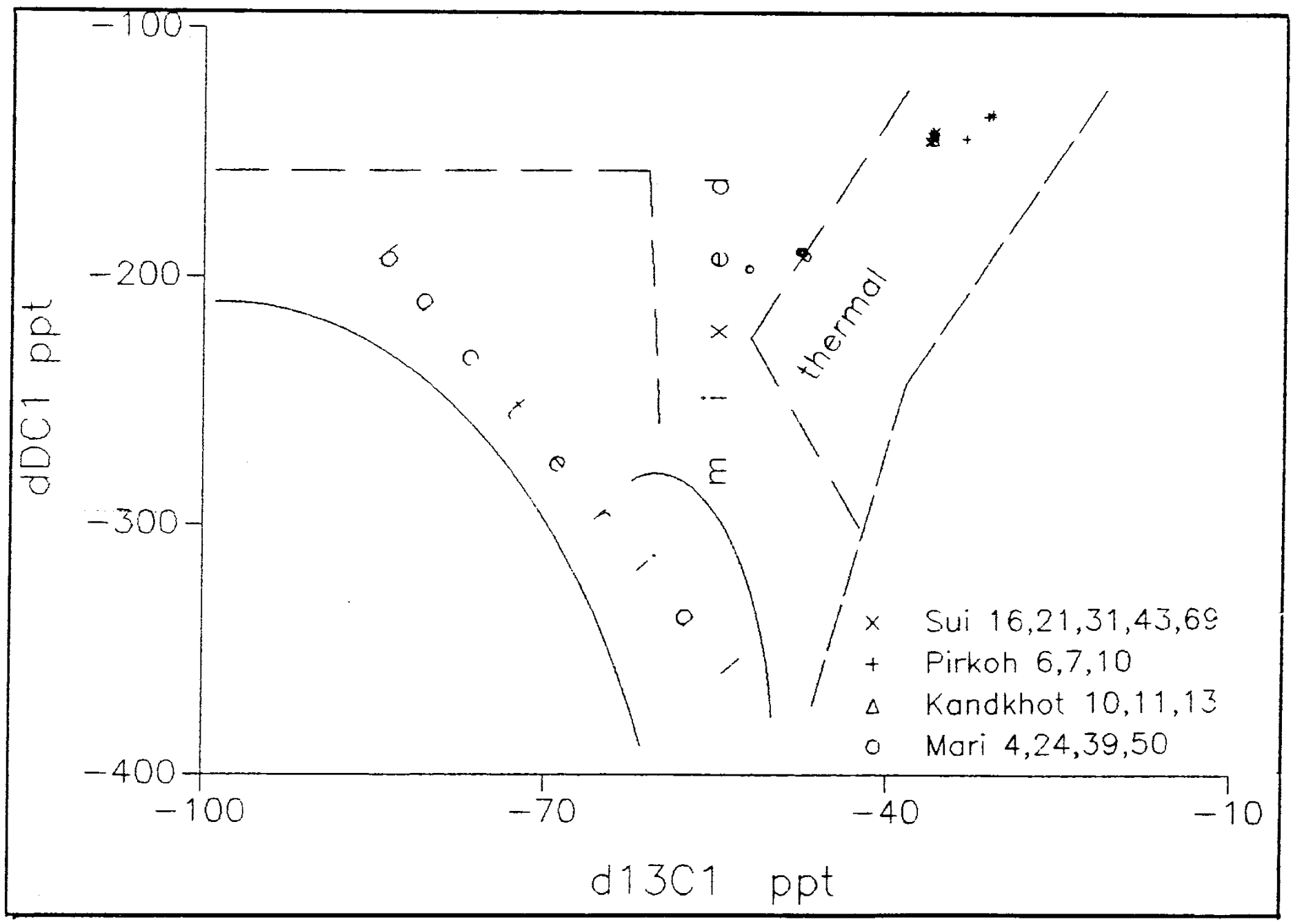

Figure 3— Natural gas samples from selected producing wells of gas fields of Sulaiman area. Isotope ratios given in part per thousand (ppt) relative to PDB and SMOW standards.

other hydrocarbon compounds was relatively low and these gases can be termed as dry. The samples from Sui were less dry than those from Pirkoh.

