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Mineralogical Analysis of Paleocene Shales from Western Salt Range and Hazara Area, Pakistan

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ABSTRACT

The Paleocene shales of Patala Formation exposed in western Salt Range (Khairabad Section) and its time-equivalent Kuza-Gali Shales from southern Hazara area have been analyzed and compared for the source rock characteristics, based on their mineralogical compositions, diagenetic changes and hydrocarbon generating potential during basin evolution. Qualitative and semi-quantitative analyses were carried out using X-ray diffraction, Coulometric, Scheibler, and scanning electron microscopic techniques for mineral identification and to estimate their concentrations in the sediments.

The samples from western Salt Range are mostly calcareous claystones, whereas the sediments from Hazara area can be classified as sandy claystones on the basis of their grain size and composition. The main constituents of the sediments are: calcite, quartz and clay minerals; however, dolomite has also been detected in a few samples from Khairabad section. The organic matter in the sediments ranges from 0.5 to 1.2%.

The principal clay minerals identified in the < 2 micron fraction are mixed-layer illite/smectite, chlorite/smectite, illite, kaolinite and chlorite, in both the areas. In the Salt Range sediments, randomly stratified mixed-layer illite/smectite is dominant; small amounts of kaolinite and chlorite are also present. The sediments from Hazara area contain mainly corrensite and illite/smectite mixed-layers. However, the samples belonging to northernmost section are mainly composed of illite.

The clay minerals have also revealed the burial diagenetic history of the sediments indicating, probably acid pore water environments in early stage of deposition and increasing alkaline pore water conditions with increase in burial depth. Presence of mixed-layer clay minerals in southern and central part of the study area, represents an intermediate phase of burial diagenesis, whereas, illite, the principal clay mineral present in northern part, is an indication of dehydrated phase.

The sediments, in both the areas, contain a considerable amount of swelling clays which might have acted not only as a catalyst, generating hydrocarbons, but also might have facilitated in migration of oil and gas in Potwar basin. In Hazara area, apparently, the deeper burial would have produced condensate and eventually gas, which might have been migrated.

INTRODUCTION

In Potwar basin the uppermost formation of Paleocene is the "Patala Formation". This formation is of extreme importance as it is considered to be the main source rock for oil and gas produced in the basin. Hydrocarbon Development Institute of Pakistan (HDIP), Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) studies also reveal that Patala shales are the main potential source for hydrocarbon generation (Ranke, 1986).

In Hazara area (north of Main Boundary Thrust and Potwar basin) the "Kuza Gali Shales" are considered to be the time-equivalent of Patala Fm. Previously, not much attention has been given to analyzing these shales and to exploring their source-rock potential. As the northern part of Potwar (adjacent to Hazara area) has been proven to be the main producing region of the basin, the nearby Paleocene shales of Hazara area might have played an important role in generating oil and gas.

The present study aims at analyzing and comparing the source rock characteristics of Paleocene shales, exposed in Salt Range and Hazara area, based on their mineralogical compositions, diagenetic changes and hydrocarbon generating potential during basin evolution. For this purpose 30 rock samples have been selected from both the areas for detailed study.

This study has been carried out in the Institute of Geology and Paleontology (Petroleum Geology Section), Technical University, Clausthal (Germany) during October 1990 to February 1991. The analyses comprise mainly the determination of total carbon, organic carbon and carbonate content, X-ray diffraction analysis for whole rock composition and clay mineral identification and scanning electron microscopic (SEM) studies.

SAMPLES UTILIZED FOR STUDY

As this study has been designed to analyze and compare different facies of the same age in two different areas, the samples have been collected from different locations. A

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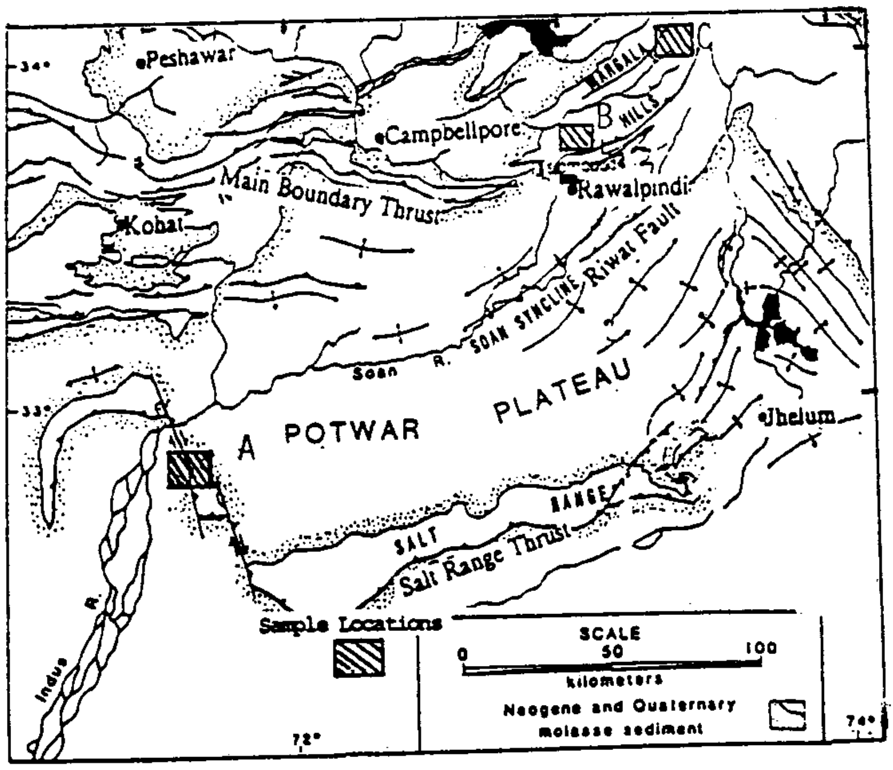

Figure 1— Location of study area showing sections from where samples have been collected. A: Khairabad, B: Margala Hills, C: Ghora Gali-Mari section (after Douglas et al, 1989).

total number of 30 samples has been collected for this study from three different locations; one, from western Salt Range, Khairabad section and other two from Hazara area (north of Potwar Plateau), namely Margala Hills and Ghora Gali-Mari section (Figure 1).

Systematic sampling could only be made for one section (Khairabad section) whereas, from the other two localities the samples have been collected randomly due to the tectonic complexity of the area.

Eleven samples (KH-2 to KH-11a), collected from Khairabad section, belong to Late Paleocene-Early Eocene "Patala Formation". Rest of the 19 samples (HZ-21 to HZ-29; HZ-42 to HZ-51) have been collected from Hazara area. These samples have been taken from Paleocene strata known as "Kuza Gali Shales" which are considered to be the time-equivalent of Patala facies exposed in the south (Salt Range). The sample description, showing brief lithology, location and other information has been listed in Table 1.

Lithological Description

The general lithology of samples from Khairabad section is calcareous claystones; some of these are grading to argillaceous limestone, especially from lower part of the formation (KH-2 & KH-3). Most of the samples are light to medium-gray in colour, few of these have brownish to yellowish weathering.

The samples of Khairabad section are generally fossiliferous, mainly forams are abundant in most of the samples. Majority of the samples, contain small coal particles and plant remains. Samples in the upper part are slightly micaceous and also show iron leaching (oxidized ?). Generally, the samples are not laminated or these are very poorly laminated.

The samples collected from Hazara area are mainly sandy claystones; some of them seem to be more calcareous e.g. HZ-25 to HZ-28 & HZ-44. The samples are light to medium-gray in colour, except HZ-25 to HZ-27, which are more yellowish and give an earthy look, probably due to weathering. All the samples seem to be unfossiliferous except HZ-42, which shows empty cavities and imprints of fossil shells. The fossil remains seem to have been altered by oxidation. The sample HZ-51 also contains shell fragments. Small coal particles and plant remains are visible in most of the samples. Presence of residual hydrocarbons has also been noticed in HZ-28.

Many of the samples from Hazara area are tectonized, especially those from the northernmost section (HZ-46 to HZ-51). In these samples, slickinsides and shiny, smooth fracture surfaces can be observed. Many of the samples are splintery and contain calcite veins.

Most of the samples are poorly laminated but a few are moderately laminated. One sample, HZ-46, shows small scale cross-stratification.

METHODS

Determination of Total, Organic and Carbonate Carbon

For the rapid determination of total carbon, non-carbonate carbon (organic carbon) and carbonate carbon in samples under study, the coulometric method has been applied.

Quantitative Chemical Determination of Carbonate Content

A quick survey of carbonate quantity, present in the sediments, has been carried out chemically by means of carbon dioxide determination. Carbon dioxide is liberated by acid treatment from carbonate minerals in a reaction flask and quantified volumetrically by the help of a gasometer. In the present study, "Scheibler" gasometer has been applied to analyze the samples.

