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Accurate source rock evaluation as the kerogen chemical structure in Paleozoic sediments from Zagros Thrust Belt of Iran

1. Introduction

The Zagros structural zone extends NW-SE across Iran, south of the Main Zagros Thrust (Figure 1). Within the Zagros Basin, this zone is divided into the Zagros Fold Belt within the southern part of zone, and the Zagros Thrust Belt within the northern part of the zone. The Zagros Fold Belt consists of a folded Paleozoic to Miocene sedimentary sequence of several thousands of meters thickness, and overlies Infracambrian and early Paleozoic platformal sediments upon a Precambrian basement. The Zagros Thrust Belt consists largely of Paleozoic, Mesozoic and Cenozoic sediments thrusted over the fold belt sediments in a southwesterly direction.

In the study area, Paleozoic sediments from Zagros Thrust Belt include the Cambrian Mila Formations, the Ordovician Ilebek, Zard Kuh, and Seyahou Formations, the Silurian Sarchahan, and the Permian Faraghan and Dalan Formations selected for details accurate source rock evaluation, as the kerogen chemical structure investigation. The outcrops from north west to south east are located in Calicheh, Gali Kuh ,Zard kuh (Tange-e-Ilebek),Kuh Dena (Dinar) and Kuh Surmeh. (Figure 1)

The type analysis of kerogen at the molecular level is important in accurate source rock evaluation, as the kerogen chemical structure is related to the composition of petroleum hydrocarbons generated from the kerogen. In this experiment, whole rock samples from the Zagros Basin were analyzed using the flash pyrolysis technique and the resulting degradation products were identified using GC/MS. Different types of kerogen produce different degradation products by pyrolysis, depending on the organic type of the kerogen. Although many pyrolysis GC/MS experiments have been performed on oil shale, coal and source rocks (Dembicki et al., 1983; Larter, 1984; Larter and Senftle, 1985; Philp and Gilbert,1984; Horsfield, 1989; Van de Meent et al.,1980), no criteria have been established for source rock potential. With a view towards future exploration in Iran, NIOC-Exploration desired to obtain geochemical data for both hydrocarbons and source rocks to determine the source of hydrocarbons in the Paleozoic sequence as joint study project with JOGMEC in 2005 and this paper described a part of results.Quantitative evaluation of hydrocarbon potential has been performed on the S2 peak

using a Rock Eval pyrolizer, but Rock Eval data provide only one peak and don't reveal details of the S2 peak. The pyrolysis GC/MS technique provides significant information on the molecular composition of the S2 peak. The 20 samples from different source rock candidate used in the experiment are summarized in Table 1. All the samples show very low hydrocarbon potential from TOC and Rock Eval data. Some samples have high TOC, but their S2 values are less than 1.0, except for two Faraghan samples. A good source rock has S2 value of greater than 3 (see Reference in Table 1).