Kirthar Area

Samples were collected from oil fields of Tando Alam, Sono, Ghotana and Zhora located at the northern border of Badin oil and gas fields area. Chemical and isotope data are presented in Tables 5 and 6.

Figure 4 shows that most of the samples contain significant amount of high molecular hydrocarbons and can be classified as wet, typical of associated gases from oil fields. The isotopic results are plotted in Figure 5, which indicate that the gases can be classified as thermogenic.

Makran Coastal Area

Nine gas samples from various seepages of Makran coastal area were collected. The results of analysis are presented in Tables 7 and 8. All samples contained methane as main hydrocarbon compound. Other hydrocarbons were very low in quantity as may be seen from high ratio of $C_1/sum(C_n)$ (Figure 6), higher molecular hydrocarbons could not be detected so far (Alam, 1989).

The isotope determinations are plotted in Figure 7, which indicates that samples from Chandragup and Goth Jumma can be classified as bacterial derived; samples from localities K1, Kandasol and Ormara can be treated as thermogenic; samples from Karial and Aghor appear to be of mixed origin. The chemical and isotope compositions of the seepage gases from Makran area cannot be interpreted

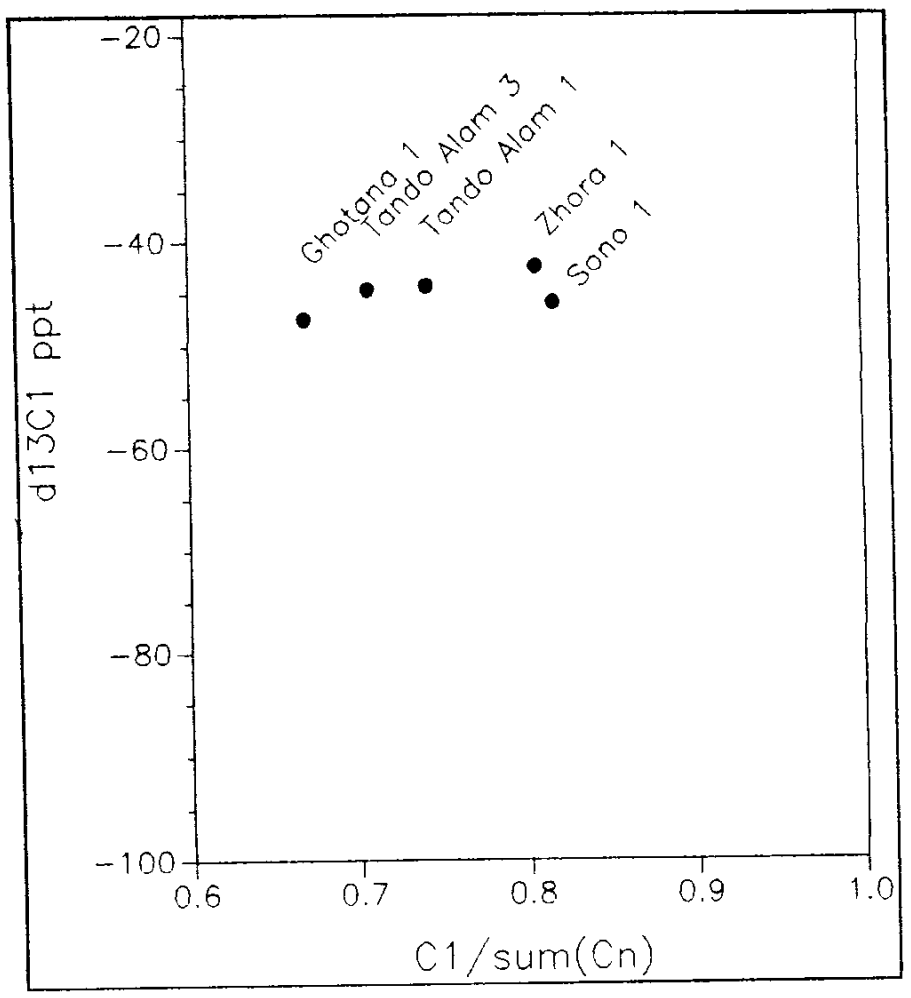

Figure 4— Isotope ratios of d13C$_1$ ppt Vs C$_1$/sum(C$_n$) from oil fields of Kirthar area.