X-ray Diffraction Analysis

X-Ray diffraction analysis has become the more accurate and quick determination method of fine-grained

Table 1. List of samples used for the study and their general lithology. Abbreviations used in the table are: sh = shale, cal. = calcareous, lith. = lithology, lam. = laminated, med. = medium, clayst. = claystone, fossil. = fossiliferous, sst. = sandstone, argille. = argillaleous, m = meter.

Sample No	Lithology	Locality	Formation
KH-2	cal. sh., medium to dark grey	East of Khairabad (Western Salt Range)	Patala Fm (Paleocene)
KH-3	same lith., 1 m above KH-2	- do -	- do -
KH-4	same lith., 3 m above KH-3	- do -	- do -
KH-5	same lith., 3 m above KH-4	- do -	- do -
KH-6	same lith. fossil. 6 m above KH-5	- do -	- do -
KH-7	sh., medium grey, 1 m above KH-6	- do -	- do -
KH-8	sh., light grey, coal particles, 2 m above KH-7	- do -	- do -
KH-9	sh, light grey, 2 m above KH-8	- do -	- do -
KH-10	sh., med. grey to yellowish 5 m above KH-9	- do -	Patala Fm/ Nammal Fm?
KH-11	same as KH-10, 1 m above KH-10	- do -	- do -
KH-11a	same as KH-11, 2 m above KH-11	- do -	- do -
HZ-21	clayst., light grey to light brown, coal particles	Margala Hills, Dunga Kasi-Pir Sohawa (Hazara Area)	Kuza Gali Shales (Paleocene)
HZ-22	sandy, clayst. med. grey , unfossil. no lam.	- do -	- do -
HZ-23	Argill.sst., med. grey mod. lam.	- do -	- do -
HZ-24	clayst., med. grey unfossil., lam.	- do -	- do -
HZ-25	cal. clayst. yellowish mod. lam. weathered	- do -	- do -
HZ-26	cal. clayst. same as HZ-25	- do -	- do -
HZ-27	same as HZ-25	- do -	- do -
HZ-28	cal. clayst., med.grey, poorly lam.,carbonaceous	- do -	- do -
HZ-29	clayst., light greenish-grey, splintery, sideritic, slightly tectonized	- do -	- do -
HZ-42	clayst., light grey to yellowish, fossil., coaly particles	Pir Sohawa-Pholira Rest House (Hazara Area)	- do -
HZ-43	sandy clayst., yellowish-grey, plant remains, lam.	- do -	- do -
HZ-44	clayst., light grey, coaly, lam.	- do -	- do -
HZ-45	same as HZ-44, poorly lam.	- do -	- do -
HZ-46	sandy clayst., med.to dark grey, tectonized cross-bedded, calcitie veins, bituminous?	Ghora Gali-Mari Section (Hazara Area)	- do -
HZ-47	same as HZ-46	- do -	- do -
HZ-48	same as HZ-46	- do -	- do -
HZ-49	same as HZ-46, fossil. fragments ?	- do -	- do -
HZ-50	same as HZ-49	- do -	- do -
HZ-51	same as HZ-49	- do -	- do -

materials, especially in the identification of clay minerals. Two analytical methods have been combined in the present study; the (001) reflections for quick and proper identification of species/groups of clay minerals; the powder preparations provided the entire (hkl) spectra for whole rock analysis (bulk mineralogy). The technique has also been applied for the estimation of mineral quantities present in the sediments.

Whole-rock qualitative analysis.— Randomly oriented powder mounts were analyzed by a Phillips PW 1710 X-ray diffractometer having completely automated instrument operations and data processing capabilities.

A Copper-K (alpha) radiation has been applied using a graphite curved monochromator and automated divergent slit, with a generator setting of 30 KV and 30 mA. The powder samples were scanned from 3° to 65° ($2\emptyset$) with a step-size of 0.02° (2Ø) and scanning speed of 0.25 sec/step. The diffractometer tracings for each sample were plotted, calibrating the 2Ø difflections on X- axis and recording X-ray intensities in counts per second on Y- axis. These tracings were then further analyzed for the mineral identification and compared with the standard patterns compiled by the Joint Committee on Powder Diffraction Standards (JCPDS, 1974).

Semi-Quanitative Analysis.— In the present study, semi-quantitative analysis have also been conducted by preparing calibration curves. For this purpose, external standard method has been applied by measuring the peak intensities of selected diffraction lines of binary mixtures of quartz and calcite in known quantities.

Clay Mineral Analysis.— Air-dried, glycol-saturated and heated clay samples were subjected to X-ray diffraction in the same instrumental conditions as used for the powdered mounts, except for the scan- range and scan-speed. These samples were scanned from 2° to 28° (2Ø), with a step-size of 0.02°(2Ø) and 1.0 sec/step.

Electron Microscopic Analysis

In the present study, the electron microscopic analysis has been carried out using the scanning electron microscope of type "ISI Super III A" with a magnification of X10 - X160,000 (incl. zoom) and maximum resolution of 70A. An accelerating voltage of 25-30 KV was applied in much of the analysis. In the present study, six samples were selected, from both Salt Range and Hazara areas, for electron microscopic analysis (EDX).

RESULTS

Whole Rock Composition

The composition and concentration of various minerals present in the sediments have been measured by different methods e.g. XRD: mainly used for whole rock composition and clay mineral analysis; Coulometric method: to determine the total, carbonate and organic carbon content and Scheibler method: for carbonate content estimation. The values obtained by various methods, indicate little difference in the quantities of mineral contents. The comparison of the results achieved by different techniques has been made and is given in Tables 2, 3 and 4. The mineral constituents and their quantities determined by various analyses are as follow:

Total Carbonates

The determination of carbonate carbon and total carbon content of the sediments, which leads to estimation of the calcite fraction, was made by Scheibler and Coulometric methods, respectively. The comparison of the results from these methods have been given in Table 2. The results show that the measurement values, obtained by these techniques for different fractions are close to each other (less than 5% difference), except in a few cases.

According to Coulometric method, the percentage of carbonate carbon content in Khairabad section is higher in comparison to Hazara area and ranges from 3.12 to 7.33% C. The carbonate carbon content values in sediments of Hazara also shows great variation which ranges from 0.07 to as high as 4.31% C, where half of the samples contain less than 1.0% C. The values determined by Scheibler method are slightly higher. It has been noticed that, generally, the samples rich in carbonate content also show higher organic contents in contrast to samples low in carbonate content.

The estimation of calcite and dolomite content has additionally been carried out by X-ray diffraction method (Figures 2 to 5).

Calcite.— The results obtained from the analyses indicate that samples from Khairabad section (KH-2 to KH-11a) contain fairly high amounts of calcite content, and these sediments can easily be classified as "calcareous claystone" (Selley, 1988). Two samples (KH-2 & KH-3) from lower part of the section can be regarded as "argillaceous limestone", containing more than 50% of calcite.

The sediments in lower part of the section contain upto 60% of calcite, which decreases gradually upward to 30%. The results obtained from Scheibler method also verify these percentages. The calcite composition of all the samples, obtained by different methods including XRD are listed in Table 3. It has been observed that carbonate content measured by Coulometric method shows relatively lower amounts in comparison with other two methods.

Calcite content of the samples from Hazara area is found to be varying significantly from sample to sample. The maximum calcite content in some of the samples from Margala Hills (HZ-25 to HZ-28 & HZ-44) range from 40 to 45%, whereas rest of the samples contain less than 25% and a few samples in this area contain less than 2%. The stratigraphic position of the samples in this area is not clear; therefore, it is not possible to establish any trend in the stratigraphic sequence.

Shale samples (HZ-46 to HZ-51) collected from further north in Hazara area (Ghora Gali-Mari section) show very low amount of calcite content. Only one sample contains about 5% calcite, whereas all of the others possess less than 2%.

Dolomite.— Dolomite content, identified by X-ray diffraction (Figure 3) and also observed in electron microscope (EDX), is present in some of the samples from Khairabad section. The maximum percentage encountered

Table 2. Chemical composition of the samples showing carbon content (organic, total and carbonate) & carbonate content(as calcite) measured by two different methods.