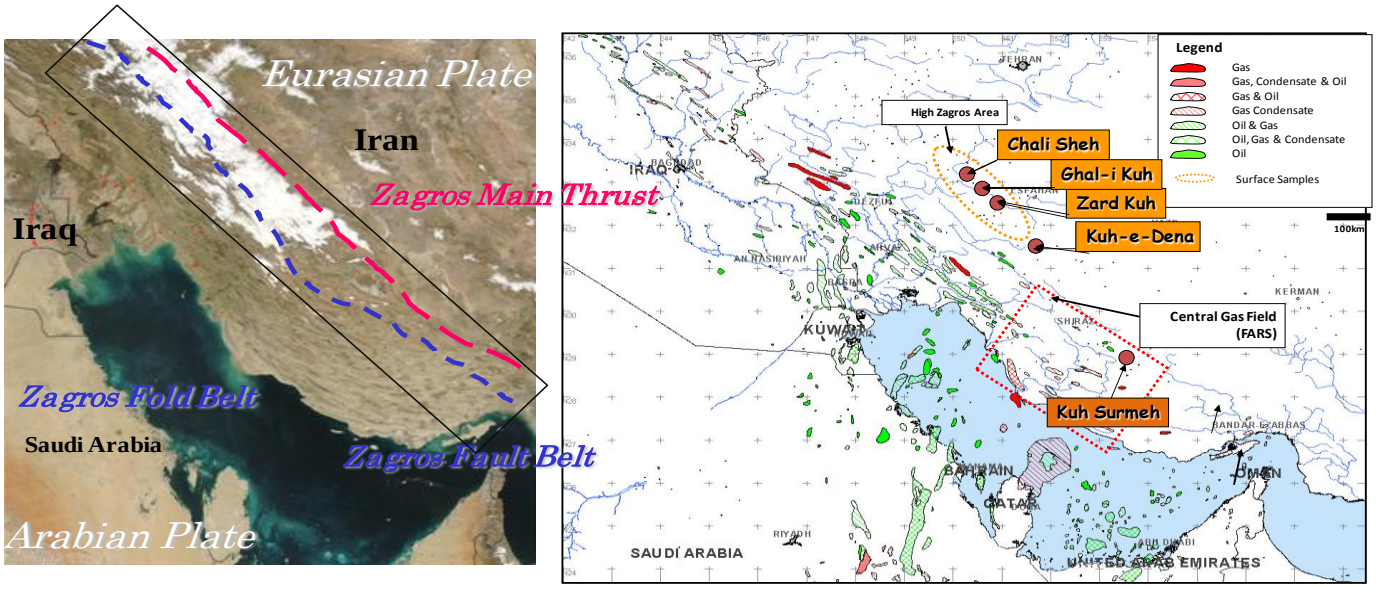

Figure1: position of Zagros basin in Iran and location of Paleozoic outcrops under of studied

		Section	Formation	TOC & RE (JOGMEC)				
				S1	S2	Tmax	HI	TOC
1	D-PTK-20	Kuh-e-Dinar	Dalan	0.06	0.14	457	19.7	0.71
2	D-PTK-23	Kuh-e-Dinar	Dalan	0.04	0.17	493	23.1	0.74
3	CH-SH-2A	Chal-i-Shir	Faraghan	0.12	1.21	467	22.1	5.47
4	CH-SH-7	Chal-i-Shir	Faraghan	0.3	3.33	465	44.3	7.52
5	Ilbk-1	Tang-e-Ilebek	Faraghan	0.01	0.05	460	35.9	0.14
6	Ilbk-2A	Tang-e-Ilebek	Faraghan	0.06	0.45	474	11.3	3.97
7	Ilbk-2	Tang-e-Ilebek	Faraghan	0.05	0.3	538	12.0	2.49
8	Ilbk-14	Tang-e-Ilebek	Zard Kuh	0.22	0.2	462	24.0	0.83
9	Ilbk-40	Tang-e-Ilebek	Zard Kuh	0.17	0.58	455	44.7	1.30
10	Ilbk-45	Tang-e-Ilebek	Zard Kuh	0.04	0.32	460	27.5	1.16
11	Ilbk-58	Tang-e-Ilebek	Ilebek	0.15	0.81	458	45.6	1.78
12	Ilbk-67	Tang-e-Ilebek	Ilebek	0.05	0.09	466	23.7	0.38
13	Ilbk-72	Tang-e-Ilebek	Ilebek	0.01	0.02	×	66.6	0.03
14	D-PTK-13	Kuh-e-Dinar	Mila	0.09	0.03	507	57.0	0.05
15	GH-AS-12	Ghali Kuh	Mila	0.01	0.02	516	44.0	0.05
16	Ilbk-96	Tang-e-Ilebek	Mila	0.1	0.04	×	24.5	0.16
17	Ilbk-110	Tang-e-Ilebek	Mila	0.01	0.03	×	20.6	0.15
18	MRA-1	Kuh-e-Surmeh (SW)	Silurrian Shale	0.03	0.04	×	18.6	0.21
19	MRA-8	Kuh-e-Surmeh (SW)	Silurrian Shale	0.03	0.03	×	13.1	0.23
20	MRA-21	Kuh-e-Surmeh (SW)	Silurrian Shale	0.01	0.02	×	11.0	0.18

Table-1: Samples and geochemical data used for pyrolysis-GC analysis.

The Faraghan sample (CH-SH-7) shows a good S2 value, but its Hydrogen Index (HI) is low at 44.3. A good source rock generally has a HI of more than 250.

Tmax values of all samples are greater than 455 ℃, indicating a late stage oil-generation zone or over-mature zone (gas generation zone). As the results, organic matter (residual kerogen) of the rocks has low S2 values. In this stage, rocks have almost no oil producing potential. The Tmax of some of the potential source rocks could not be obtained, as their S2 values were too low. Samples with low organic matter and high maturity are generally not subject to further analysis. Previous Pyrolysis-Gas Chromatography (Py-GC) experiments have used samples with high TOC and low maturity levels; however, in this study we performed Py-GC experiments on Zagros rocks to obtain significant information on the characteristics of the residual kerogens.