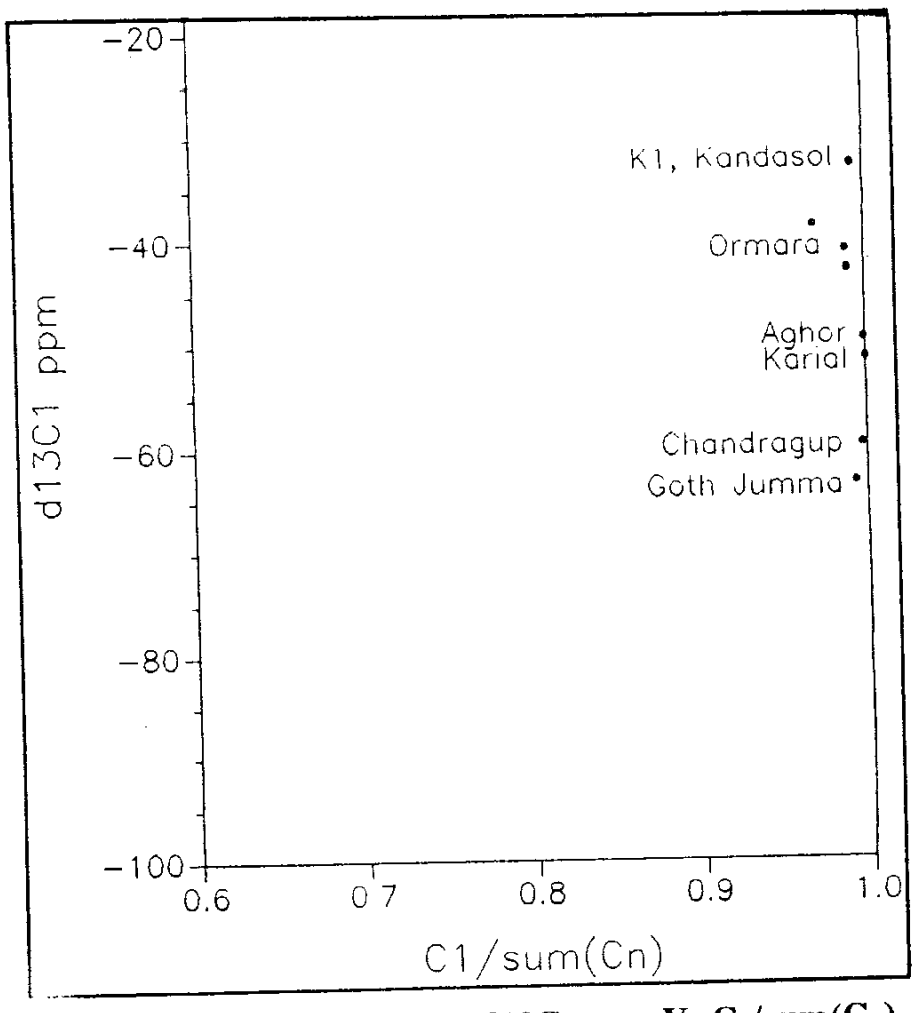

Figure 6— Isotope ratios of d13C$_1$ ppm Vs C$_1$/sum(C$_n$) from gas seepages of Makran coastal area.