	COULOMETRIC				SCHEIBLER	
Sample No.	Organic Carbon (%)	Total Carbon (%)	Carbonate Carbon (%)	Carbonate (%)	Carbonate Carbon (%)	Carbonate (%)
KH-2	0.50	7.83	7.37	61.17	7.74	64.46
KH-3	0.61	7.80	7.91	60.00	7.34	61.16
KH-4	0.40	5.00	4.60	39.25	5.42	45.18
KH-5	0.30	4.84	4.54	39.80	5.40	45.00
KH-6	0.30	5.10	4.80	39.87	5.32	38.00
KH-7	0.40	4.00	3.60	29.37	4.14	34.53
KH-8	0.35	3.90	3.65	29.70	4.02	33.42
KH-9	0.35	6.57	6.22	51.83	6.68	55.67
KH-10	0.75	3.93	3.12	26.50	3.86	31.60
KH-11	0.55	4.43	3.88	32.33	4.08	34.00
KH-11a	0.50	5.53	5.03	41.43	5.46	45.48
HZ-21	0.25	3.36	3.11	25.83	4.20	33.80
HZ-22	0.30	1.50	1.20	10.00	1.42	12.36
HZ-23	0.10	0.17	0.07	0.70	0.21	1.75
HZ-24	0.10	1.00	0.90	7.11	0.96	8.00
HZ-25	0.45	4.37	3.93	32.50	5.00	42.00
HZ-26	1.11	4.37	4.80	40.00	5.34	44.58
HZ-27	0.90	5.21	4.31	36.10	5.25	43.00
HZ-28	0.74	4.71	3.97	33.00	4.90	40.80
HZ-29	0.20	0.30	0.10	0.75	0.15	1.30
HZ-42	0.90	3.30	1.40	9.33	1.90	16.00
HZ-43	0.30	0.40	0.10	0.50	0.24	2.00
HZ-44	0.90	4.80	4.00	33.33	4.40	36.60
HZ-45	1.20	4.30	3.10	25.00	3.65	30.46
HZ-46	0.50	1.00	0.50	4.50	0.61	5.10
HZ-47	0.35	0.60	0.25	2.00	0.30	2.44
HZ-48	0.32	0.42	0.10	0.42	0.18	1.52
HZ-49	0.25	0.40	0.15	1.25	0.18	0.17
HZ-50	0.30	0.40	0.10	0.50	0.18	1.50
HZ-51	0.30	0.45	0.15	1.17	0.18	1.46

(measured by XRD in relation to calcite content) in one of the samples (KH-9) is upto 35%. In rest of the samples, collected immediately above and below the strata containing maximum dolomite content, less than 10% of dolomite is present. An upward gradual increase in dolomite content can be observed (Table 4). The lower beds contain less than 2% of dolomite.

No dolomite has been found in the samples collected from Hazara area.

Quartz

Quartz is one of the major constituents present in the whole suite of samples in varying amounts. The quantitative estimation of quartz content depends upon X-ray diffraction method. These estimations (Table 4) have been made through the "straight-line model" but unfortunately no other comparative analyses could be carried out to confirm these estimations. The samples from Khairabad section contain quartz concentrations from 15 to 18%. The samples relatively poor in carbonates contain slightly higher percentages of quartz content but this increase in quartz fraction is not very great. Whereas, the sediments with high concentration of carbonates (about 60%), like KH-2 and KH-3, contain < 10% quartz content.

In contrast to the Salt Range area, the samples from Hazara area show higher quartz concentrations. Some samples e.g. HZ-23 and HZ-43, show more than 45% of

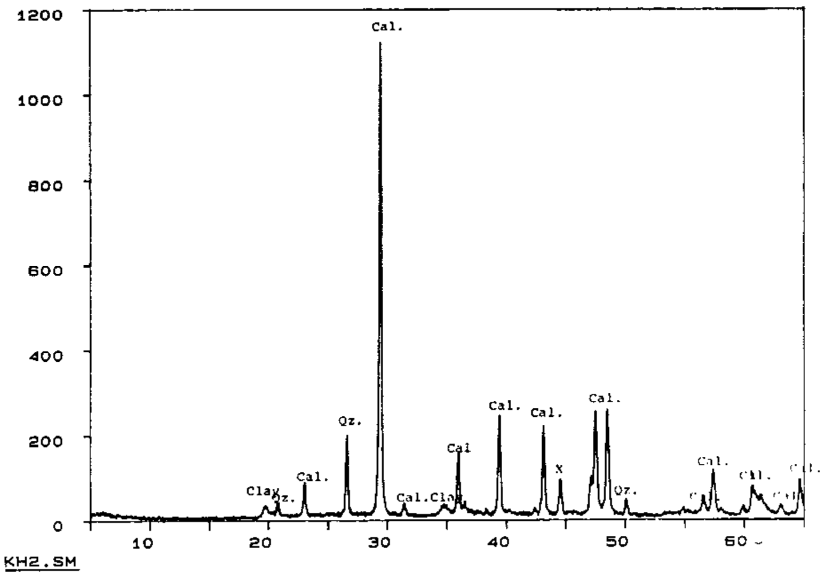

Figure 2— Diffractometer tracing of sample KH-2: random powder mount, analyzed to determine the whole rock mineral composition, showing peak intensities of different minerals.

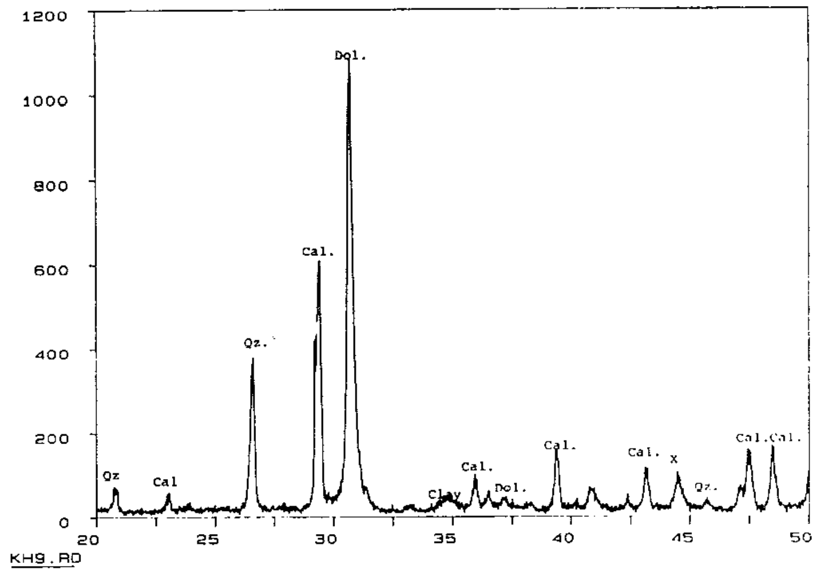

Figure 3— Diffractometer tracing of sample KH-9: random powder mount analyzed for whole rock mineral composition, showing peak intensities of different minerals. The strong peak at 30.7° (2Ø) corresponds to dolomite.

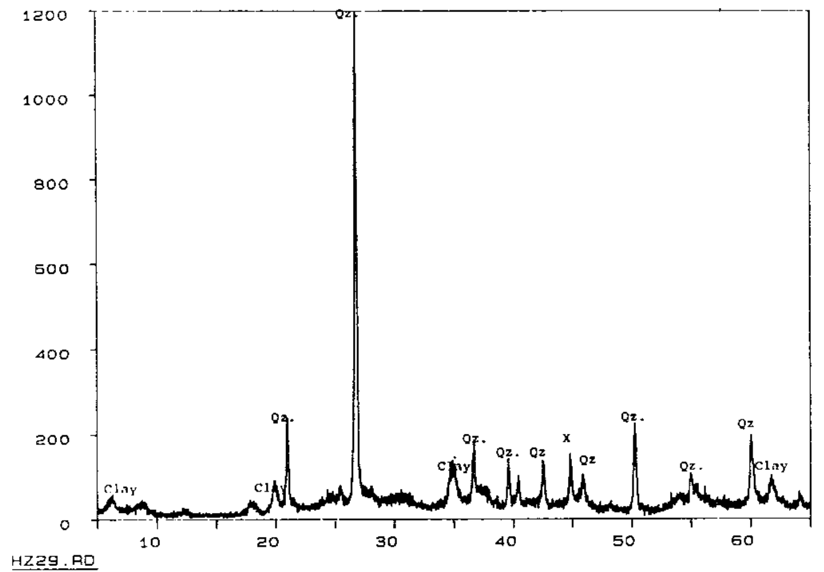

Figure 4— Diffractometer tracing of sample HZ-29: randomly oriented powder mount analyzed for whole rock mineral composition, showing peak intensities of different minerals. A considerable increase in quartz and clay content can be noticed, whereas calcite content is almost lacking.

