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CHEMISTRY AND MINERALOGY OF SOME EOCENE AND ASSOCIATED LIMESTONES OF KOHAT DISTRICT,N.W.F.P.

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Very large deposits of limestone ranging in age from Jurassic to Eocene are found in Kohat area. X-ray, differential thermal analysis and chemical data are presented for the rock samples from different sections of Eocene, Paleocene and Jurassic. These limestones are mainly composed of calcite, dolomite and subordinate amounts of quartz, illite and sometimes kaolinite.

The complete absence of titania and small amount of quartz indicate that the sedimentation of limestone occured away from the shoreline. The Eh and pH conditions during the formation of these limestones have also been discussed.

INTRODUCTION

North West Frontier Province of Pakistan has enormous resources of limestone, but little efforts were made in the past to study the properties of these deposits which would have led to its proper utilization. The present paper deals with the mineralogy and chemistry of some of the Eocene, Paleocene and Jurassic Limestone deposits of Kohat District. They were studied by Eames[1] and Meissner *et al.* [2].

LOCATION AND ACCESSIBILITY

Kohat City is about 64 km. south of Peshawar. Togh Bala and Babri Banda are on Kohat – Rawalpindi Road and the Eocene Limistone outcrops are found along the road sides. In the south of Kohat, Shiwakki, Jatta, Banda Daud Shah, Jarma and Latambar are located. The Paleocene limestone outcrops at Handyside and the Jurassic at Narai Khadai both these places are north of Kohat on Kohat – Peshawar Road.

The terrain in general, is mountaineous but the hills are low lying.

GENERAL GEOLOGY OF THE AREA

Jurassic to Paleocene age rocks are found in Kohat District. Rocks from Jurassic to Paleocene are exposed in the northern and northwestern part of Kohat, whereas southern part has the exposure of Eocene to Paleocene. The Eocene formation comprises of limestone, clay, salt and gypsum. The rocks are tightly folded and form low-lying hills. These hills and ridges are separated by valleys. General strata is E-W and dip is towards north. The stratigraphic succession of Kohat area as given by Siddiqi[3].

The present investigation deals with Habib Rahi member of the Kohat Formation, Lockhart limestone (Paleonce) and Samana Suk limestone (Jurassic). A brief account of these groups is given as follows:

Kohat Formation. The Kohat shales of Eames[1] with their three sub-divisions "Nummulitic Shales," "Kohat Limestone" and "Sirki Shales," were formally accepted as Kohat formation by the Stratigraphic Committee of Pakistan. The Kohat formation has been sub-divided into the following three members:

Upper part.	1. Habib Rahi member	Limestone.
Middle part.	2. Sadkal member	Limestone and shale.
Lower part.	3. Kaladhand member	Shale and limestone.

The present investigation has been confined to Habib Rahi member of the Kohat formation.

The formation is located at Kohat, northern Potwar and Kala Chitta areas. The formation had yielded abundant foraminifers and few molluses (Eames) [1]. Meisner *et al.* [2] include Assiline Concellata, Dictyocoroids Verdenburgi, Fasciolites oblonga, Orbitolites, Complantatus and various species of Nummulites. The fauna indicates a late Early Eocene to Middle Eocene age.

Lockhart Limestone. Davies[4] introduced the term Lockhart limestone for a Paleocene limestone unit in the Kohat area and this usage has been extended by the Stratigraphic Committee of Pakistan to similar units in the other parts of the Kohat, Potwar and Hazara area. This unit thus represents the Nummulitic series of Middlemiss[5], the