3. Experiments

Pyrolysis conditions for the rock samples and GC analytical conditions are shown in Table 2. Each rock was crushed to a powder using an agate crusher, and 10-20 mg of sample (approximately 100 meshes) was used for the experiment. Because of the low organic carbon content of samples, bitumen was not removed from the rock sample.

4 .Results and Discussion

More than 100 degradation products have been described in the PY-GC reports listed above in the Introduction. These products can be grouped into four components: aromatic hydrocarbons (aromatic HC), phenolic compounds (phenolics), saturated alkanes, and unsaturated alkenes. The characteristics of Type 1, 2 and 3 kerogens are summarized as follows.

Type 1 kerogen produces predominantly alkanes and alkenes.

Type 2 kerogen is composed of various products.

Type 3 kerogen generates mainly aromatic HC and phenolics.

To provide a simple comparison of the chemical nature of each formation, we arbitrarily selected the following compounds from the 4 groups described above.

1. Dimethyl-benzen (xylene) from the aromatic HC group.
2. Phenol from the phenolic compounds group.
3. n-C11 and n-C14 alkanes from the alkane compounds group.
4. n-C11 and n-C14 alkenes from the alkene compounds group.

Characterization of each formation was achieved by comparison of these four components. Figure 3 shows the percentage of aromatics (aromatic HC plus phenol) and aliphatics (n-alkanes plus n-alkenes) in each formation.

Although both aromatics and aliphatics were detected in all the formations, the Dalan, Faraghan and Zard-Kuh Formations record relatively high amounts of aromatics. In contrast, the Mila Formation is rich in aliphatics. Unfortunately, the TOC content of Mila samples is extremely low at 0.05-0.16%, and Tmax indicates over-maturity (507 ℃, 516 ℃). The results indicate that all the samples analyzed here are residual kerogens that have almost no oil potential, as mentioned above.

It is difficult to estimate the original type of the residual kerogen from the present results only, but we can speculate that the results for the residual kerogen reflect the characteristics of the original kerogen. That is, immature kerogen also has an aliphatic nature.

Three Silurian shales show similar molecular composition to the Mila Formation, as shown in Figure 6-8. We did not determine Tmax values in our study due to extremely low TOC (0.18-0.23%) and small S2 peaks. According to NIOC data, Tmax values for the Silurian samples are 473 ℃ and 480 ℃, indicating that they are also over-mature. As in the case of Mila samples discussed above, we speculate that the original Silurian kerogen may have contained significant amounts of aliphatic chains during its immature stage.

Figure 3 show the quantities of aromatic HC, phenol, and aliphatics. Here, peak height (mm) is divided by the TOC of each sample. A quantitative calculation using a standard compound

was not performed in this experiment. The Mila samples are rich in aliphatic HC. This result is very different from the results for the five other formations. Phenol is detected in all rocks, indicating a contribution of woody lignin from higher land plants.