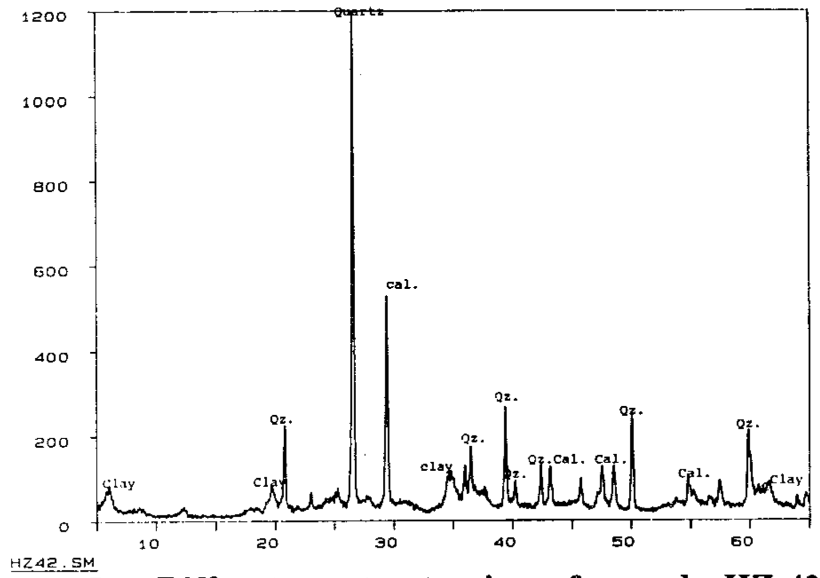

Figure 5— Diffractormeter tracing of sample HZ-42: randomly oriented powder mount analyzed for whole rock mineral composition, showing peak intensities of different minerals.

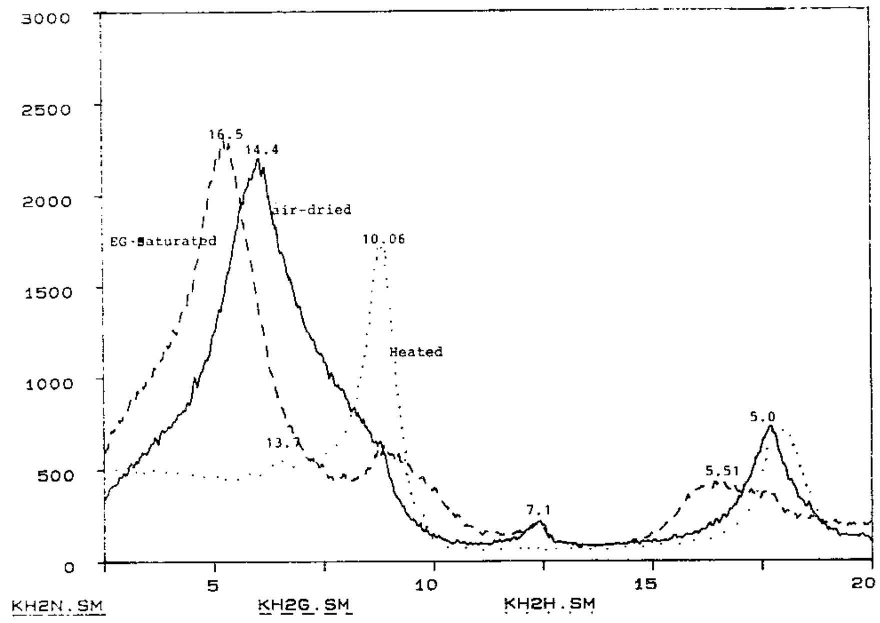

Figure 6— Diffractometer tracing of sample KH-2 illustrates the clay mineral peaks of mixed-layer illite/smectite, 50% illite, RO. The influence of different sample treatments can be noticed, how it helps in identification of clay minerals. Kaolinite and/or chlorite peak (7.1 Å) is also visible which eliminates in heated sample trace.

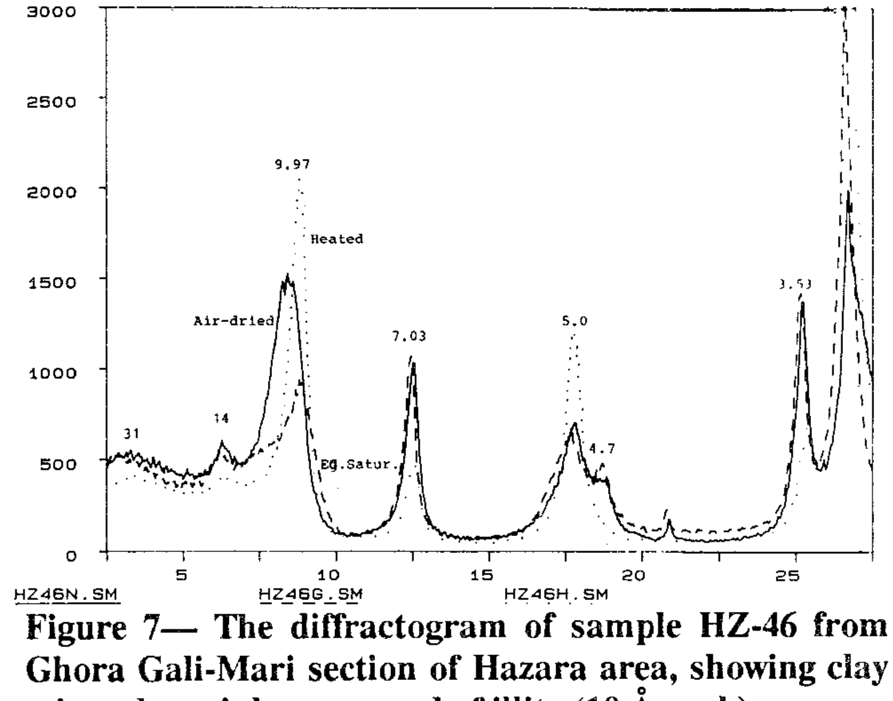

Figure 7— The diffractogram of sample HZ-46 from Ghora Gali-Mari section of Hazara area, showing clay minerals mainly composed of illite (10 Å peak).

Table 3. Carbonate content percentages in the samples measured chemically and by X-ray method.

Sample No.	Coulometric	Scheibler	X-ray Diffraction
KH-2	61.17	64.46	57
KH-3	60.00	61.16	60
KH-4	39.25*	45.18*	40
KH-5	39.80*	45.00*	42
KH-6	39.87*	44.26*	38
KH-7	29.73*	34.53*	32
KH-8	29.70*	33.42*	30
KH-9	51.83*	55.67*	25
KH-10	26.50*	31.60*	28
KH-11	32.33*	34.00*	24
KH-11a	41.43*	45.48*	38
HZ-21	25.83	33.80	26
HZ-22	10.00	12.36	11
HZ-23	0.70	1.75	<2
HZ-24	7.11	8.00	8
HZ-25	32.50	42.00	40
HZ-26	40.00	44.58	39
HZ-27	36.10	43.00	35
HZ-28	33.00	40.80	38
HZ-29	0.75	1.30	<2
HZ-42	9.33	16.15	16
HZ-43	0.50	2.00	<2
HZ-44	33.33	36.60	38
HZ-45	25.00	30.46	27
HZ-46	4.50	5.10	<2
HZ-47	2.00	2.44	<2
HZ-48	0.42	1.52	<2
HZ-49	1.25	0.17	<2
HZ-50	0.50	1.50	<2
HZ-51	1.17	1.46	<2

* % Dolomite content is also included.

quartz, but in majority of the samples, it ranges between 20 to 35%. It appears that sediments containing low carbonate content (<2%) show high quartz contents (>30%).

Organic carbon

The organic carbon content has been measured by Coulometric method. The organic content measurements indicate that the analyzed sediments are not rich in organic carbon. The samples from Khairabad section show organic contents ranging from 0.30 to 0.75% (Table 4).

The organic contents in samples of Hazara region range widely, but most of the values range from 0.30 to 0.90%. The highest values determined for organic content are 1.20 and 1.10% in samples HZ-45 and HZ-26 respectively.

Table 4. Mineralogical composition of the samples determined by X-ray diffraction and Coulometric method.

	XRD				Coulometric
Sample No	Calcite (%)	Quartz (%)	Clay (%)	Dolomite (%)	Organic Carbon (%)
KH-2	57	7	36	-	0.50
KH-3	60	10	30	-	0.60
KH-4	40	14	44	<2	0.40
KH-5	42	14	42	<2	0.30
KH-6	38	15	45	<2	0.30
KH-7	32	18	48	<2	0.40
KH-8	30	18	47	<5	0.35
KH-9	25	15	20	35	0.35
KH-10	28	17	49	4	0.75
KH-11	24	18	46	10	0.55
KH-11a	38	16	43	3	0.50
HZ-21	26	27	47	-	0.25
HZ-22	11	33	56	-	0.30
HZ-23	<2	48	50	-	0.10
HZ-24	8	28	64	-	0.10
HZ-25	40	24	36	-	0.45
HZ-26	39	20	41	-	1.10
HZ-27	35	20	45	-	0.90
HZ-28	38	22	40	-	0.74
HZ-29	<2	25	72	-	0.20
HZ-42	16	26	58	-	0.90
HZ-43	<2	45	45	-	0.30
HZ-44	38	22	40	-	0.90
HZ-45	27	26	47	-	1.20
HZ-46	<2	30	68	-	0.50
HZ-47	<2	32	66	-	0.35
HZ-48	<2	38	60	-	0.32
HZ-49	<2	30	68	-	0.25
HZ-50	<2	36	62	-	0.30
HZ-51	<2	36	62	-	0.30

Clay minerals

The clay mineral concentration in the sediments has been estimated indirectly by subtracting the amount of non-clay minerals from the whole rock composition (100%), determined by X-ray diffraction method (Table 4).