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STRATIGRAPHY

Age	Group / Formation		Average thickness	Lithology
Pliocene	Siwalik	Dhock Pathan Fm.	5500′	Sandstone, clay, conglomerate.
		Nagri Fm.	5750′	Sandstone, conglomerate, clay.
		Chinji Fm.	3100′	Sandstone, claystone, siltstone.
Miocene	Rawalpindi	Kamlial Fm.	1865′	Sandstone, clay, claystone.
		Murree Fm.	335′	Sandstone, conglomerate.
Eocene	Cherat	Kohat Fm.	550′	Limestone
		Mamikhel clay	230′	Clay, conglomerate.
	Shekhan Lst.	Jatta Gypsum	205/100′	Limestone/Gypsum
	Panoba shale.	Bahadurkhel salt.	403/320′	Shale/Salt.
Paleocene	Patala Fm.		420′	Shale, nodular limestone
	Lockhart Lst.		340′	Limestone
	Hangu Fm.		400′	Sandstone, limestone.
Cretaceous	Darsmand Lst.		300′	Limestone.
	Lumshiwal Fm.		380′	Sandstone.
	Chichali Fm.		90′	Sandstone.
Jurassic	Samana Suk Lst.		505·	Limestone.
	Datta Fm.		1180′	Limestone.

lower part of the "Hill Limestone" of Wynne[6] and Cotter[7], the "Khairabad Limistone" of Gee[8] "Tarkhobi Limestone" of Eames[1] and "Mari Limestone" of Latif [9]. The limestone is generally bituminuous and gives off fetid odour on a fresh surface.

The limestone contains abundant foraminifers, corals, molluses, echinoids and algae.

Samana Suk Formation. Davies[4] introduced the name Samana Suk for the Jurassic limestone in Samana Range. The name has been extended to include similar limestone sequence in the Salt Range and Trans-Indus Ranges. In Hazara, Kala Chitta and eastern Kohat, it is thin to thick bedded, and includes some dolomitic and ferruginous sandy and oolitic beds. Brachiopods bivalves, gastropods, ammonoids and crinoids have been reported from the limestone. The formation is correlated with the Chiltan limestone and Mazar Drik formation of lower Indus Basin.

DESCRIPTION OF LOCALITIES

The limestone used in the present investigation were collected and described by Siddiqi[3] (Fig. 1).

He measured the sections and collected samples at an interval of 3 and 15 metres. Composite samples were prepared for the chemical and mineralogical investigations.

FK1 : Togh Bala Section. It is 6.5 km from Kohat on Kohat – Rawalpindi Road. The thickness of Eocene Limestone is 33.5 metres. It is medium bedded, highly fossiliferous, medium to fine-grained creamy limestone. Calcite veinlets are common.

FK2: Babri Banda Section. Babri Banda is 8.0 km from Kohat on Rawalpindi Road. Small exposures of Eocene limestone are found on both sides of the road. Sampling and measurement were conducted on the southern exposure of the road. Dipping at the roadside is almost vertical and towards south it is gentle. Limestone is creamy in colour, highly fossiliferous, medium to thick bedded. Calcite veinlets are very common.

FK3: Shiwakki Section. Shiwakki village is about 8 km east of Jatta, at a distance of about 32 km from Kohat. East of Jatta Salt Quarries, section was measured in Shiwakki gorge. The limestone is 41 m thick, grey to pink in colour. It is thin to thick bedded, having intercalations of yellowish marl. Middle zone is highly fossiliferous.

FK 4: Jatta Diversion Section. Eocene rocks are exposed on Kohat – Bannu Road near the diversion from main road to Jatta salt mines. The thickness of the limestone beds is 15 metres.

FK 5: Banda Daud Shah Section. Banda Daud Shah is about 48 km from Kohat on Kohat – Bannu Road. Two

