An Overview of the Distribution of Inert Gases in Deeper Reservoirs of the Sulaiman Fold Belt, Pakistan*

Adeel Nazeer[1], Tabinda Tariq[3], Ghulam Murtaza[3], S. Habib Shah[2], and Aisha Danyal[3]

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[1]Exploration Department, Pakistan Petroleum Limited (PPL), Islamabad, Pakistan (A_nazeer@ppl.com.pk)
[2]Exploration Department, Pakistan Petroleum Limited (PPL), Islamabad, Pakistan (S_Habib@ppl.com.pk)
[3]Exploration Department, Pakistan Petroleum Limited (PPL), Islamabad, Pakistan

Abstract

Natural gas in a number of gas fields in Pakistan is associated with high percentage of inert gases. Inert gases are considered to reduce the BTU value of sweet gases. Wells of Jandran and Kandra are examples where production of inert gases (mainly CO_2) is a major problem in development of the fields. High inert gases also give clues to short or long distance migration. Previous workers presented a number of factors responsible for distribution of inert gases (CO_2 and N_2) in various basins of Pakistan; nevertheless, the issue related to the source and variable amount of inert gases is still unresolved.

Attempts were made to analyze the varying composition of inert gases along the deep seated basement faults in the Eastern Sulaiman Fold Belt but no specific relation could be established. This was not in favor of the prevailing notion of previous workers that inert gases are associated with deep seated faults. In the same way, geothermal gradient zones were identified and distribution of inert gases in these zones was studied but again no well established relation could be tracked.

However, varying composition of inert gases in two different formations of one of the wells of Jandran established important geological factors. The CO_2 in deeper Chiltan (86%) and shallower Mughalkot (3%) in Jandran indicates that the source of inert gases and hydrocarbons is not the same. Similarly, variation in amount of inert gases in the Chiltan Limestone of the Rodho Structure and Afiband reveals the generation of in-situ inert gases because both wells were drilled on the same anticlinorium, sharing the same geology and possibly the same source rock. Probably post accumulation changes play an important role in generation of in-situ inert gases in varying concentrations.

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Author: Adeel Nazeer

Pakistan Petroleum Limited

Co-authors: Tabinda Tariq, Ghulam Murtaza, S. Habib Shah and Aisha Danyal

Pakistan Petroleum Limited

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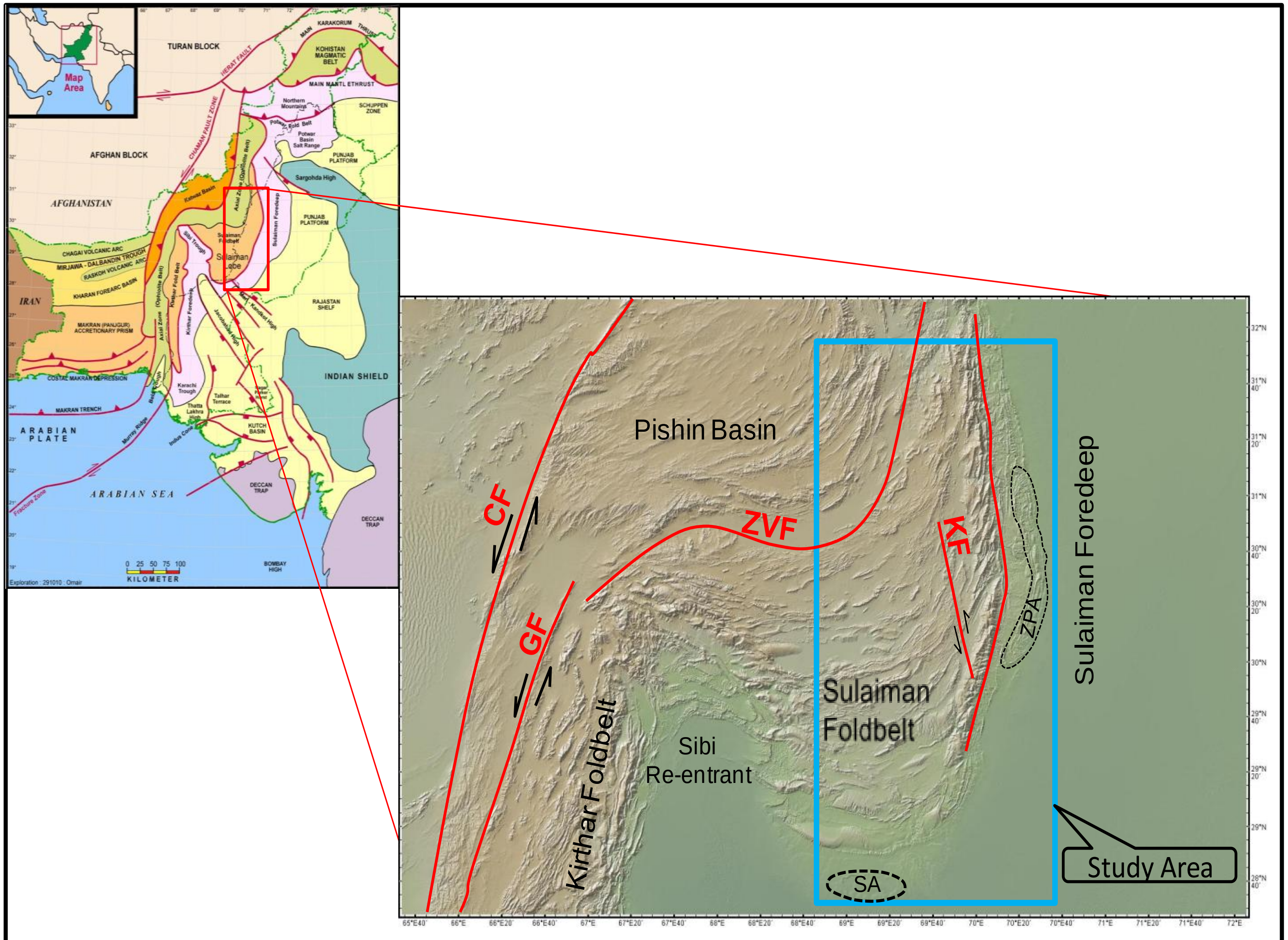
INTRODUCTION

The objectives of this presentation is to discuss the distribution of Inert gases in the Sulaiman Fold Belt on the basis of various factors which are analyzed in this paper.

Present study suggests that in-situ generation of inert gasses by various physio-chemical process as most viable reason for presence of inert gases because of various geological factors which include;

- Uneven distribution of inert gases with reference to geothermal gradient
- Major variation in concentration of inert gases along deep seated faults
- Decarbonation of CaCO3 to generate CO_2 in the lack of high temperature

STUDY AREA



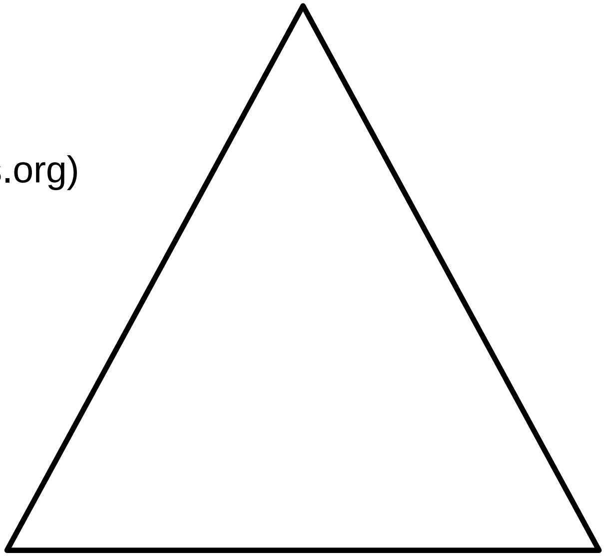
CF=Chaman Fault, **GF=**Ghazaband Fault, **KF=**Kingri Fault, **ZVF=**Zhob Valley Fault, **SA**=Sui Anticline, **ZPA**=Zindapir Anticlinorium

Map Showing major tectonic elements of Sulaiman Fold belt and location of study area.

COMPOSITION & FORMATION OF NATURAL GASES

Methane	CH_4	70-90%
Ethane	C_2H_6	0-20%
Propane	C_3H_8	
Butane	C_4H_{10}	
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.2%
Nitrogen	N_2	0-5%
Hydrogen sulphide	H_2S	0-5%
Rare gases	A, He, Ne	trace

Typical Composition of Natural Gas (Source: www.naturalgas.org)



PREVIOUS STUDIES

1) Battani et al. (1998) negated the origin of inert gasses from igneous source on the basis of ^3He which is absent in gas samples. But decarbonation of limestone was largely supported by later worker with out emphasizing the temperature required for calcination and its availability in surrounding area.

2) Carbon dioxide in Kandhkot Field is mainly derived from thermal decomposition of carbonates (Chiltan) on the basis of carbon isotopic data (Saqi et.al., 2000).

3) Carbonate decarbonation is responsible for the generation of CO_2, possibly from Chiltan Formation outside the Mari Field area where this formation has experienced temperature in excess of 300^oC. A model is suggested in which hot basement (Shallow Intrusions) and deep-seated faults (i.e., high geothermal gradients) fed the CO2 along deep seated faults (Asif et.al., 2003).