Clays are present as a major constituent in most of the samples; however, the percentages are relatively low in samples from Khairabad section in comparison with Hazara area. Possibly, this is due to the presence of high carbonate content in KH-set of samples, whereas in Hazara area, low carbonate content and moderate amount of quartz corresponds to the presence of more clay.

In most of the samples from Khairabad section, the clay content ranges from 42 to 49%, and only in three samples it is less than 36%. In these three samples, the carbonate contents are in abundance.

In Hazara samples, the clays are in abundance as compared to quartz and carbonate fractions. The majority of the sediments contain clay contents ranging from 40 to 72%, except in one sample in which it is 36 %. This is likely due to presence of a high percentage of carbonates.

The clay concentration varies also in both sections of Hazara area. The samples (HZ-46 to HZ-51), collected from northernmost region (Ghora Gali-Mari section), contain higher clay concentrations (>60%) as compared to those from Margala Hills.

Clay Mineral Analysis

In the present study, the clay mineral analysis and their identification have been made as well. The deflections from oriented air-dried, glycol-saturated and heated samples have been obtained on a single diffractogram to examine the effects of different treatments and conditions under which the samples were run. This also helped in identifying the different clay mineral groups.

The individual clay minerals and mixed-layer clays identified in the samples under study are as follow:

Kaolinite, Chlorite and Illite.— All the samples from Khairabad section (KH-2 to KH-11a) and two samples from Margala Hills (HZ- 21 and HZ-22) show moderate reflections near 21.5° (2Ø) (7.1Å) which indicates the presence of kaolinite, or chlorite, or the presence of a mixture of both (Figure 6). To verify the absence or presence of chlorite and kaolinite, the samples were heated at 550 °C for about two hours and then re-examined. The intensity of reflection near 14Å decreased greatly and a very weak peak was observed which shifted to 13.7Å (Figure 6) and the 002 reflection eliminated completely. At this temperature, kaolinite (and some chlorites) becomes amorphous to X-ray, so its diffraction pattern disappeared. This test suggests the presence of a fair amount of kaolinite (may be up to 5%); however, the presence of a very small quantity of chlorite can not be ruled out due to the presence of a weak reflection at 13.7 Å after heating.

Sediments (HZ-46 to HZ-51), especially from northernmost study area (Ghora Gali-Mari section) which contain extremely low mixed-layer contents, are almost entirely composed of illite (Figures 7 and 8) and a little amount of chlorite (Figure 7). One sample from Margala Hills (HZ-29) also shows the similar composition (Figure 9). These sediments probably, relate to the same stratigraphic horizon.

Mixed-layer illite/smectite.— The diffraction patterns of the clay samples illustrate that the samples (KH-2 to KH-11a) are dominated by the presence of mixed-layer illite/smectite. The diffraction patterns were recorded and analyzed from air-dried, ethylene glycol-saturated and heated preparations.

In air-dried condition the specimens produced a main peak near 15 Å (Figure 6). The ethylene glycol-saturated condition caused a significant change in the diffraction pattern shifting the 14.4 Å peak to 16.5 Å, indicating the presence of expandable clay minerals (mainly smectite).

The absence of 001 series of the superstructure is indicative of randomly interstratified mixed-layer. In an ethylene glycol-saturated pattern, a peak near 10 Å is indication of illite and near 5.5 Å (16° to 17° 2Ø) a broad peak shows the presence of illite/smectite phase (002/003).

The qualitative identification of mixed-layer illite/smectite has further been confirmed by obtaining diffraction pattern from heated samples (Figure 6). The pattern resumed the pure illite (10 Å structure) and 002 reflection of 5 Å.

The illite percentage has also been estimated by using the two reflections of mixed-layer illite/smectite near 9° (001/002) and 16° (002/003) 2Ø (Moore, 1989). The differential 2Ø values of two, provides a good estimate of the illite/smectite ratios, assuming that interference from other clays does not make this measurement impractical. The estimated ratios of illite/smectite range from 50 to 60% illite and from 40 to 50% smectite in Khairabad.

Mixed-layers chlorite/smectite + illite/smectite.— Samples from Hazara area mostly exhibit two kinds of mixed-layers mainly chlorite/smectite (regular) and illite/smectite (nearly regular) with a small amount of chlorite and/or kaolinite. The 1:1 mixed-layer chlorite/smectite (corrensite) with 50/50 composition and R1 ordering, produced a superstructure d(001) near 31.1 Å (14.2Å + 16.9Å) for the glycol-saturated condition (Figures 10 and 11), whereas air-dried samples also formed a rational pattern and produced regular spacings of various orders of reflections.

Another diagnostic criterion for corrensite lies in the appearance upon glycol saturation, of the 004 reflection at about 11.3° 2Ø (7.8Å) which can be seen in tracings of most of the samples from Hazara area. Confirmation of the corrensite identification has also been made by heat-treating the samples, causing the collapse of the smectite component to approximately 9.8Å and leading to a new superstructure spacing of 24Å. A weak broad peak can be observed ranging from 22Å to 24Å, whereas, at other rational spacings of the reflections e.g. near 12Å and 8Å, comparatively strong reflections can also be observed (Figures 10 and 11).

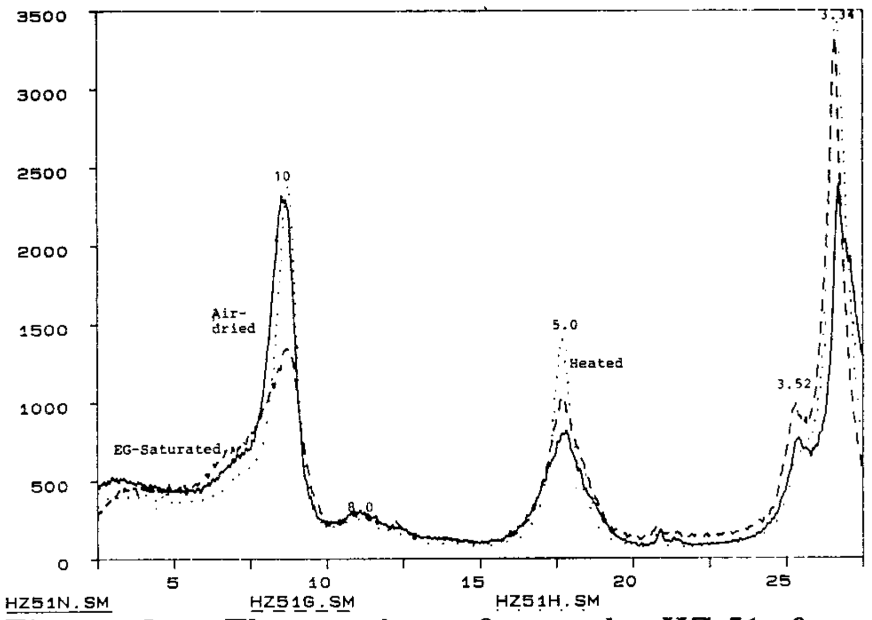

Figure 8— The tracing of sample HZ-51 from northernmost section of Hazara area, showing clay minerals mainly composed of illite.

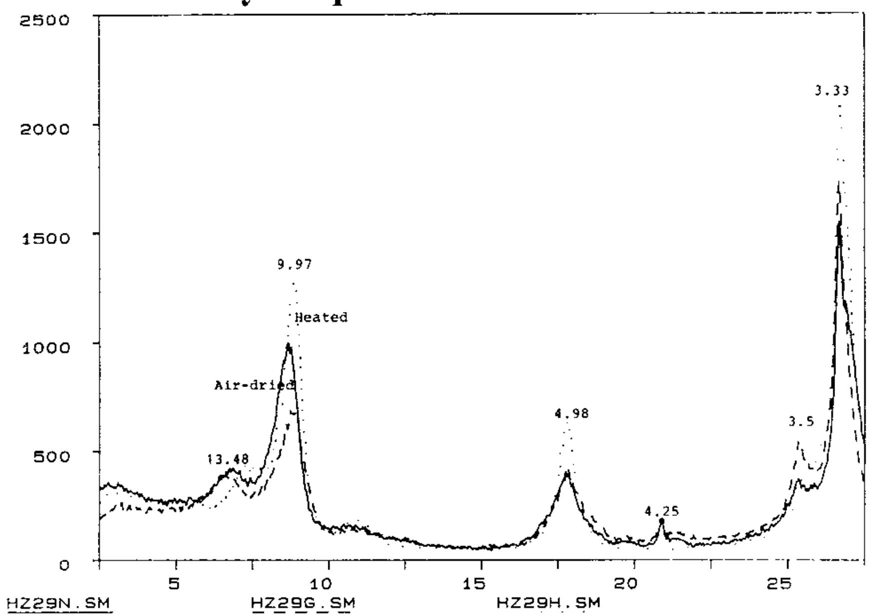

Figure 9— XRD tracing of the sample HZ-29 indicates a considerable decrease in swelling clay minerals.