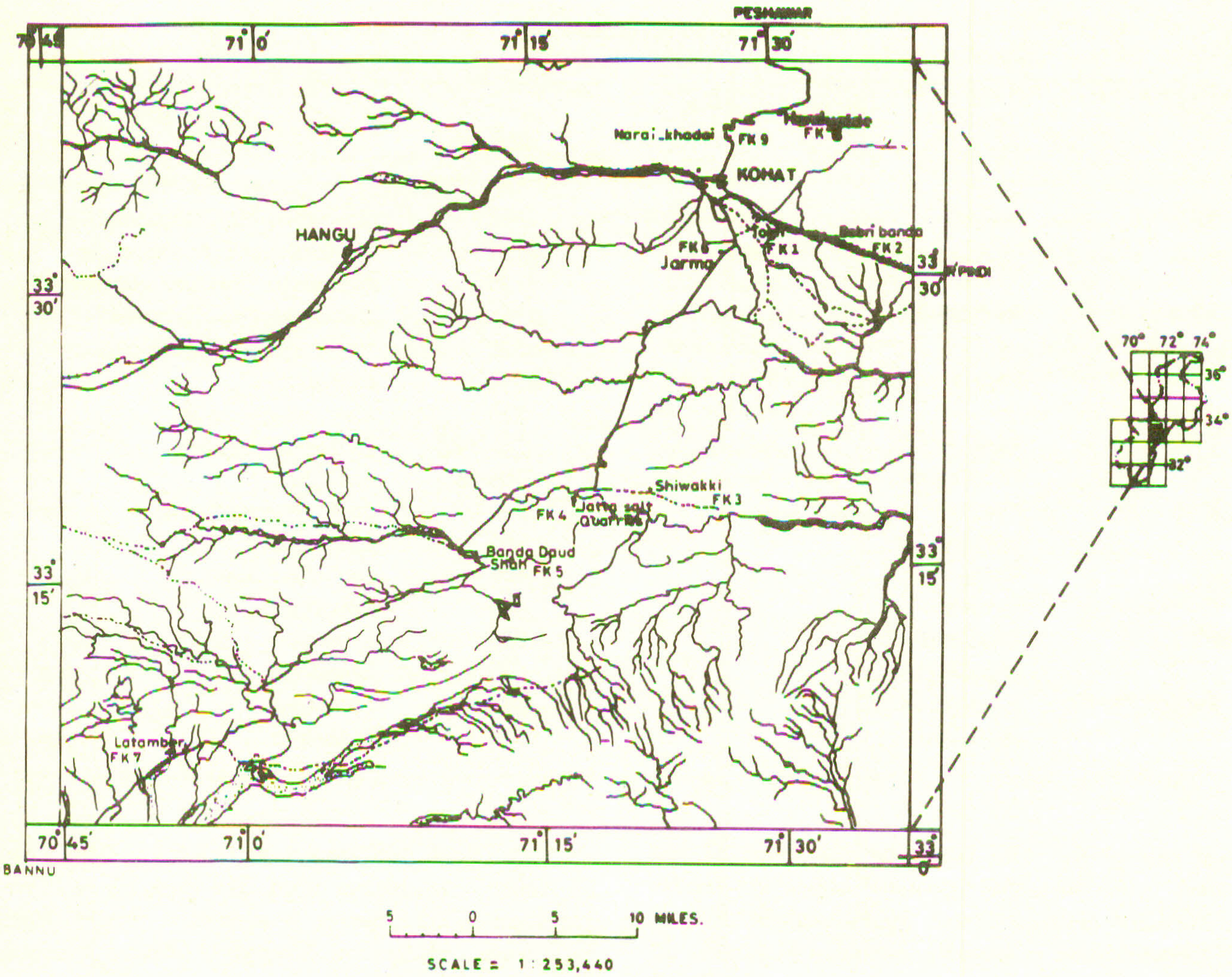

Fig. 1. Location map.

sections of Eocene rocks were examined.

EK 5 a: About 1.5 km towards east of Banda Daud Shah Dak Bungalow (Gorga Section). The thickness of the limestone beds is 24 metres. It is highly fractured and nodular.

FK 5 b: Along the road side at Banda Daud Shah – Kohat Road. It is highly fractured light grey limestone. The thickness of limestone bed is 26 metres.

FK 6: Jarma Section. This section is about 8 km from Kohat on Bannu Road. Limestone is thick bedded, light grey to brownish grey, highly fossiliferous, and medium grained. The thickness of the limestone beds is 36.5 metres.