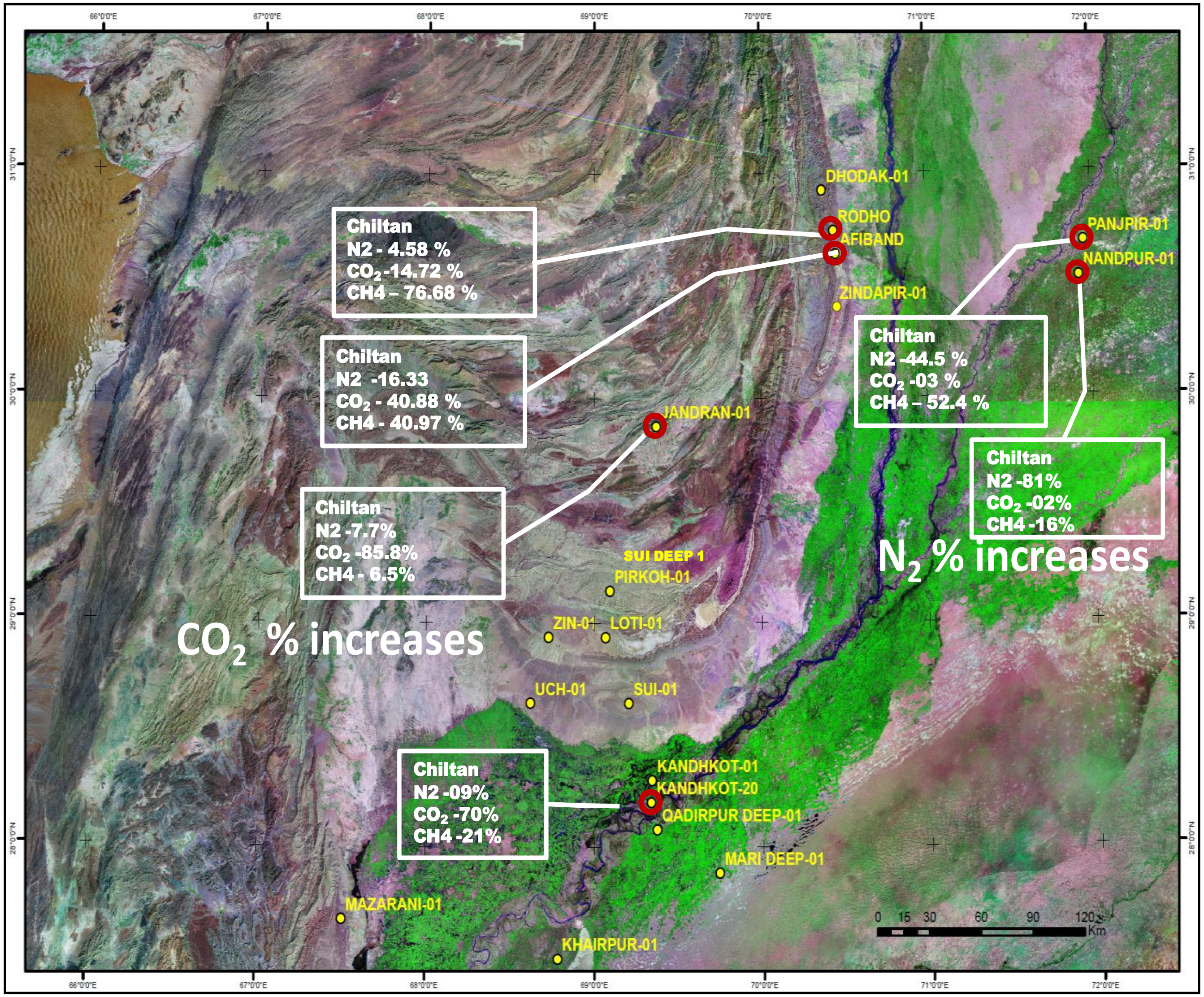
4) It is also considered that the size of molecules for transportation along deep seated faults and considered the CO2 with tendency to lag behind due to larger diameter during process of diffusion, with more possibilities to accommodated in deeper reservoir (Asif et.al., 2003).

5) Deep Seated faults are considered by previous workers as main path for transportation of inert gases i.e. CO_2 and N_2 from deeper to shallower horizons.

DISTRIBUTION OF INERT GASES IN SULAIMAN FOLD BELT & PUNJAB PLATFORM

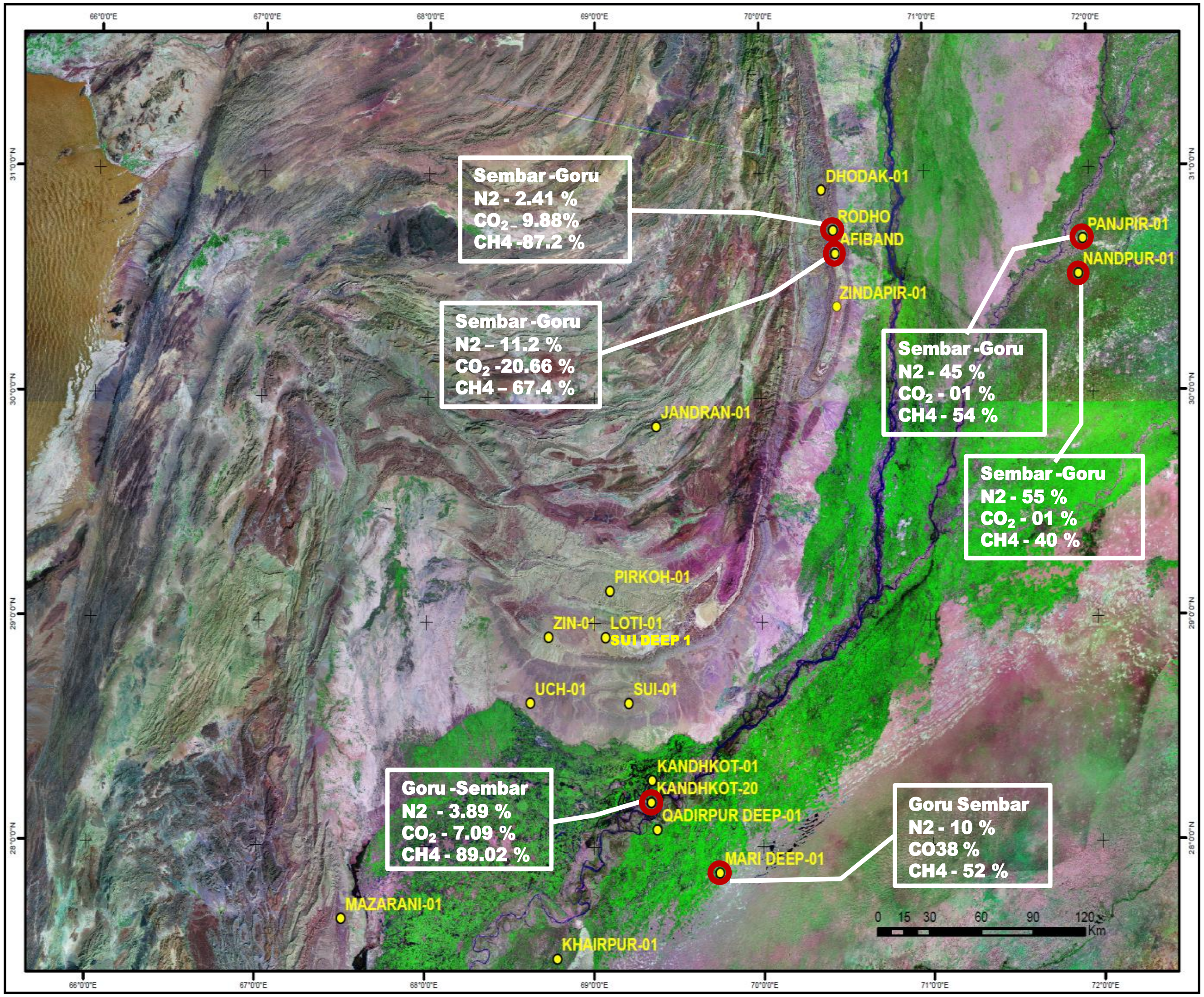
Well	Formation	N_2 (%)	CO_2 (%)	CH_4 (%)
Dhodak 1	Pab/Ranikot	4.51	1.39	**94.1**
Rodho Structure	Sembar/Goru	2.41	9.81	87.2
	Chiltan	4.58	**14.72**	**76.68**
Afiband Structure	Sembar/Goru	11.2	20.66	61.53
	Chiltan	16.33	**40.88**	**40.97**
Jandran 1	Mughalkot	3.8	3	93.2
	Chiltan	7.7	**85.8**	6.5
Zin 1	SML	8.5	44.7	46.8
Uch 1	SML	25.2	46.2	28.6
Pirkoh 1	Pab/Ranikot	8.01	6.76	85.23
Sui Deep 1	Sembar/Goru	3.89	7.09	89.02
Kandhkot-20	Chiltan	9	**70**	21
Mari Deep-1	Goru	10	38	52
Nandpur-1	Sembar/Goru	55	01	40
	Chiltan	81	02	16
Panjpir-1	Sembar/Goru	45	1	54
	Chiltan	44.5	03	52.4