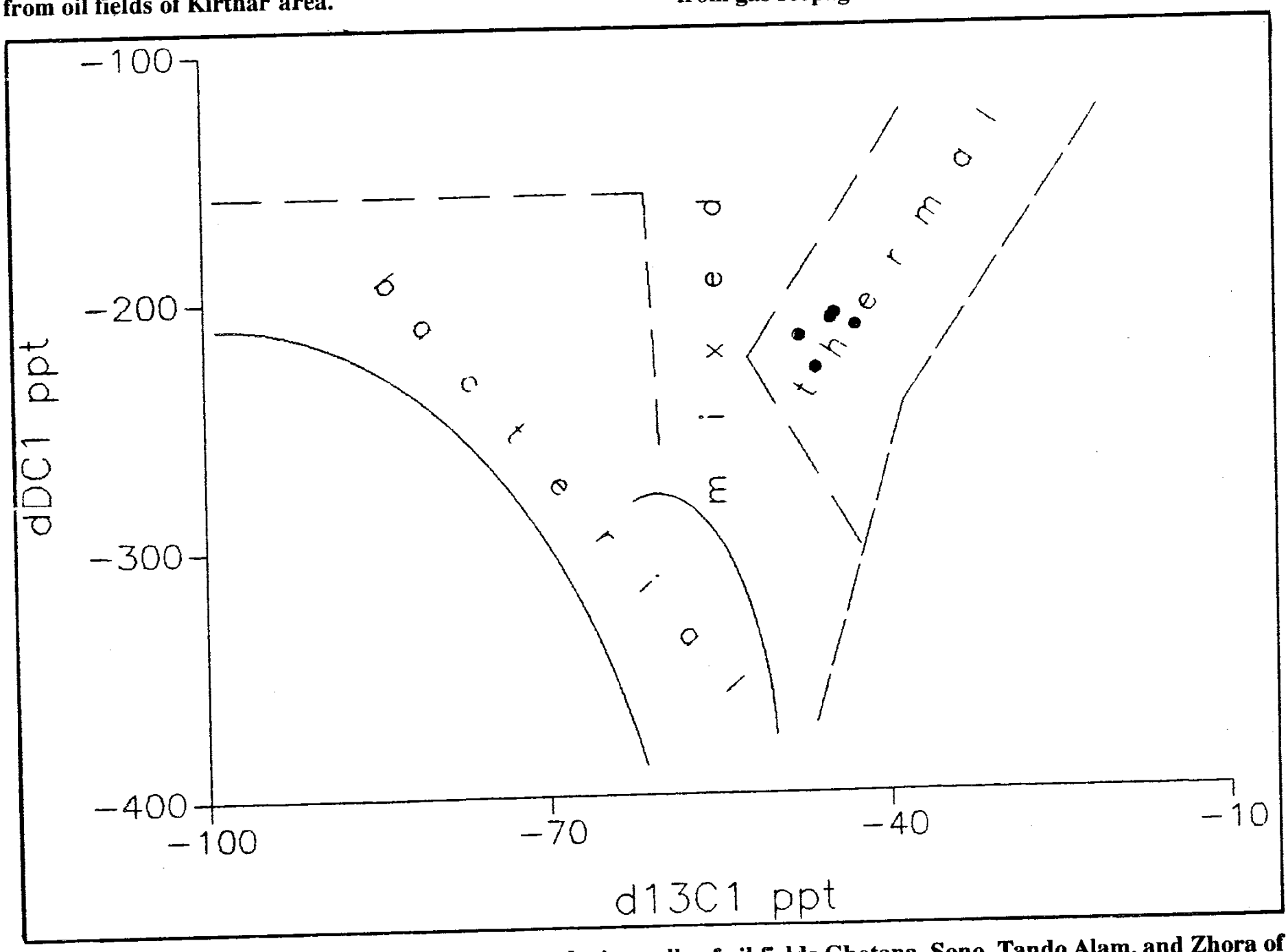

Figure 5— Natural gas samples from selected, producing wells of oil fields Ghotana, Sono, Tando Alam, and Zhora of Kirthar area. Isotope ratios given in part per thousand (ppt) relative to PDB and SMOW standards.

Table 5. Isotope ratios of natural gas samples from selected oil producing wells of the Badin oil and gas fields area.

Lab-#	Locality/Well	Depth (m)	d13C_1	dDC_1	d13C_2	d13C_3	d13CO_2
			(p p t)				
1694	Tando Alam 1	2162-2180	-44.4	-207	-27.2	-25.1	-0.8
1695	Tando Alam 3	2186-2231	-44.7	-209	-27.8	-25.4	-1.6
1696	Sono 1	2233-2244	-46.1	-229	-29.1	-25.8	-1.0
1697	Ghotana 1	--	-47.5	-216	-30.7	-27.0	-3.2
1698	Zohra 1	1980-2023	-42.6	-212	-28.9	-26.0	-1.8

Table 6. Chemical composition of natural gas samples from selected oil producing wells of the Badin oil and gas fields area.