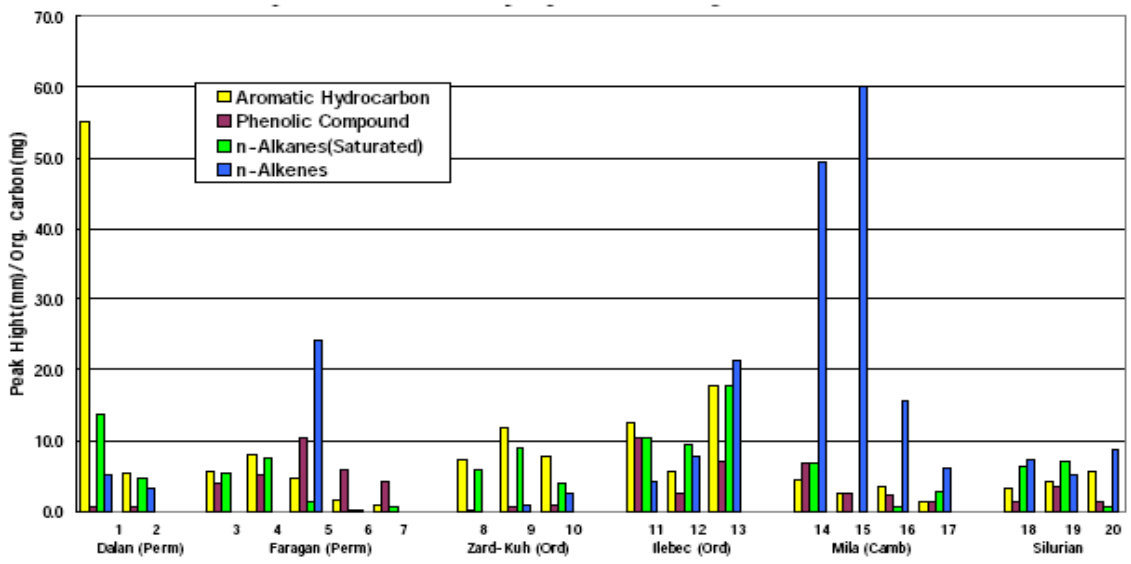

Figure 3: Yield of Aromatic HC, Phenol, n-Alkanes and n-Alkenes.

Figure 3 show the concentrations of the four components outlined above. Mila samples are extremely rich in alkenes. As basic, when aliphatic chains are ruptured, two unpaired electrons are formed. One chain then becomes saturated alkane and the other becomes unsaturated alkene; the two molecules are then stable.

Type 1 and 2 kerogens from various sedimentary basins show a doublet of n-alkanes and n-alkenes. The famous Green River shale produces n-alkanes and n-alkenes as doublet peaks. Dalan, Faraghan and Zard-Kuh rocks provide only n-alkanes, with no alkenes. These n-alkanes are considered to be derived from bitumen in the rocks when they were heated in the Py-GC experiment. As unsaturated alkenes were not detected, these saturated n-alkanes are not derived from the bond cleavage of aliphatic chains.

NSO compounds in pyrolysis products

The following NSO compounds were found in the programs (a gas chromatogram of pyrolysis products).

N-compounds: Benzonitrile, Quinolin and Carbazole.

S-compounds: Benzothiophene, Dibenzothiophene and Methyl-benzothiophene.

O-compounds: Phenol, Methyl-phenol, Naphthalenol, Dibenzofuran, Fluorenone and Anthrone.

The pyrogram of six formations (Dalan, Faraghan, Zard Kuh, Ilebek, Mila and Silurian), and identified peaks for NSO compounds. These compounds have been found previously within petroleum and reported in the Biomarker Guide (Peters et al., 2004).

The retention time of the pyrograms was widened from 13-36 minutes for exact peak identification. A phenol peak is indicated, as its retention time was short and not included in the 13-36 minute interval. For all the samples, the above NSO compounds were minor peaks compared with major aromatic compounds (Naphthalene, Biphenyl, Anthracene, etc) and aliphatic compounds (n-alkanes and n-alkenes).

In these pyrolysis experiments, we did not extract bitumen from the rock sample, as the TOC content of some samples is very low (e.g. 0.18-0.23% for Silurian shales and 0.05-0.16% for Mila Formation samples). When rock is heated at high temperatures of 700 ℃, organic compounds in bitumen are easily evaporated, expelled from rock and detected on the pyrogram. The NSO compounds found in this experiment are therefore a mixture of bitumen and kerogen decomposition products.

5. Results

The following chemical characteristics are revealed by Py-GC analysis of the Zagros samples.

1. Kerogen of the Mila Formation is rich in aliphatic chains and poor in aromatic structure compared with the other five formations.

2. Silurian rocks are also aliphatic in nature.

3. We speculate that Mila (and Silurian) rocks had Type 1 characteristics during their immature stage. If this is the case, these rocks could be potential source rocks for producing aliphatic hydrocarbons (condensates and oils).

4. Dalan, Faraghan and Zard-Kuh samples show aromatic characteristics. Their original immature kerogen might be Type 3.

6. Conclusions

The 20 samples from different source rock candidate frome palezoic sediments from Iran selected for accurate source rock evaluation, as the kerogen chemical structure is related to the composition of petroleum hydrocarbons generated from the kerogen. The kerogen derived from Mila Cambrian formation and Sarchahan Silurian are related to marine organisms yield because of mainly aliphatics chains and producing aliphatic hydrocarbons (condensates and oils).The kerogen of Permian Dalan, Faraghan and Zard-Kuh samples from Permian to Silurian in high zagros area derived from terrestrial plant produced alkyl-phenols in significantly higher amount than the other kerogen. Their original immature kerogen might be Type 3.

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