FK 7: Latambar Section. The last exposure of Eocene Limestone on Kohat Bannu Road is at Latambar, about 72 km from Kohat. The thickness of limestone is 32 metres.

FK 8: Handyside Section. A section of 30.5 metre thick Lockhart limestone is exposed at about 6.5 km from Kohat on Kohat – Peshawar Road. It is light grey, nodular to massive and medium crystalline. Fresh surface is of dark grey colour and gives fetid odour. Thin marly zones are interbedded. Calcite veinlets are common. The upper contact is conformable with Patala Shales.

FK 9: Narai Khadai Section. The Jurassic limestone is exposed in the north of Kohat town, extending from east to west for about a distance of 64 km. A section, 5 km from Kohat on Kohat – Peshawar Road was sampled. Here the thickness of the Jurassic limestone is 696 metres which is due to the repeatition of strata by folding. It is grey to dark grey in colour, dense to coarsely crystalline and cliff forming.

EXPERIMENTAL

X-ray photographs were taken with 114.6 mm. diameter Debye-Scherrer, Camera using Cu-Kα radiation. DTA was carried out with a uniform rise of temperature of the furnace (10° per minute). DTA curve was recorded on a Servogor S recorder. Chemical analyses were made following the classical methods and methods given by Riley[10].

RESULTS

X-ray Diffraction. 9 samples were examined by X-ray diffraction technique. Table 1 shows spacings and relative intensities, estimated by visual inspection from powder photographs of typical samples FK 3 (Eocene), FK4 (Eocne), FK 8 (Paleocene) and FK 9 (Jurassic). Table 2 gives the summary of the minerals identified in each sample. All the samples gave reflections of calcite (d = 3.03, 2.28, 2.09 and 1.87). The strongest reflection 2.88 A° of dolomite is present in samples FK 4, FK 5a and FK 9. Similarly the strongest quartz reflection of 3.33 A° is present in all except FK 1, FK2 and FK 5b.

All the samples were treated with 1:1 HCl solution. The results of the acid insoluble fraction examined by X-ray diffraction are summarised in Table 3. the sample FK 8 (Paleocene) contains only quartz. The rest of the samples contain quartz and illite. A very small amount of kaolinite seems to be present in samples FK 3, FK 5a, FK 5b and FK 7.

Table 1. X-ray diffraction data for FK 3, FK 4, FK 8 and FK 9

FK 3		FK 4		FK 8		FK 9	
dA°	I	dA°	I	dA°	I	dA°	I
3.86	30	3.85	30	3.85	20	3.86	20
						3.69	1
3.36	10	3.35	10	3.33	5	3.35	10
3.02	100	3.02	100	3.03	100	3.03	100
2.84	10	2.88	10			2.88	50
		2.67	½			2.67	2
2.49	40	2.49	40	2.49	30	2.49	40
						2.40	3
2.28	50	2.28	60	2.28	40	2.28	45
		2.19	1			2.19	20
2.09	50	2.08	60	2.09	30	2.09	40
		2.01	1			2.01	10
1.91	60	1.91	70	1.91	40	1.91	40
1.87	60	1.87	70	1.87	40	1.87	40
		1.80	½			1.80	10
						1.79	10
1.62	10	1.62	15	1.62	5	1.62	5
		1.60	30	1.60	10	1.60	10
1.52	10					1.54	2
1.51	2	1.52	20	1.51	10	1.51	8
1.47	10	1.46	20			1.46	5
1.44	20	1.43	30	1.43	10	1.44	10
1.42	15	1.41	25	1.41	10	1.42	5
						1.39	1
1.35	5	1.35	10			1.33	5
1.34	5	1.33	15	1.29	5	1.29	5
1.29	10	1.29	20			1.23	5
1.24	2	1.23	10			1.18	2
1.23	5	1.18	10	1.18	2		
1.18	10	1.15	20	1.15	2	1.15	2
1.15	10	1.14	10			1.14	2
1.14	5						

Table 2. Summary of minerals detected by x-ray diffraction.