DISTRIBUTION OF INERT GASES IN SULAIMAN FOLD BELT & PUNJAB PLATFORM



Gas Composition Variation in Chiltan Formation in the Sulaiman Fold Belt

DISTRIBUTION OF INERT GASES IN SULAIMAN FOLD BELT & PUNJAB PLATFORM



Gas Composition Variation in Sembar /Goru in the Sulaiman Fold Belt

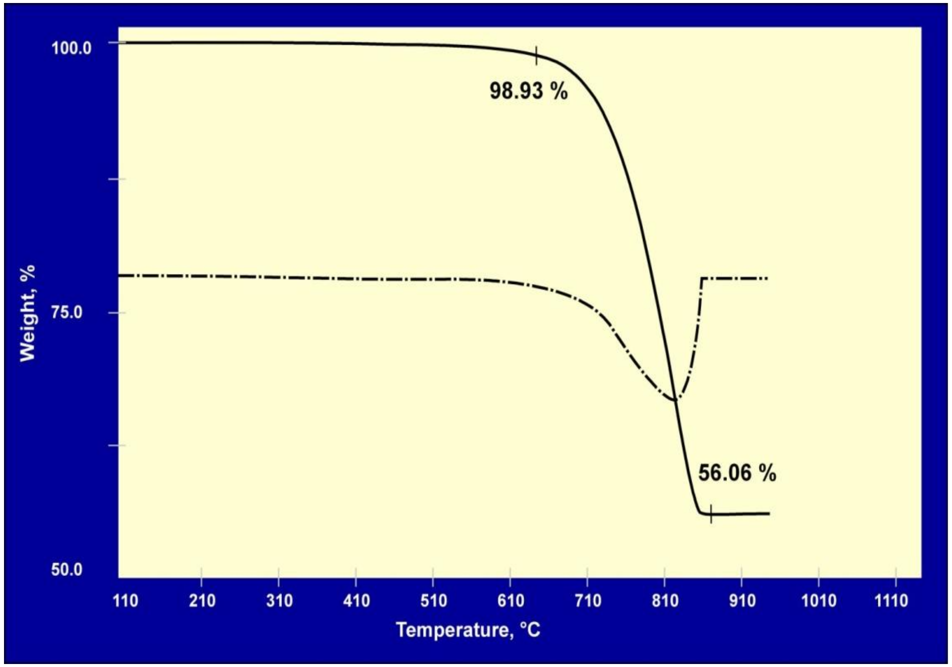
DECARBONATION OF CALCIUM CARBONATE

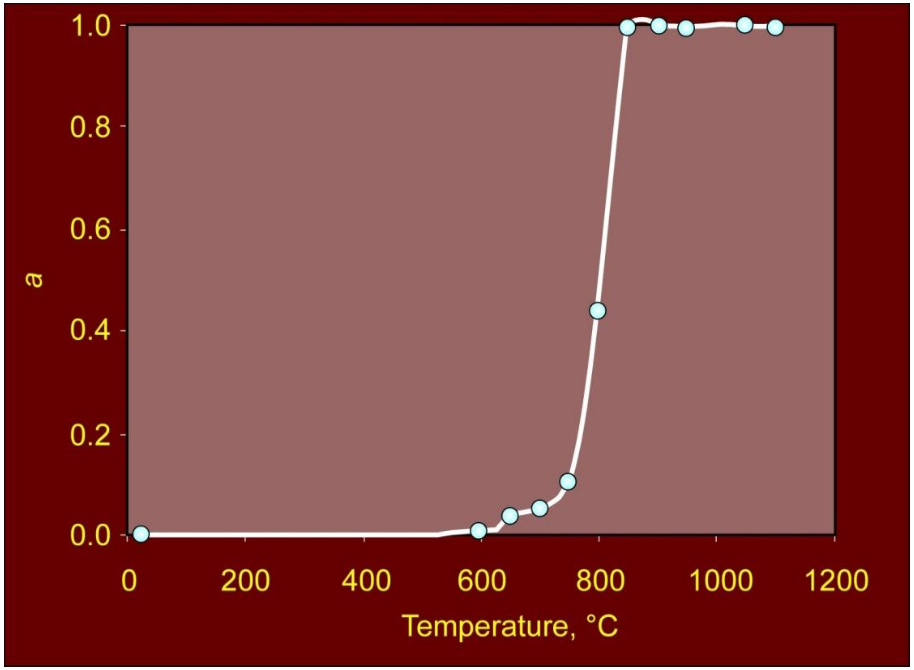
Early Studies about the Source of Co_2 in Study Area

- Thermal Decarbonation of $CaCo_3$
- Role of Pressure for Thermal Decarbonation of $CaCo_3$
- Role of Geothermal Gradient

Decomposition of $CaCO_3$ is endothermic reaction which required tremendous amount of energy for the complete decomposition of $CaCO_3$. Moreover , thermal decomposition is dependent up upon the composition, nature of impurities, texture of grains, size of grains, and type of environment.

DECARBONATION OF CALCIUM CARBONATE

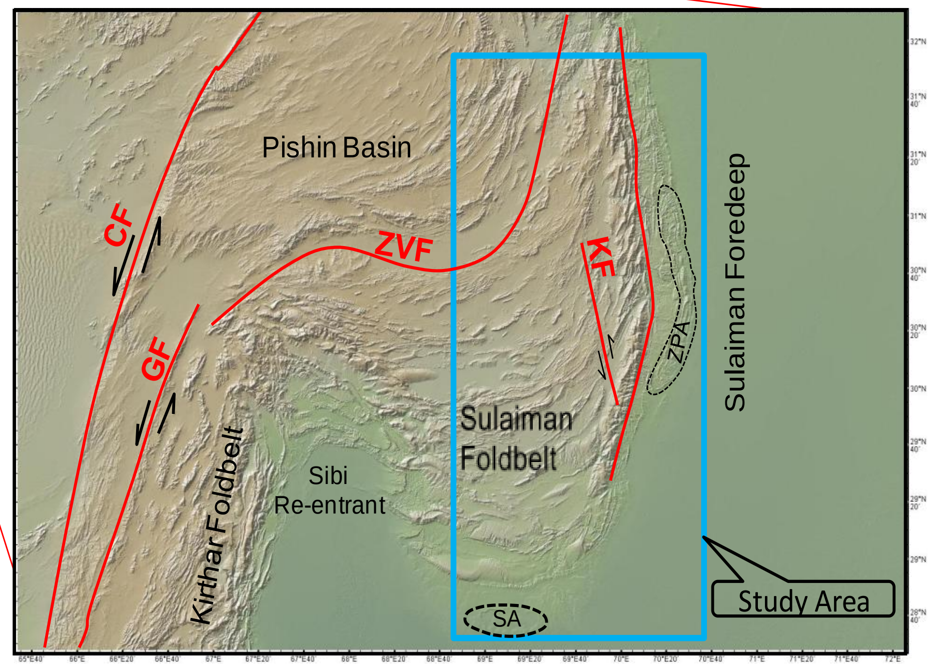




Thermal Decomposition of $CaCO_3$ in thermo gravimeter (Halikia et. al, 2002) shows that high temperature is required for the process of thermal decomposition and it could not be possible without process of metamorphism and igneous activity. As igneous activity is not related with study area, therefore decarbonation of Limestone is not possible in study area.

Rodriguez-Navarro et.al, 2009 observed rate of conversion α vs. *T*. Conversion started at *T* ~ 600 °C, and was completed at 850 °C; i.e., when a loss of 44 wt% cor-responding to the stoichiometric CO_2 amount in CaCO3 was achieved. This temperature ranges in study area is not possible in study area because igneous activity is not associated with study area.

DECARBONATION OF CALCIUM CARBONATE



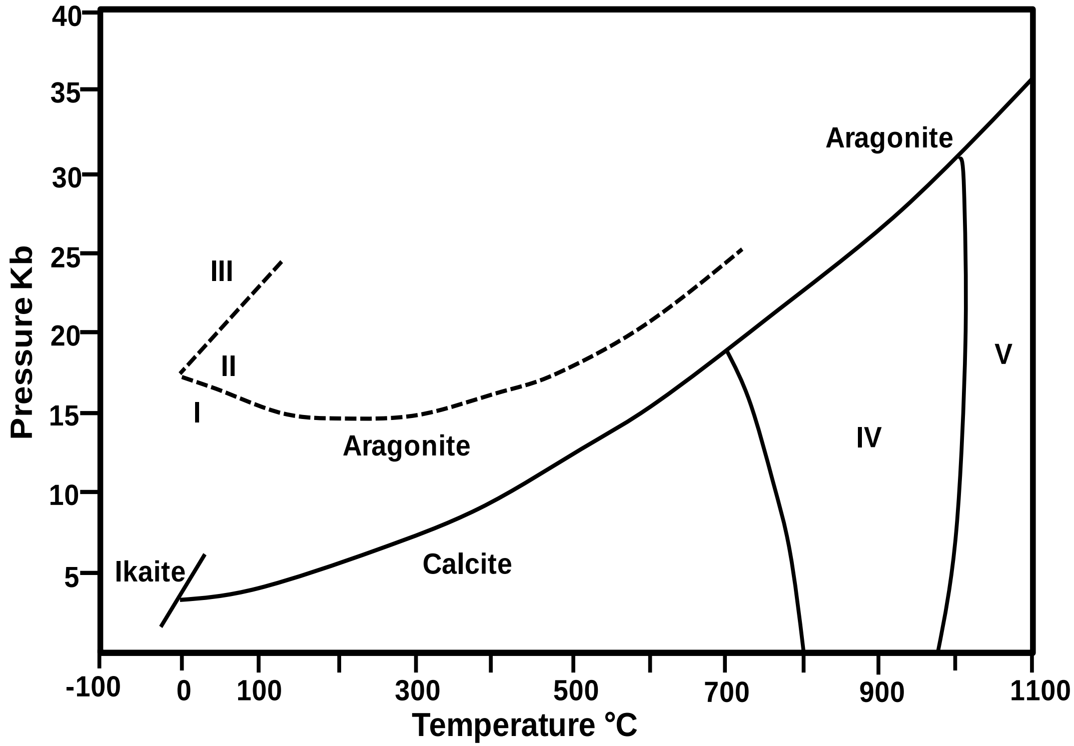
CF=Chaman Fault, **GF**=Ghazaband Fault, **KF**=Kingri Fault, **ZVF**=Zhob Valley Fault, **SA**=Sui Anticline, **ZPA**=Zindapir Anticlinorium

1) Youngest igneous activity is associated with Indian Plate boundary along Ghazaband Fault and Ornach Nal Fault in the form of Ophiolitic Melange and far away from study area. While folding is younger than Ophiolitic Melange Zone. It is not possible that inert gases which are released from magma, charged the CO_2 in study area. Existing seismic data does not support the possible pathway which connect Ophiolite Melange with study area. Moreover, there is no evidence of intrusion in Neogene in the study area and it's surrounding area which is necessary condition to attain the desired temperature to trigger the process of decarbonation.