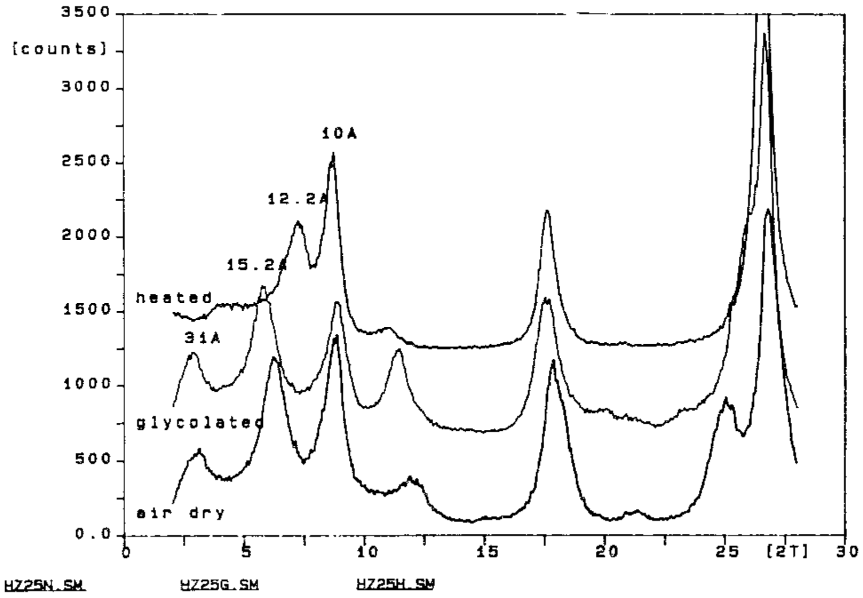

Figure 10— Diffractometer tracing of sample HZ-25 illustrates the clay mineral peaks of corrensite plus mixed-layer illite/smectite and their positions, shifting due to different sample treatment conditions can be observed.

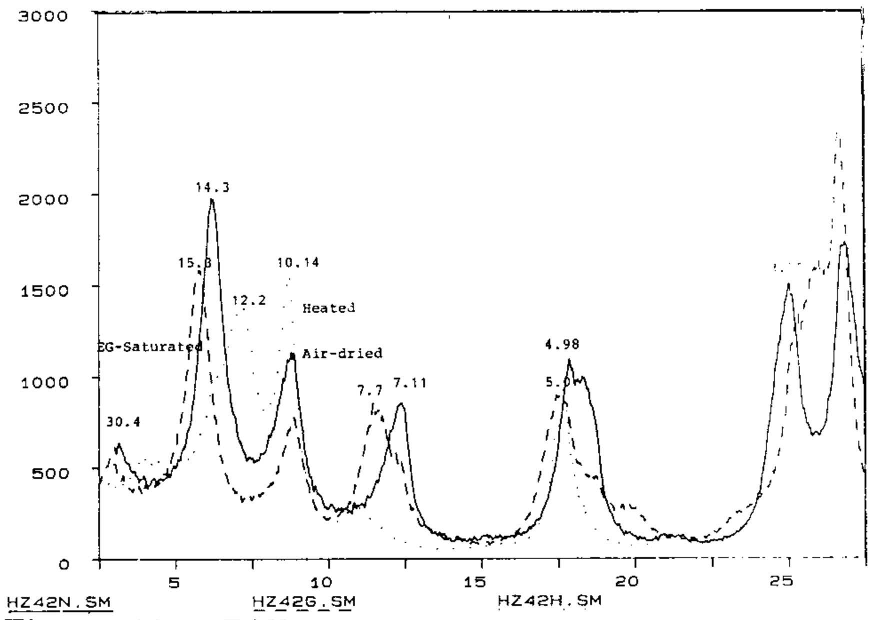

Figure 11— Diffractometer trace of sample HZ-42 illustrates the clay mineral peaks of corrensite and mixed-layer illite/smectite. Superstructure near 30.4 Å in EG-saturated condition can be observed, which shifts after heating near 23 Å.

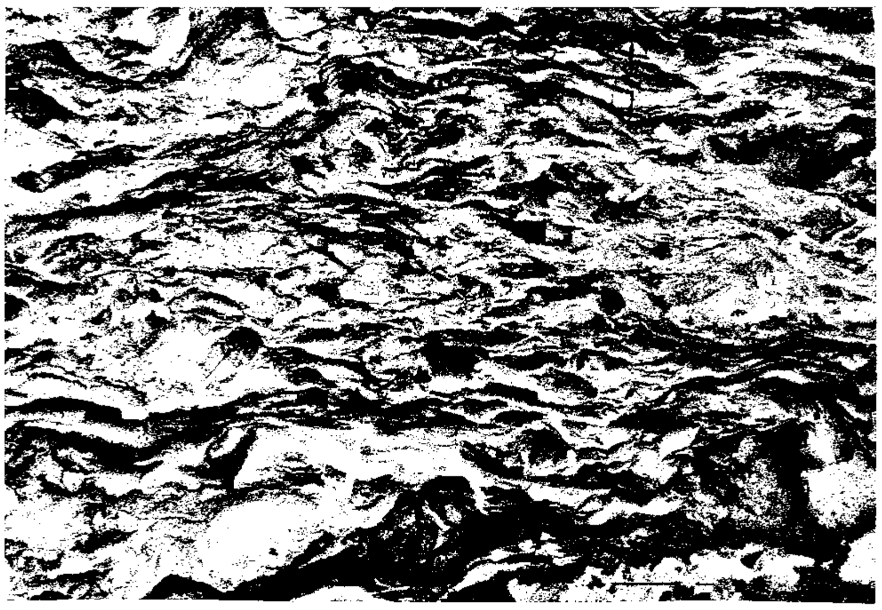

Figure 12— (HZ-29). Preferred orientation in this sample is apparent. Clay flakes are wrapped around the silt (quartz) grains. Left scale bar = 10μm.

Figure 13— (KH-4). The sediment exhibits moderate parallelism of platy minerals. Notice how the fossil fragments are making the fabric random, especially in the right corner of the photo. Left scale bar = 10μm.

The mixed-layer illite/smectite seems to be more or less regular (ordered) R1, containing 70% or more illite. One factor indicating "ordering" is the greater sharpness of illite peaks at high angles in case of EG-saturation. Moreover, a strong reflection is present at low diffraction angle, near 6.2° (2Ø) (Figures 10 and 11) which contains a dominating component of the second-ordered superstructure reflection (002), whereas, randomly stratified layers show reflection near 5° (2Ø) (Moore, 1989).

The illite/smectite content of the mixed-layers seems to be comparatively higher than chlorite/smectite fraction (Figure 10) in Margala Hills' samples (HZ-21 to HZ-28) but the situation is reversed in the specimens taken from further north, where the samples (HZ-42 to HZ-45) are comparatively rich in corrensite (Figure 11).

Electron Microscopic Analysis

In the present study an attempt has been made to identify small textural and structural features of the sediments to understand and identify the depositional and post-depositional environments. For this purpose six representative samples have been analyzed and photographed. The results obtained are as follow:

Preferred Particle Orientation.— Most of the sediments under study, macroscopically, seem not to be well-laminated. However, some samples show moderate preferred particle orientation for example HZ-29, which contains about 70% clay minerals. The orientation, probably was produced upon sediment compaction by reorientation of flocculated clay (Figure 12). The SEM micrograph indicates that silt content has influenced the rock fabric, making it random at places. Parallelism of clay minerals can also be observed in Figure 13, where microfossils have played a part in disrupting the parallel fabric.

Random Particle Orientation.— The SEM microphotograph (Figure 14) of a sample from Hazara area is showing dominant random particle orientation with no evidence of bioturbation in hand specimen. This randomness might have been produced by rapid deposition of flocculated clays, or high salinity of depositional environments (?).

Fossil Fragments and Other Features.— The sediments collected from Khairabad section contain microfossils (Figure 15), mainly planktonic foraminifera (*Globigerina sp.*?). The fossils, embedded in finely crystalline micritic calcite, are poorly preserved (Figure 16).