Lab-#	Locality/Well	C_1	C_2	C_3	i-C_4	n-C_4	i-C_5	n-C_5	N_2	0_2	CO_2
		(M o l %)									
1694	Tando Alam 1	65.3	10.8	8.0	1.5	1.7	0.5	0.3	5.6	2.7	3.6
1695	Tando Alam 3	64.1	13.5	8.4	1.7	1.9	0.6	0.4	4.1	1.1	4.1
1696	Sono 1	68.6	7.7	4.7	1.0	1.3	0.4	0.3	68.6	1.4	4.7
1697	Ghotana 1	54.7	9.3	9.5	3.1	3.2	1.1	0.8	12.6	1.7	4.0
1698	Zohra 1	15.7	1.6	1.1	0.3	0.4	0.2	0.1	62.8	16.6	1.2

Table 7. Isotope ratios of natural gas samples from gas seepages at Makran coastal area.

Lab-#	Locality	grid		d13C_1	dDC_1	d13C_2	d13C_3	d13CO_2
		^oE	^oN			(p p t)		
2410	Chandragup C-4	65.8	25.4	-59.8	-220	--	--	-0.6
2411	Goth Jumma JG-1	66.0	25.7	-63.5	-217	--	--	-0.2
2412	Aghor A-1	65.5	25.4	-49.7	-339	--	--	3.0
2413	Ormara 0-7	64.7	25.3	-38.8	-157	-23.9	-19.2	13.9
2414	Ormara 0-6	64.7	25.3	-41.2	-181	-22.5	-19.2	7.1
2415	Ormara 0-3	64.7	25.3	-43.1	-179	-22.5	-19.1	17.2
	K-1	--	--	-33.0	-143	-24.9	--	-6.4
	Karial	--	--	-51.6	-179	--	--	5.2
	Kandasol	--	--	-32.9	-147	-25.4	--	-6.8

Table 8. Chemical composition of natural gases from gas seepages at Makran coastal area.

Lab-#	Locality	C_1	C_2	C_3	i-C_4	n-C_4	i-C_5	n-C_5	N_2	O_2	CO_2	C_1/ sumC_n
		(M o l %)										
2410	ChandragupC-4	85.3	0.1	0.1	0.1	0.1	0.1	0.1	9.3	4.6	0.6	0.997
2111	Goth Jumma JG	87.6	0.1	0.1	0.1	0.1	0.1	0.1	9.4	2.3	2.3	1.000
2412	Aghor A-1	63.7	0.1	0.1	0.1	0.1	0.1	0.1	5.1	2.5	28.7	0.999
2413	Ormara 0-7	87.9	2.0	0.5	0.2	0.1	0.1	0.1	6.1	1.1	2.1	0.970
2114	Ormara 0-6	48.8	0.4	0.1	0.1	0.1	0.1	0.1	42.2	5.6	2.8	0.989
2415	Ormara 0-3	89.0	0.7	0.1	0.1	0.1	0.1	0.1	4.6	1.7	3.7	0.990
	K-1	61.7	0.5	0.0	0.0	0.0	0.0	0.0	29.3	7.1	--	0.993
	Karial	48.1	0.0	0.0	0.0	0.0	0.0	0.0	40.9	10.4	--	1.000
	Kandasol	25.7	0.2	0.0	0.0	0.0	0.0	0.0	58.6	14.8	--	0.993