2) Battani et. al (1978) analyzed 25 samples of gas from Pakistan to understand the presence of extremely variable amounts of carbon dioxide and nitrogen, reaching values of 69% and 23% respectively. Carbon isotope ratios and noble gas concentrations were measured on these samples. The authors suggest, based on the absence of ^{3}He, that there appears to be no trace of mantle fluxes. Consequently, the authors had to contemplate another origin for both nitrogen and carbon dioxide, other than igneous activity.

3) Therefore, process of thermal decomposition of carbonates backlash in study area and its surroundings to consider it as origin of source rock in the absence of intrusion in Neogene and especially in the absence of ^{3}He isotopes on available data.

ROLE OF PRESSURE FOR THERMAL DECARBONATION OF CaCO3



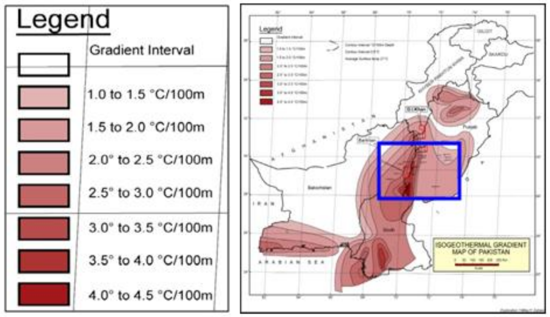
Phase relations [after Marland (1975) and Carlson (1980)] of the $CaC0_3$ system is shown in diagram, where 1-V calcite polymorphs are metastable. At high pressure, various polymorphs of calcite are produced with change in structural orientation. But calcite remains calcite in low grade metamorphism (green schist facies) with out production of CO_2. This shows that production of CO_2 is not possible in study area because contact metamorphism and magmatic chamber is not available in study area to decarbonate the limestone.

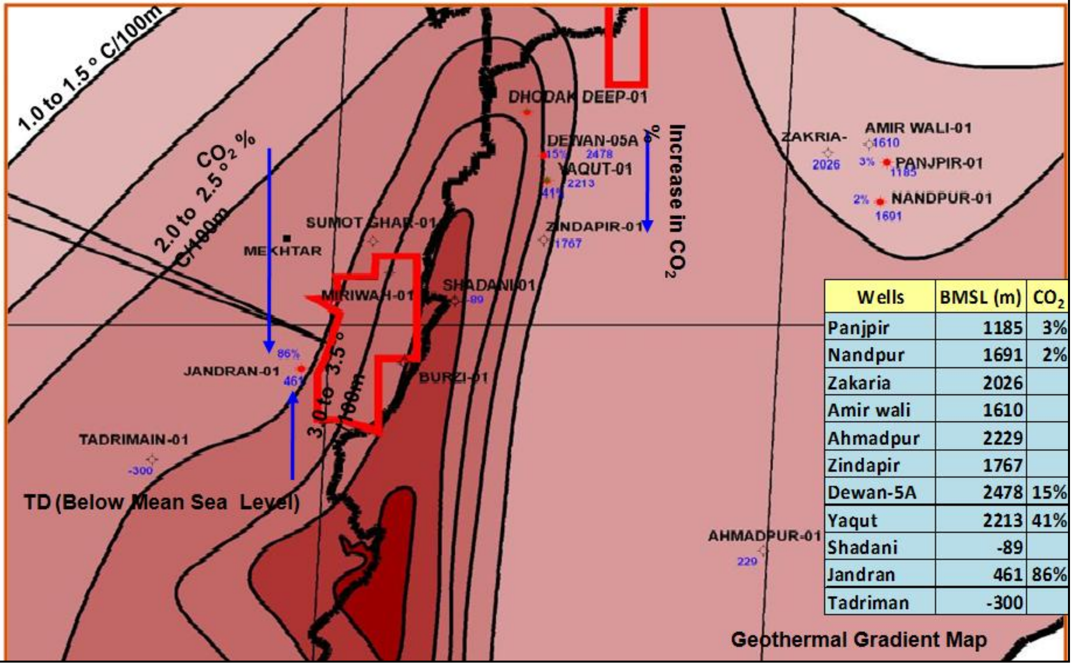
ROLE OF GEOTHERMAL GRADIENT

3 geothermal gradient zones identified

- **Punjab Platform with gradient 1-2° C /100 m and < 5 % CO_2**
- **Safed Koh EL with gradient 2-2.5° C / 100 m and < 40 % CO_2**
- **Jandran EL with gradient 2-2.5° C / 100 m and > 80 % CO_2**

No precise geological reason can be offered for such uneven distribution





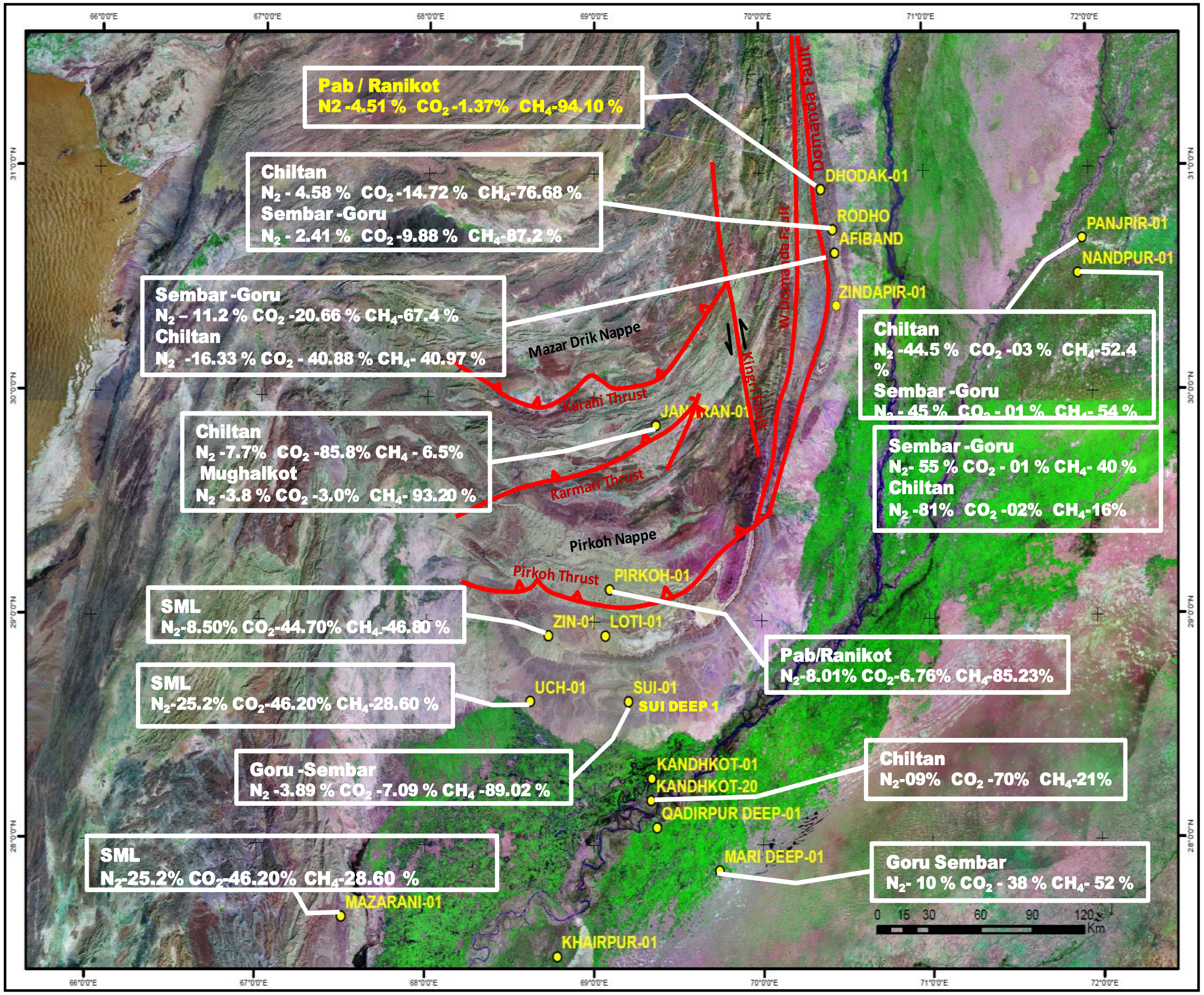
Wells	BMSL (m)	CO_2
Panjpir	1185	3%
Nandpur	1691	2%
Zakaria	2026	
Amir wali	1610	
Ahmadpur	2229	
Zindapir	1767	
Dewan-5A	2478	15%
Yaqut	2213	41%
Shadani	-89	
Jandran	461	86%
Tadriman	-300	

There is uneven relationship for the distribution of CO_2 along Geothermal Gradient. Basically maturity depends upon geothermal gradient but thermal decarbonation of carbonates in study area is not responsible for the generation of CO_2. A large burial depth is required to generated from calcareous rocks.