FK 1	FK 2	FK 3	FK 4	FK 5a	FK 5b	FK 6	FK 7	FK 8	FK 9
Calcite	Calcite	Calcite Quartz	Calcite Dolomite Quartz	Calcite Dolomite Quartz	Calcite	Calcite Quartz	Calcite Quartz	Calcite Quartz	Calcite Dolomite Quartz

Table 3. Summary of minerals detected in-acid-in soluble fraction.

FK 1	FK 2	FK 3	FK 4	FK 5a	FK 5b	FK 6	FK 7	FK 8	FK 9
Quartz Illite	Quartz Illite	Quartz Illite Kaolinite	Quartz Illite	Quartz Illite Kaolinite	Quartz Illite	Quartz Illite	Quartz Illite Kaolinite	Quartz	Quartz Illite

Table 4. Chemical analyses of limestone.

	FK 1	FK 2	FK 3	FK 4	FK 5a
SiO_2	0.70	1.30	1.00	4.40	2.40
Al_2O_3	1.90	1.70	2.49	2.24	2.05
Fe_2O_3	0.60	0.40	0.01	0.80	0.80
TiO_2	Nil	Nil	Nil	Nil	Nil
CaO	50.23	50.96	53.30	42.68	43.50
MgO	3.60	2.8	0.60	7.75	8.40
Na_2O	0.14	0.12	0.23	0.16	0.16
K_2O	0.14	0.08	0.05	0.12	0.22
P_2O_5	0.18	0.12	Trace	0.16	0.22
MnO	Nil	0.03	Trace	0.04	Nil
L.O.I	43.25	43.06	42.20	41.94	42.15
TOTAL:	100.74	100.61	99.88	100.23	99.90

	FK 5b	FK 6	FK 7	FK 8	FK 9
SiO_2	1.10	2.60	0.80	0.72	3.17
Al_2O_3	1.10	1.56	2.55	2.30	4.22
Fe_2O_3	0.50	0.40	0.30	0.60	1.20
TiO_2	Nil	Nil	Nil	Nil	Nil
CaO	51.52	49.22	50.63	52.13	41.64
MgO	2.6	3.20	2.00	1.60	7.60
Na_2O	0.12	0.12	0.12	0.15	0.16
K_2O	0.15	0.07	0.08	0.08	0.22
P_2O_5	0.22	0.14	0.12	0.35	0.22
MnO	0.03	0.00	0.03	0.07	0.03
L.O.I.	43.12	42.06	43.35	42.2	42.04
TOTAL:	100.8	99.37	99.98	100.8	100.80

Table 5. Calculated mineral composition.

Normative minerals	FK 1	FK 2	FK 3	FK 4	FK 5a	FK 5b	FK 6	FK 7	FK 8	FK 9
Calcite	80.30	83.87	93.50	57.00	55.50	85.00	79.60	85.40	88.20	54.50
Dolomite	16.56	12.88	2.76	34.96	38.64	11.96	14.72	9.20	7.34	34.96
Apatite	0.40	0.27	Nil	0.37	0.50	0.50	0.33	0:27	0.84	0.50
Muscovite	1.19	0.64	0.40	1.03	1.59	1.27	0.56	0.64	0.80	1.83
Paragonite	Nil	1.53	Nil	1.99	1.99	1.53	1.53	Nil	Nil	1.99
Chlorite	0.17	Nil	Nil	0.62	0.32	Nil	0.31	0.23	0.47	0.99
Quartz	0.04	0.09	0.84	2.78	1.75	Nil	1.51	0.42	0.21	1.10
Al_2O_3	1.44	0.84	2.31	2.05	0.63	Nil	0.70	2.30	2.04	2.58
Na_2O	0.14	0.12	0.23	0.16	0.16	0.12	0.12	0.12	0.15	0.16
TOTAL:	100.24	100.25	100.04	100.96	101.08	101.38	99.39	98.20	100.05	98.61

Differential Thermal Analysis. The DTA curves of the nine samples gave the strong endothermic peaks at about 950°. The $MgCO_3$ endotherm appears only in samples FK4, FK 5a and FK 9. Jehan *et al.*[11] have already shown that the endothermic peak of $MgCO_3$ does not appear below 30% dolomite. The Paleocene limestone FK 8 shows a broad exothermic curve with a peak at about 365° due to the oxidation of organic matter. The DTA curves of the typical samples FK 3, FK 4, FK 8 and FK 9 are given in Fig. 2.