Microscopic examination reveals well rounded and well sorted (silt-size) quartz particles cemented by crystalline calcite cement (Figure 17). The frosty and pitted surface on quartz grain is an indication of mechanical weathering. In intrabiotic empty chambers of the forams, euhedral calcite crystals can develop. In SEM micrograph of sample KH-9, probably such a chamber filling by calcite cement and calcite overgrowth have occurred (Figure 18). In SEM photograph of a sample (KH-6) from Khairabad section (Figure 19), a distinctive "worm-like" morphological feature seems to be an organic remnant (?).

DISCUSSION

For the study of mud rocks, X-ray diffraction analysis is the basic tool to determine the nature and properties of clay minerals present. Clay mineral analysis further leads to construction of the likely provenance of the sediments, the conditions of deposition, paleoclimate, diagenesis and burial history.

In the following section, a brief attempt has been made to interpret the environmental conditions of the sediments during deposition and their diagenetic history. A full review is not intended and also not possible due to lack of sufficient data and other relevant information.

Distribution and Lateral Variations of Clay Minerals

There are differences in the grain size of the clay minerals which affect their distribution in a sedimentary basin. These variations can be used to determine the regional distribution of clays within a sedimentary basin and to infer the direction of sediment transport and distance from source area. Figure 20 illustrates the generalized picture of lateral variations in clay assemblages (Parham, 1966). One or more of the clay mineral groups may be absent from a given sediment but the general relationship remains the same. However, this generalized concept may not hold for some data where exceptions are present which do not agree entirely with the concept. The reasons for such exceptions may be presence of more than one source area, or the origin of clays and the diagenesis which also accounts for the lateral variations.

The presence of kaolinite in samples from Khairabad section (western Salt Range) and its absence in samples from Hazara area might be an indication of basinward decrease in its amount. The increase in amount of illite, chlorite and presence of corrensite and mixed-layer illite/smectite are well in accordance with the model presented in Figure 20 and indicate northward deepening of the basin.

Environments of Deposition

In the present study, the presence of marine fossils (planktonic forams; Figures 15 and 16) in Khairabad

Figure 14— (HZ-25). This micrograph shows randomness of clay fabric plus some individual flakes. Massive detrital illite is mainly composed of irregular clay particles with curved edges.

Figure 15— (KH-6). SEM micrograph shows planktonic foraminifera (*Globigerina sp.* ?) test, observed to be very common in most of the sediments of Khairabad section. Small calcite crystal growths can be seen in test pores. Left scale bar = 10μm.

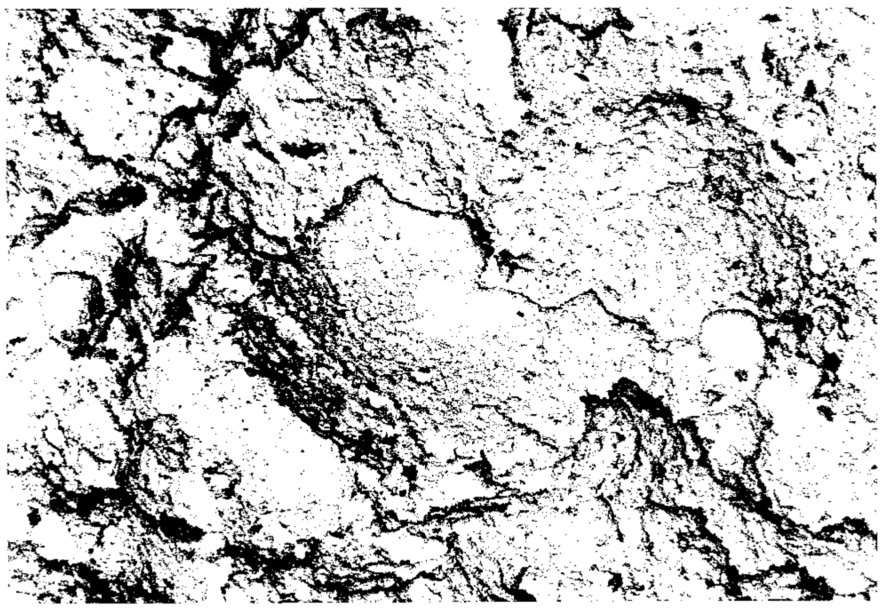

Figure 16— (KH-6). Micrograph shows the characteristic random fabric due to abundant biogenic (mostly planktonic forams) and lithogenic fragments.

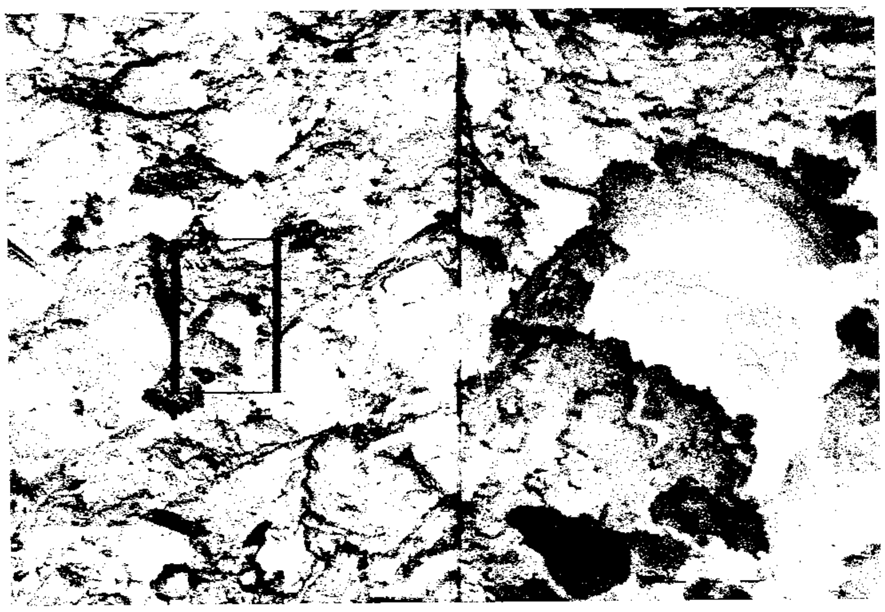

Figure 17— (KH-9) The micrograph shows well-rounded, silt-size quartz grain embedded in calcite cement. Large, well-preserved euhedral dolomite crystals in calcite matrix probably indicate late dolomitization of calcite diagensis (?). Left Scale 10μm (for left half of the scale).

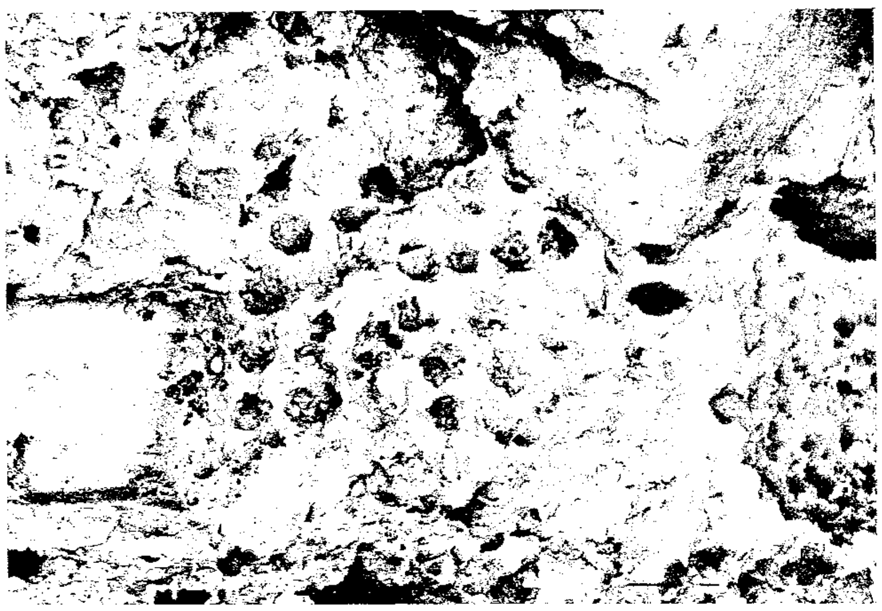

Figure 18— (KH-9). Enlarged area of a foram chamer (?) partly filled with euhedral calcite crystals. Left scale bar = 10μm.