TRANSPORTATION OF INERT GASES ALONG DEEP SEATED FAULTS

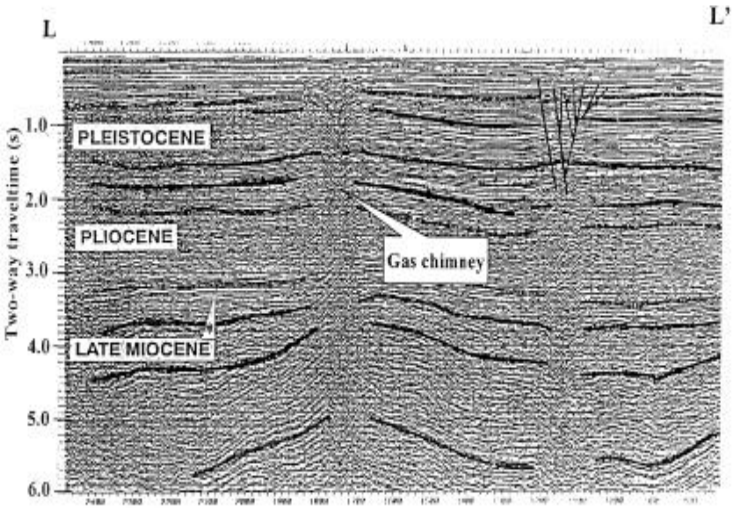
- Faults are responsible for the transport of natural gases. Normally geometry of faults plays important role. If fault is deep seated and exist as lineation without major truncation, transportation should be even and distribute in multiple reservoirs with considerable amount.
- Amount of CO_2 is higher in carbonates only, even 85.8 % in Chiltan of Jandran, 44.7% in SML (Eocene) of Zin Field, 46.2 % in SML (Eocene) of Uch Field and therefore lithology of carbonate has certain relation with production of CO2 but not only related to transport of inert gases along deep seated faults.

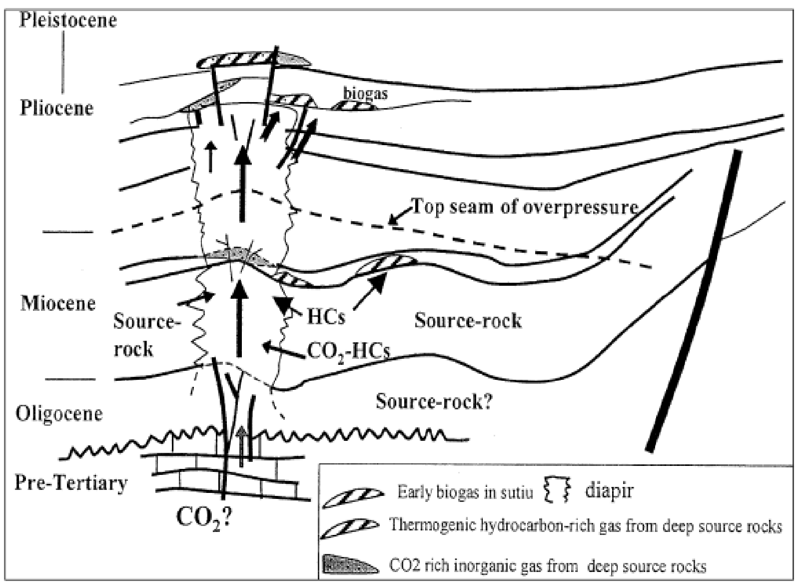
TRANSPORTATION OF INERT GASES ALONG DEEP SEATED FAULTS

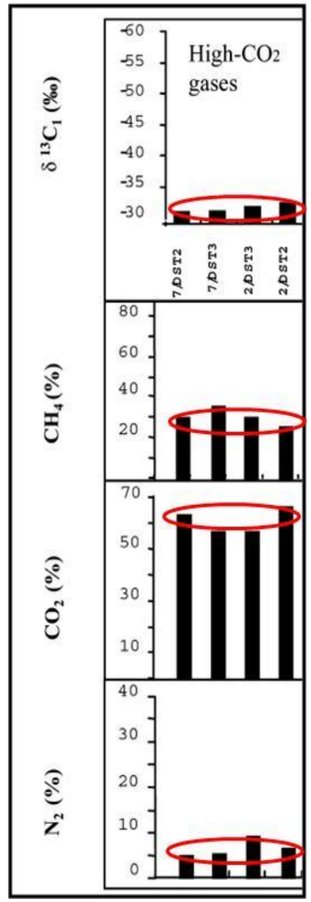


Gas composition variation along major faults in the Sulaiman Fold Belt. Rodho and Afiband varies in composition not as different reservoirs in single well but also varies in same reservoir of two different parts of Zindapir Anticlinorium, sharing similar structural style along deep seated fault.

DF1-1 GAS FIELD, SOUTH CHINA SEA (CASE STUDY)





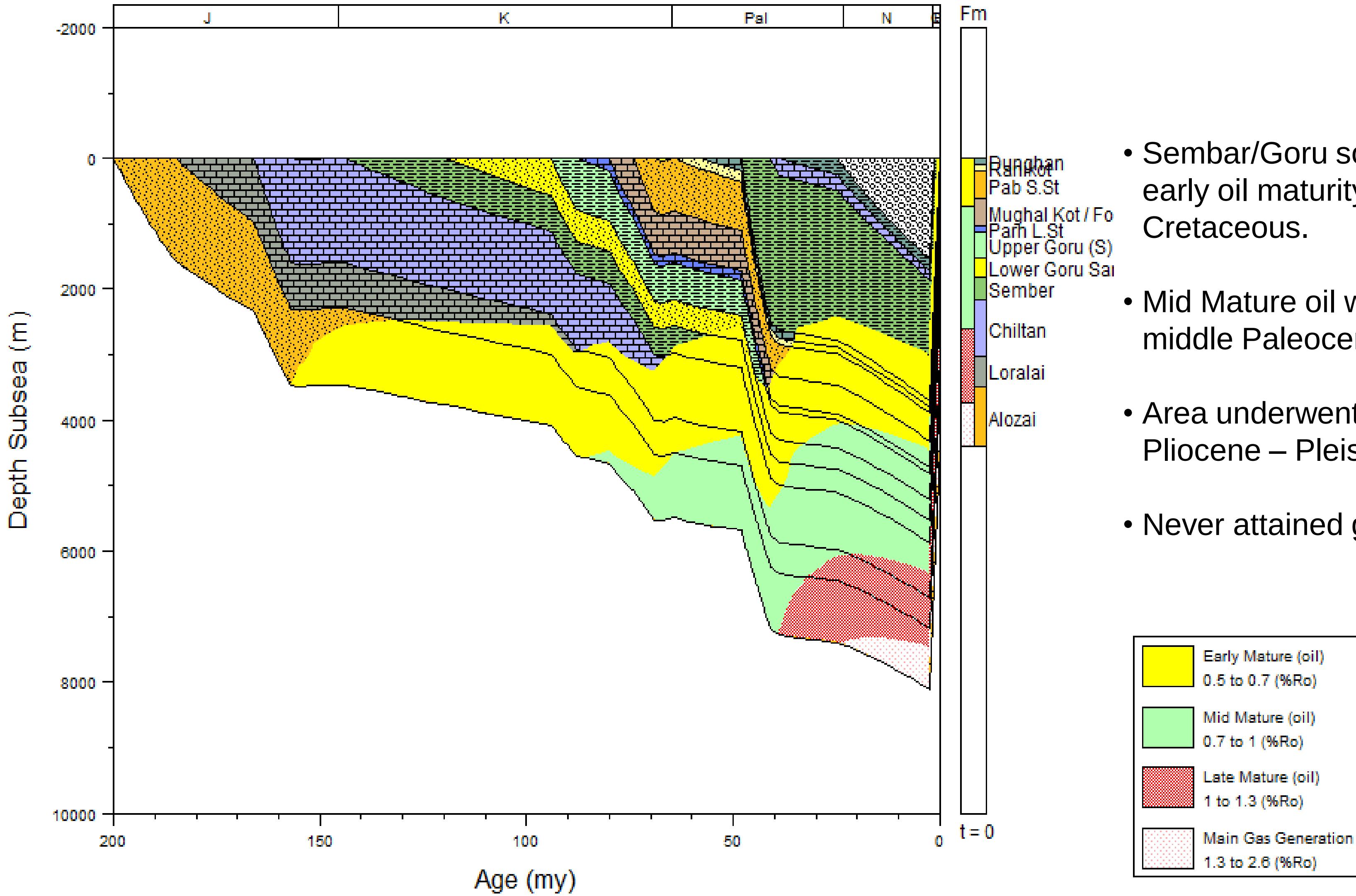


The Dongfang1-1 (DF1-1) gas field was discovered in 1992. It is located in the northern part of the Yinggehai Basin, South China Sea with various composition of gas. The biogenic gas generation from shallowly-buried Pliocene source rocks. In 1st episode. The second and third episodes are followed by the migration of thermogenic gases from deep Miocene source rocks containing type III.