Chemical Analysis. The chemical analyses of the 9 samples are given in Table 4 and the calculated norms in Table 5. A plot of chemical changes (Fig. 3) shows no correlation between the elements.

The calculated composition have been worked out on the assumption that phosphorous is located in apatite, $Ca_5(PO_4)_3(OH)$. Magnesium is located in dolomite, $CaCO_3$ $MgCO_3$. The lime left over after forming apatite and dolomite gives the figure for calcite ($CaCO_3$). The potash is present as muscovite $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$ and soda as paragonite $Na_2Al_4(Si_6Al_2)O_{20}(OH)_4$. When silica is

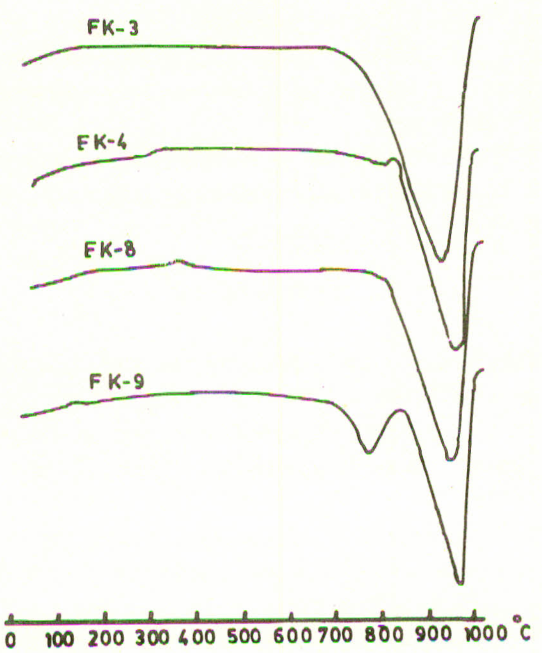

Fig. 2. The DTA curves of samples FK3, FK4, Fk8 and FK9.

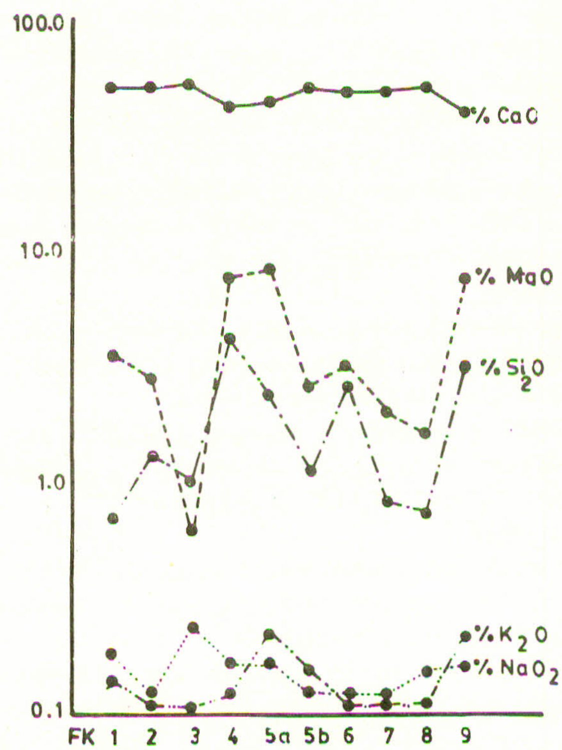

Fig. 3. Semilogarithmic plot of the major of the limestone.

insufficient to form paragonite, soda is reported as Na_2O. Small amount of iron has been reported as chlorite, $Fe_{12}Si_8O_{20}(OH)_{16}$. The silica left over after forming silicates is reported as quartz and the alumina as excess Al_2O_3.