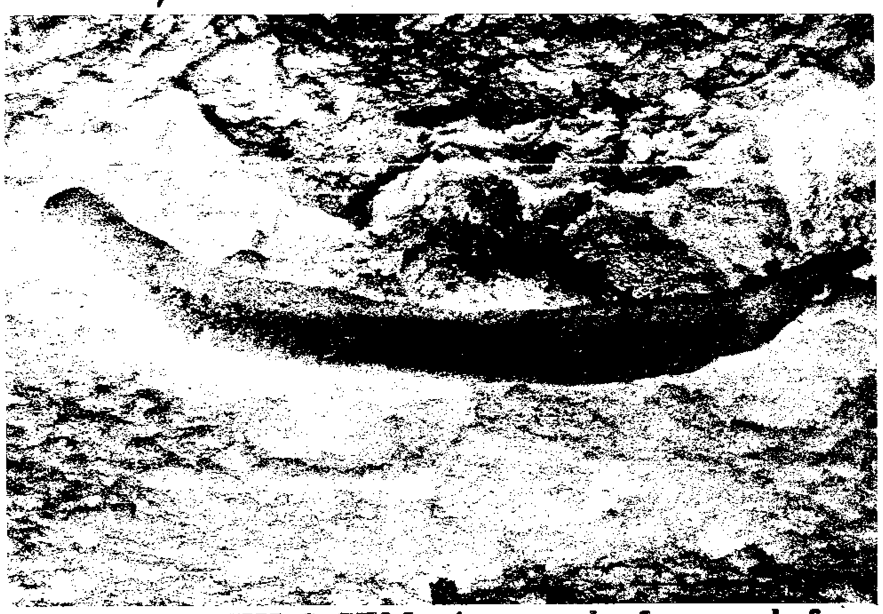

Figure 19— (KH-6) SEM micrograph of a sample from Khairabad section, showing a distinctive "worm-like" morphological feature which seems to be an organic matter remnant (?). Left scale bar = 10μm.

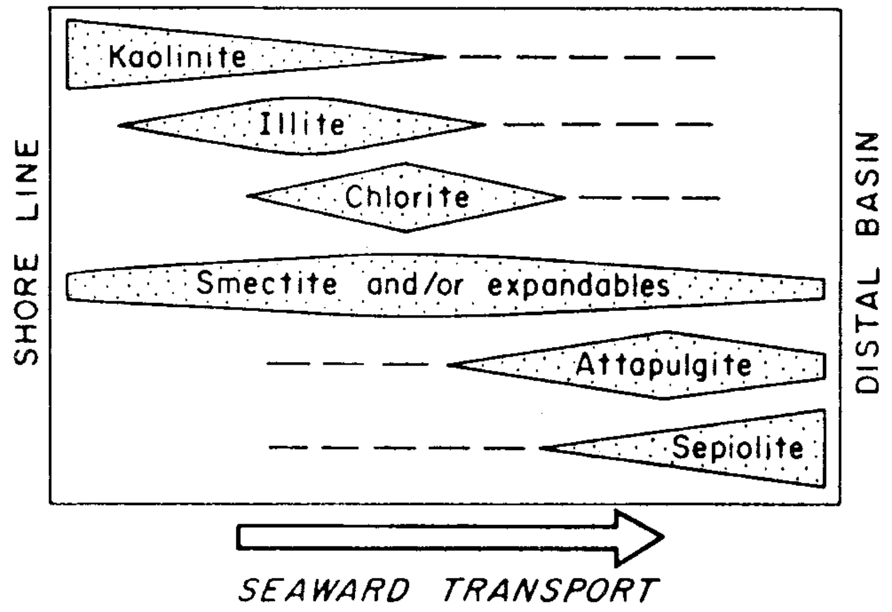

Figure 20— Schematic variation of clay minerals from shoreline to deep, distal basin. (Redrawn from Parham 1966, Figure 6).

section clearly indicates the marine environments. The presence of dolomite in upper part of the formation suggests the shallowing upward conditions in the area.

Diagenesis

After deposition, argillaceous sediments undergo important mineralogical, geochemical and physical changes. In the burial diagenetic environments, there is a progressive alteration of clay minerals with rising temperature. The transformation and neoformation of clay minerals during burial diagenesis are not only a function of burial temperature but also of pore water chemistry, porosity and permeability.

In Khairabad section, the presence of kaolinite, though in very small amount, would be an indication of acid pore water environments at the initial stage of burial and later, most of it might have been transformed to illite or smectite which are stable in alkaline pore waters.

During burial diagenesis, smectite and vermiculites dehydrate and transform via intermediate mixed-layer clay phases to illite and/or chlorite depending on whether the alkaline pore waters are enriched in K^+ and/or Mg^{2+}. These changes are thought to occur progressively over the temperature range of 80 to 200°C (Shaw, 1985).

In Khairabad section, the presence of mixed-layer illite/smectite and in Margala Hills, chlorite/smectite + illite/smectite mixed-layers are the indications of intermediate phase of burial diagenesis. Whereas, the samples from northernmost section (HZ-46 to HZ-51), which contain mainly illite, represent the dehydrated end product of clay minerals and alkaline pore water environments enriched in K^+ ions. It also clearly indicates a gradual increase in the intensity of burial diagenesis northward.

Role of Clay Minerals in Hydrocarbon Generation

In the present study, most of the samples contain organic matter ranging from 0.5 to 1.2% which may rank the formation as a fair source rock, depending upon the kerogen type. In addition, these shales contain a considerable amount of swelling clays (smectite/montmorillonite) which might have acted not only as a catalyst generating hydrocarbons but also might have facilitated in the migration of oil and gas in Potwar basin.

In Hazara area, apparently, the deeper burial would have produced condensate and eventually the gas, as the vitrinite reflectance values measured from sediments of Hazara area by BGR (Hannover), are considerably high. Further more, little water would have been available due to gradual decrease in swelling clay quantity and increase in illite proportion northward. However, the greater solubility of gases, which increases with increasing temperature and pressure, may mean that some of the gas might have been migrated in solution.

CONCLUSIONS

The mineral composition of Paleocene shales, both in western Salt Range (Khairabad Section) and Hazara area, varies slightly. The sediments from Salt Range area are mainly "calcareous claystones", whereas, the samples collected from Hazara area can be classified as "sandy claystones".

Total carbonate concentration in Salt Range samples ranges between 30 to 60%. In Hazara area, the calcite content in the sediments analyzed, ranges from <2% to 40%, whereas, nearly half of the samples contain less than 10%. Dolomite has been found in some of the samples from Khairabad section, especially in the upper part of the sequence. In one of the samples, the dolomite concentration is up to 35%. No dolomite content has been detected from Hazara area.

The quartz percentages (whole rock composition) in the sediments have been estimated by X-ray diffraction method. In most of the samples from Khairabad section, quartz content ranges from 15 to 18%, whereas in Hazara area its quantity ranges between 20 to 40%. The samples showing low calcite concentrations, generally contain high percentage of quartz fraction.

The organic carbon content determined in the samples, both from Salt Range and Hazara area ranges from 0.5 to 1.2%. These values are indicative of a fair source rock generative potential of the sediments, if type of organic matter is prone to hydrocarbons.

The clay mineral concentration in the sediments has been estimated indirectly using mainly XRD technique. The clay mineral percentages are relatively lower in calcareous claystones, mostly in samples of Khairabad section, as compared to Hazara area. The clay minerals in the Salt Range samples range from 40 to 50%, though, in few samples these are less than 30%. In Hazara area, the clay mineral concentration is higher ranging from 40% to 70%. All the samples from northernmost area show more than 60% of clay minerals.

The principal clay minerals identified in the < 2 micron fraction are mixed-layer illite/smectite, mixed-layer chlorite/smectite, illite, kaolinite and chlorite, in both the areas. In the Salt Range sediments, randomly stratified mixed- layer illite/smectite is dominant, small amounts of kaolinite and chlorite are also present. The sediments from Hazara area contain mainly corrensite (regular mixed-layer chlorite/smectite) and nearly regular mixed-layer illite/smectite. However, the samples belonging to northernmost section are mainly composed of illite and chlorite.

The lateral variation and distribution pattern of clay minerals point to a shoreward situation (shallow-marine) in western Salt Range area and basin-ward conditions (deepening) toward north, in Hazara area. A gradual increase of dolomite content in upper part of Khairabad section shows a shallowing upward sequence.

The clay minerals have also revealed the burial diagenetic history of the sediments indicating, probably acid pore water environments in early stage of deposition and increasing alkaline pore water conditions with increase in burial depth. Presence of mixed-layer clay minerals in southern and central part of the study area represents an intermediate phase of burial diagenesis, whereas, illite, the principal clay mineral present in northern part, is an indication of dehydrated phase. Evidently, the modification in clay mineral composition was controlled, to some extent, by increasing grade of burial diagenesis and tectonism towards north.

The sediments, in both the areas, contain a considerable amount of swelling clays (smectite) which might have acted not only as a catalyst generating hydrocarbons but also might have facilitated in migration of oil and gas in Potwar basin. In Hazara area, apparently, the deeper burial would have produced condensate and eventually the gas. Little water would have been available due to gradual decrease in swelling clays and increase in illite proportion northward. However, the greater solubility of gases, which increases with increasing temperature and pressure, may mean that some of the gas might have been migrated in solution.

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