Hydrocarbon rich CO_2 were generated from thermal decomposition of calcareous shales with a burial depth of over 6000m, and pre-Tertiary carbonates in the basin in fourth zone. But distribution of Hyrocarbon rich CO_2 is considerable in multiple reservoirs because flow of gas along deep seated fault is uniform. Palaeotemperature gradients is 45oC/km which is much higher than Palaeotemperature of study area. Moreover Basin evolution includes two rift episodes: an earlier Eocene–Oligocene rift period, and a later Neogene to Quaternary post-rift.

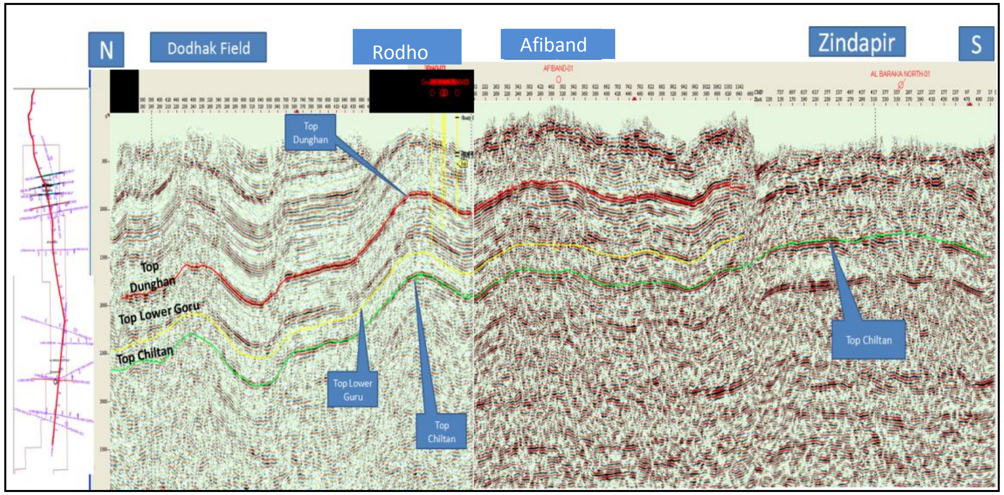
Ref : B. J., Huang, 2002

AGE OF GENERATION/ EXPULSION OF HC's

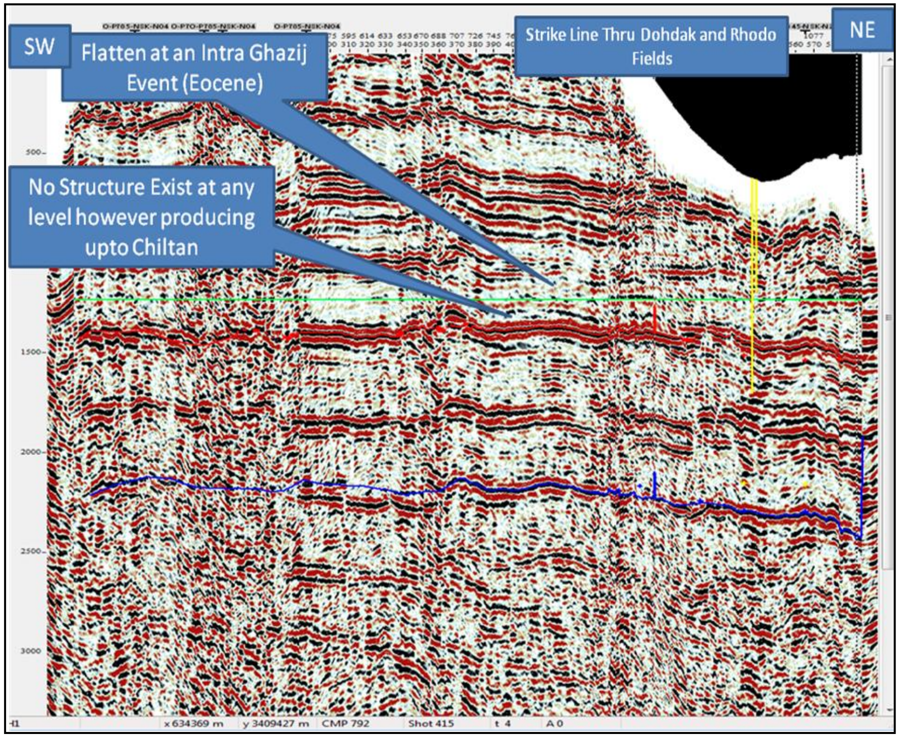


- Sembar/Goru source attained early oil maturity during Late Cretaceous.
- Mid Mature oil window in the middle Paleocene.
- Area underwent uplift during Pliocene – Pleistocene.
- Never attained gas maturity

AGE OF STRUCTURATION



Interpreted seismic line 785-SK-85

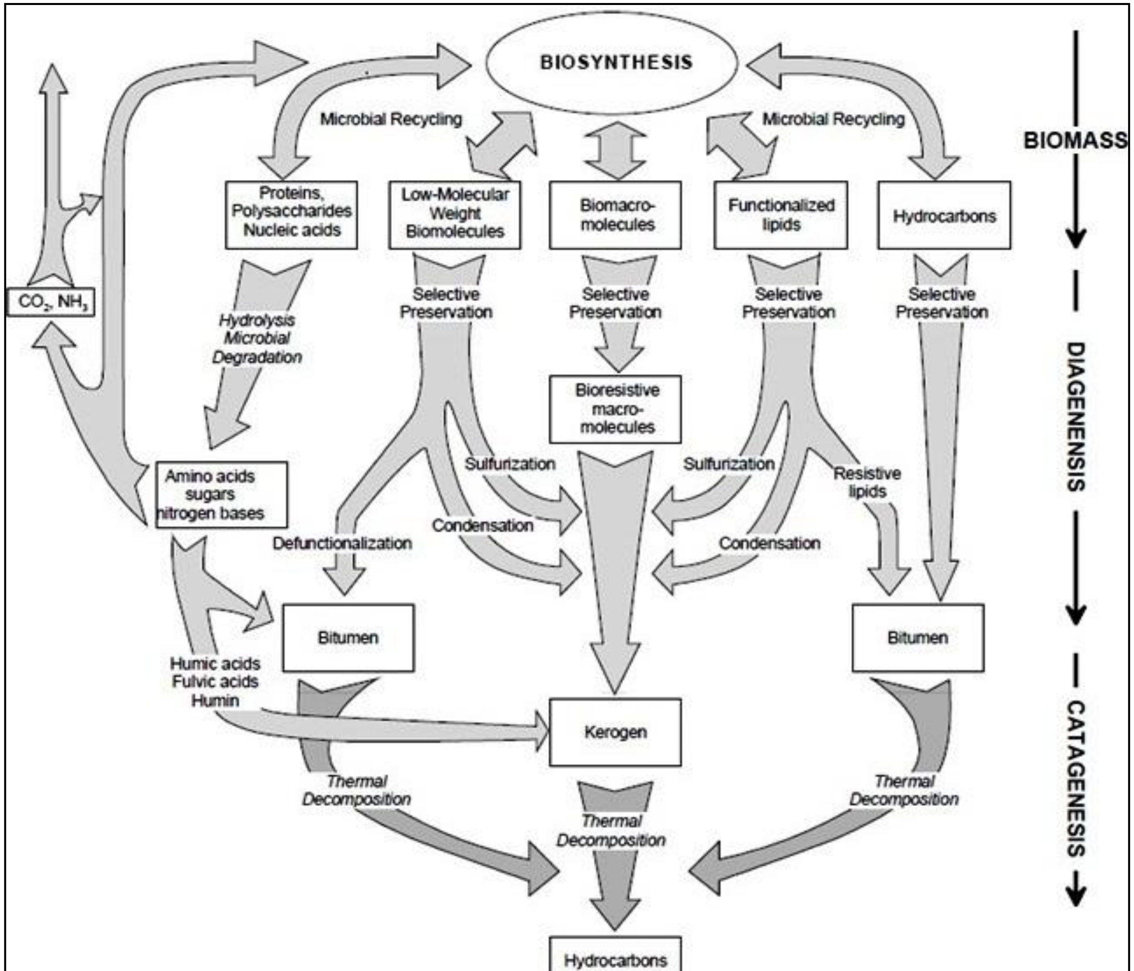


Interpreted seismic line 785-SK-85 , which is flattened over Ghazij. It shows that there was no structure at the time of Middle Eocene. Structures were under filled by migrated hydrocarbons in Neogene

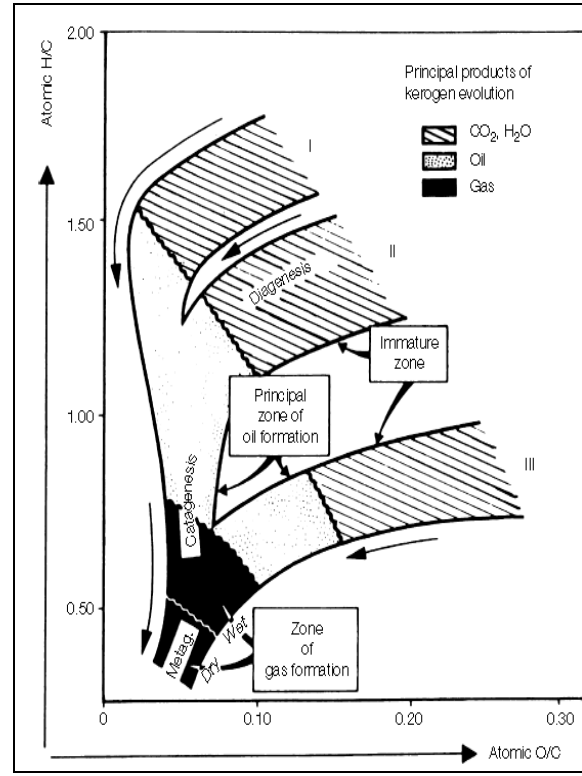
GENERATION OF INERT GASES FROM SEDIMENATRY ORIGIN

Inert gases formed during the process of diagenesis, catagenesis and metagenesis, depends upon the availability of desired paleo temperature during burial depth.