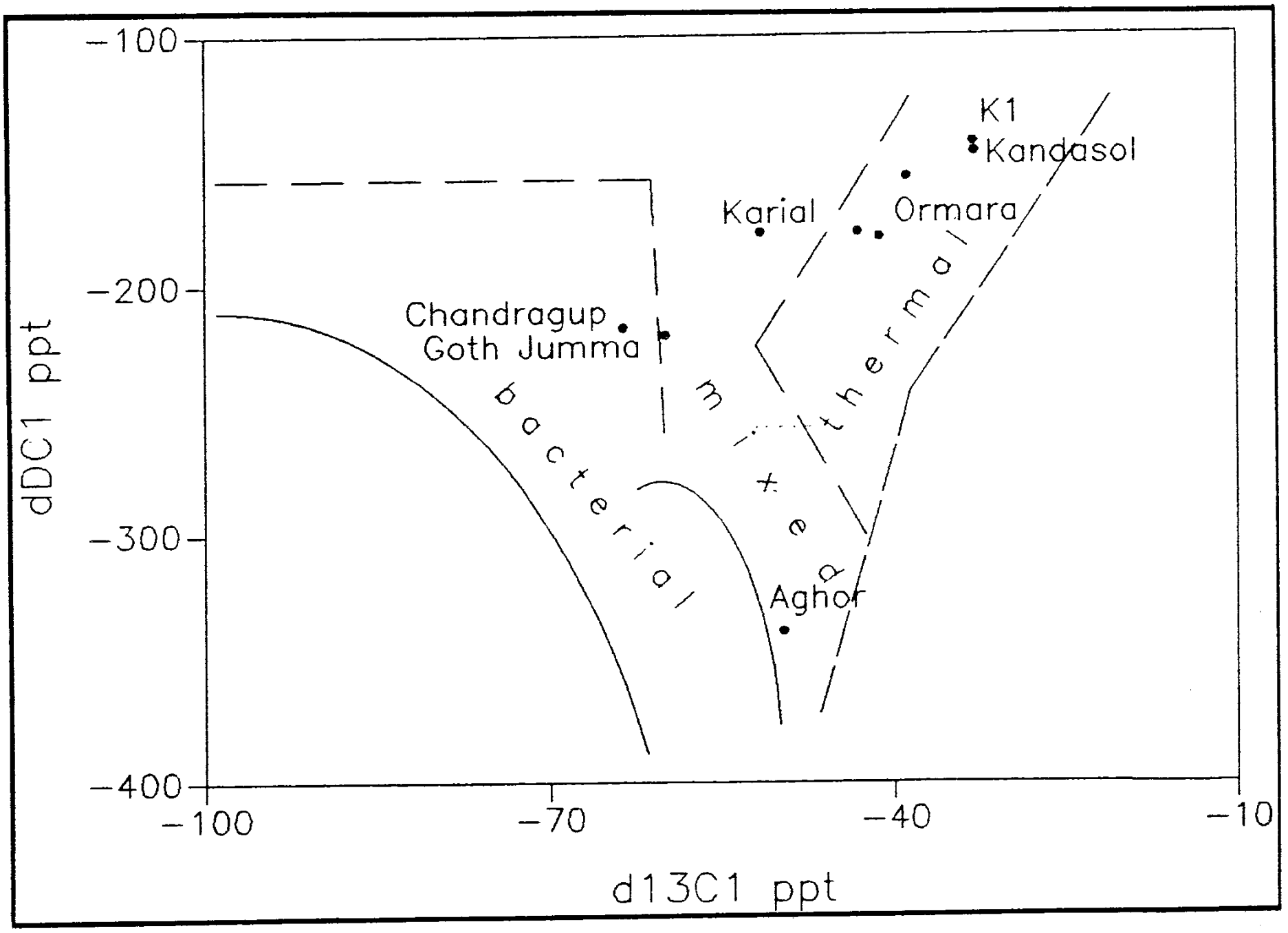

Figure 7— Natural gas samples from seepages of Makran coastal area. Isotope ratios given in part per thousand (ppt) relative to PDB and SMOW standards.

without ambiguity due to the possibility that the original composition might have been changed because of oxidation processes and possible contamination by atmospheric gases.

Nevertheless thermogenic gases of a maturation level above 2 % vitrinite reflectance seem to be present in samples from Ormara, K1 and Kandasol. Bacterial derived methane appear to be present in samples from Aghor on one side and Chandragup and Goth Jumma on the other.

CONCLUSION

The chemical and isotope analysis indicate that:

1) Gas samples from producing wells of Potwar basin are of thermogenic origin and exhibit typical properties of associated gas.

2) The gas produced from Kandhkot, Sui and Pirkoh are unambiguously of thermogenic origin. In Mari gas field, isotopically there seem to be two groups of methane. The samples from the western, central and northern part of the fields are homogeneous and are classified as thermogenic gases containing a small admixture of bacterial derived methane only. Methane from the carbon dioxide rich zone is isotopically lighter and possibly contains more bacterial methane than the other samples.

3) Though chemical and isotope compositions of the seepage gases from Makran area indicate mixed origin but it can not be interpreted unambiguously due to oxidation processes and contamination by atmospheric gases.

4) Gases samples from producing wells of Kirthar area contained a significant amount of high molecular hydrocarbons and can be classified as wet typical of associated gases from oil fields.

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