The calcite content of Eocene limestone varies between 55.5% and 93.5% dolomite content waries between 2.76 and 38.64 %. The calcite content of Paleocene and Jurassic limestone are 88.20 and 54.5 % respectively, and dolomite content 7.34 and 34.96%.

The amounts of quartz in all the samples are low and varies between nil and 2.78 %. The muscovite (or illite) content of the samples varies between 0.4 and 1.83 %.

DISCUSSION

Among the Eocene limestones of Kohat, the presence of folomite in FK 4 and FK 5 (a) is confirmed by X-ray and DTA examinations. Similarly the Jurassic limestone (FK 9) also contains sufficient amount of dolomite. The x-ray and DTA do not indicate the presence of dolomite in other samples. The normative calculation shows that the $MgCO_3$ content varies between 1.26 % and 7.55%; Calcite, however, ordinarly can contain only 1 or 2 % $MgCO_3$ in solid solution. Thus most of the samples contain some amount of dolomite admixed with calcite.

The variable amount of dolomite may have originated either biochemically or chemically. Higher amount of dolomite at Jatta Diversion Section, Banda Daud Shah (Gogra) and Narai Khudai may be the effect structures such as faults[12] or folds[13].

The great difference in the amount of dolomite in the two sections of Banda Daud Shah (sample FK 5a and Fk 5b) may be due to paleogeography. Pettijohn[14] has mentioned that dolomite is more commonly a near-shore facies, and limestone is the product of off-shore and deeper water sedimentation.

The complete absence of titania and small amount of quartz indicate that the sedimentation of the limestone studied, occured away from the shore-line.

In the acid-insoluble fraction, quartz and illite seem to be common in all the samples. However, Shiwakki (FK 3) and Banda Daud Shah (FK 5a and FK 5b) also contain some kaolinite.

In a general way sediments are deposited under either oxidizing or reducing conditions. The measure of oxidizing capacity of the environment is the Eh, or the oxidation reduction potential. The absence of pyrite in the limestone apparently indicates that there was probably a normal marine open-circulation environmnet. The presence of large amounts of calcite indicate alkaline conditions, pH probably ranging between 7.5 and 8.0 and Eh remained near zero. Small amount of organic matter is present in the Paleocene limestone (FK 8). Normal microbiological and scavenger action tends to destroy the organic residues which settle to bottom. Inhibition of such action due to oxygen deficiency leads to the presence of organic matter in sediments. Therefore, it is suggested that the Eh during the sedimentation of FK 8 was most probably within the range 0 to 0.35 volts (Krumbein and Garrels) [15].

In the study of ancient sediments it is only possible to suggest the relative rate of sedimentation. The geological approach is by evaluating the rates at which different types of sedimentary materials have been deposited. Schuchert [16] has derived that the rate of sedimentation of limestone is about 14cm/1000 years. This rate is for shallow water deposits, and thus similar rate of sedimentation could probably be suggested for the Eocene, Paleocene and the Jurassic sediments.

Siddiqi[3] has estimated that Kohat area contains about 7000 million tons of Eocene limestone, 20,000 million tons of Paleocene limestone and 15,000 million tons of Jurassic limestones. Besides these 42,000 million tons, about 1000 million tons of Cretaceous limestone also occur in this area but has not been included in the present investigation. Thus great prospect lies for industries based on limestones such as cement and soda ash. The first cement plant is under construction at Babri Banda. The limestones of the Jatta Diversion Section (FK4), Banda Daud Shah (FK 5a) and the Jurassic limestone at Narai Khudai (FK 9) contain objectionable amount of dolomite and thus are not suitable for the production of ordinary portland cement. These limestones may be used advantageosly as an agricultural limestone especially on soils developed on Siwalik sandstones.

Efforts may be made to establish soda ash industry in the Kohat area as the other raw material common salt also occur nearby.

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