FORMATION OF KEROGEN AND GENERATION OF INERTS (CO_2)

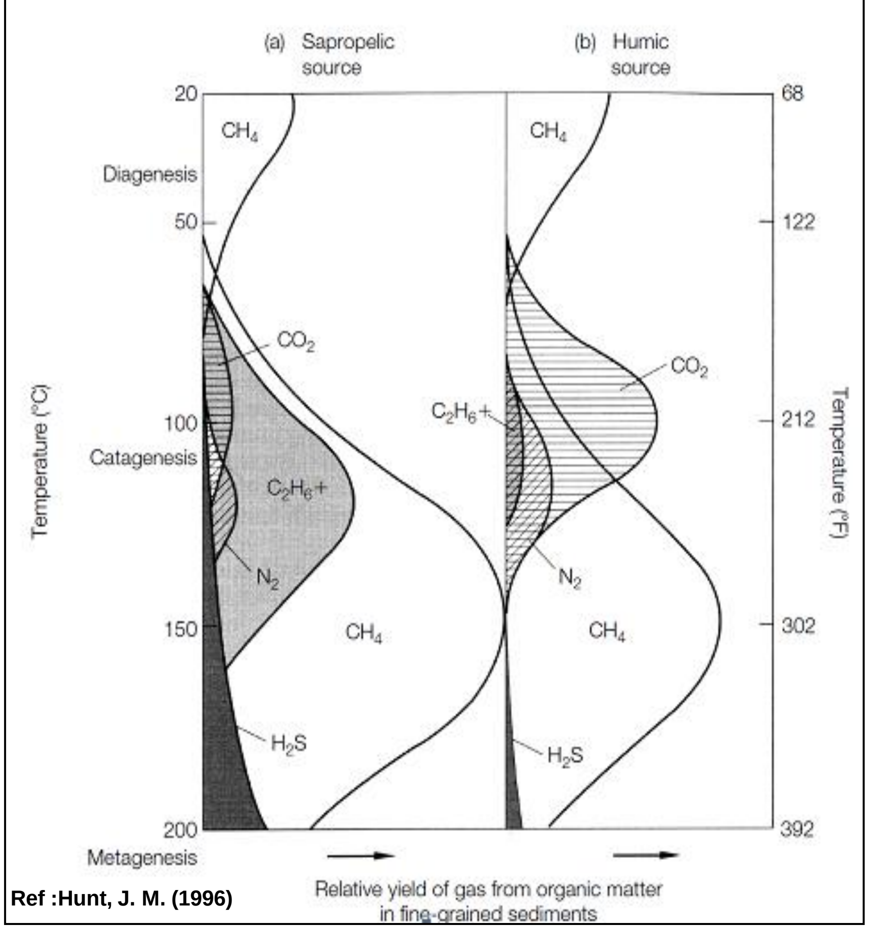


Ref: Clifford C. Walters (2006



Process of diagenesis formed kerogen from the organic content present in sediments. During the formation of Kerogen, inert gases (CO_2) will produced. Probably some amount of inert was produced at the time of diagenesis in study area. Kerogen Type III is common type in Sulaiman Indus Basin.

GENERATION OF INERTS (CO_2-N_2) DURING CATGENESIS



Ref :Hunt, J. M. (1996)

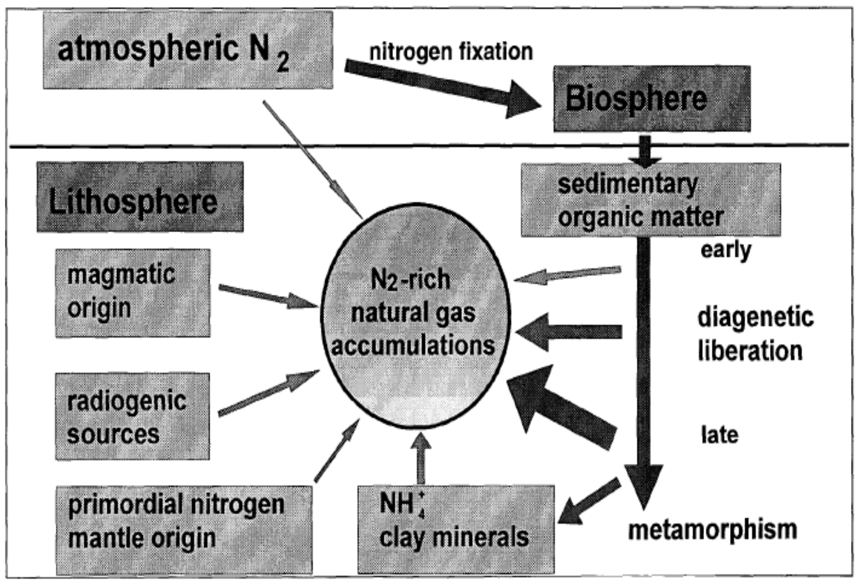
Inert gasses (CO_2-N_2) also produced during the process of Catagenesis. Kerogen Type III generate more inerts because they consist of oxidized woody carbohydrate which is smaller in molecular size and easily break down into furthar smaller size.

FORMATION OF KEROGEN AND GENERATION OF INERTS (N_2)

Sample	Humic coal		Sapropelic coal		Anthracite		Torbanite	
% R_r	0.76		0.79		2.30		0.48	
Gas	kg/t TOC	Std. m^3/t TOC	kg/t TOC	Std. m^3/t TOC	kg/t TOC	Std. m^3/t TOC	kg/t TOC	Std. m^3/t TOC
CH_4	38.04	56.21	32.73	48.37	14.4	21.28	21.6	31.92
N_2	14.85	12.54	8.54	7.21	4.91	4.15	4.88	4.12

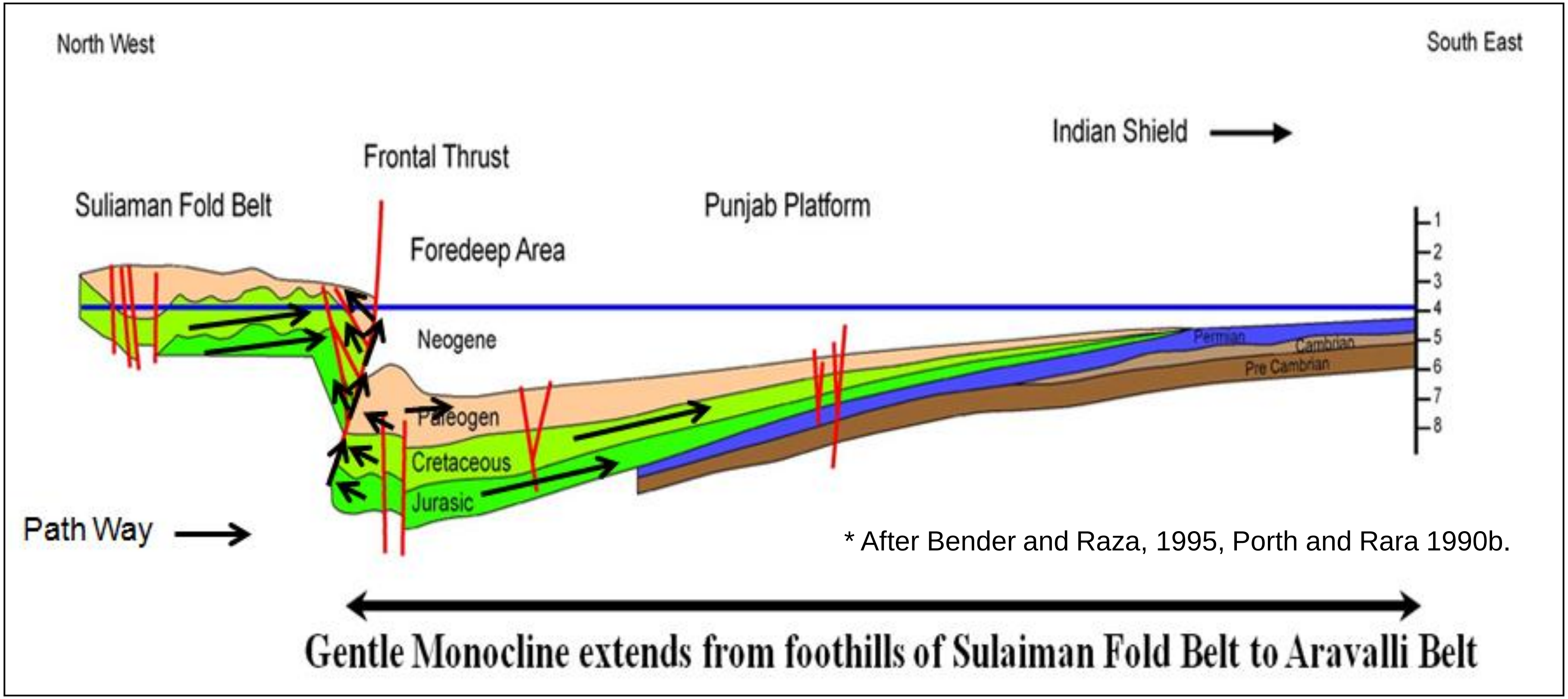
1 Std. m^3/t = 1 cm^3/g.

Quantities of methane and nitrogen generated during non-isothermal pyrolysis experiments up to 1000°C (heating rate 0.1 K/min)



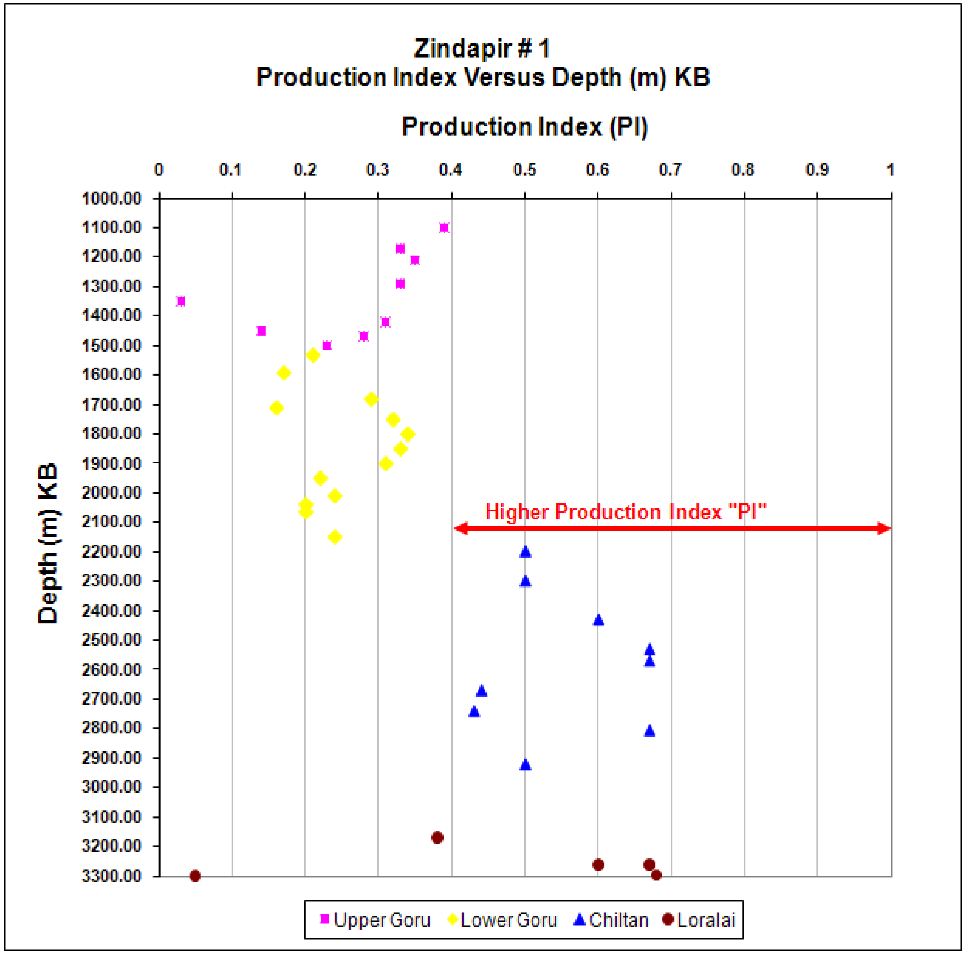
Krooss B.M et.al concluded the even relationship of nitrogen in North Germany and concluded Kerogen Type III and coal as main source for the production of Methane and N_2, especially for the production of N_2 in Nandpur-1 and Panjpir-1 because shallow shelf exist in Punjab Platform. Kerogen Type III is also present in Chiltan Limestone of Ahmedpur-1 and Zindapir-1 wells.

TRANSPORTATION OF INERT GASES ALONG CARRIER BEDS



Carrier beds play a vital role for heterogeneous composition of hydrocarbons, it may accommodate generated hydrocarbons of various levels of maturity of same source rock, that may be from varying kitchen area. It may be from varying source rock, at varying geological times. However, this mechanism requires further research.

DIFFERENT SOURCE ROCKS

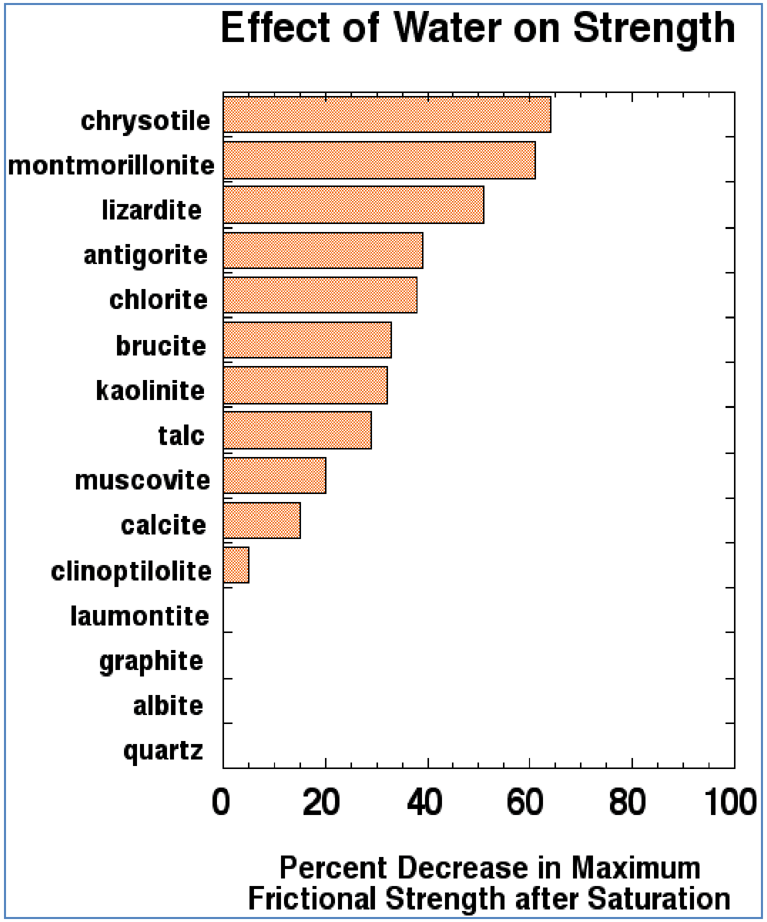


Production Index (S1+S2/S1) differ in Chiltan and Goru in Zindapir-1, which simply shows that hydrocarbons generated in two reservoir at variable rate and variable temperature during pyrolysis. PI is higher in Chiltan Limestone. Probably different source rock belong to varying origin, may belong to varying kitchens, plays important role in generation of Hydrocarbons in Zindapir Anticlinorium.

ROLE OF WATER & CLAY MINERALS

Siskin and Katritzky (1995) proved that (a) presence of clay minerals as catalyst (in the presence of water soluble products), b) effect of salt present in water and c) temperature of burial for catagenesis process as important factors for the depolymerization of kerogen and considered 25°C as minimum temperature for the beginning of depolymerization. This shows that generation of some content of Co_2 can also be considered at low temperature, especially at the beginning of digenesis in study area.

SOLUBILITY OF CALCITE



a) C. A Marrow (2000) proved that calcite has a tendency like other fault gouge minerals to take on adsorbed water may strongly influence their frictional strength.

b) It means that calcite adsorbed the water to some extents, formed Calcium Bicarbonate which is not stable solution and precipitate the calcite with varying geochemical process.

c) Perach Nuriel (2012) found that faulting and striation in limestone involve calcite precipitation during the various stages of the seismic cycle of Dead Sea fault zone in northern Israel.

d) There adsorption and absorption of calcite and its re-precipitation play vital role in production of CO2

CONCLUSION

- Previous worker considered thermal decomposition of calcite which requires very high temperature. As igneous activity is not associated with study area, therefore, major contribution of CO_2 due to thermal decomposition is not possible in study area.
- Present study shows that empirical values of inert gases (percentage) has uneven distribution along geothermal gradients & major faults. Hence, this major contribution of inerts resulted from post-accumulation changes
- Present study shows that age of generation, expulsion and accumulation is post Eocene. While formation of structuration is also started at the same time and this structuration became trap for the accumulation of hydrocarbons
- Probably heterogeneous flow of hydrocarbon plays along carrier beds plays vital role for varying composition of inert gasses but may require further investigation.
- Present studies shows that composition of existing hydrocarbons consist of hydrocarbons of different levels of maturity. Therefore early matured Kerogens have more capacity to generate CO2
- Probably various source rock (especially older than Sembar) also contributed in production of CO2
- Probably gouge containing calcite mineral produced at the activation of fault was dissolved by water and formed bicarbonate. As geochemical condition changes, CO2 was released with precipitation of calcite. but process may require further investigation.

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