

CHEMISTRY AND MINERALOGY OF LITHOMARGES FROM THE AREA AROUND AGARIA, SIHORA TALUKA, JABALPUR DISTRICT, MADHYA PRADESH, INDIA

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ABSTRACT : DTA, XRD and IR spectroscopic studies of the lithomarges from the area around Agaria, Jabalpur district, Madhya Pradesh, have shown that they are predominantly made up of kaolinite group of clay minerals including kaolinite, dickite, halloysite and fire-clay variety of kaolinite. Chlorite and smectite group of minerals and iron minerals like goethite occur in minor quantities. The lithomarges have resulted from the weathering of argillites of Precambrian age, under tropical wet-dry climatic conditions. Absolute and relative accumulation of iron has given rise to the ferricrete in upper horizons, while relative enrichment of aluminium in the lower horizons has led to the formation of lithomarges. The lithomarges show good refractory properties. Low iron and titanium oxides and alkalies content make them suitable for use as refractory materials, foundry molds, etc. Kaolins which form major portion of the lithomarges are poorly crystallised and moderately stacked. This make them suitable for use in paper industry.

INTRODUCTION

In recent years there has been an increased use of clay and related minerals in modern industries for various purposes which necessitates precise identification of the clay minerals along with proper characterisation of the clay deposit. Precise identification of clay minerals can be done by X-ray diffraction (XRD), infrared spectroscopic (IR) and differential thermal analytical (DTA) studies. Clay mineralogical characterisation of the lithomarges occurring in the area around Agaria, Sihora taluka of Jabalpur district, Madhya Pradesh, has been done by the XRD, IR and DTA techniques, as these clay deposits are being reported for the first time. In the present paper an attempt has been made to discuss the genesis of the lithomarges in the light of clay mineralogical and physico-chemical data.

PHYSIOGRAPHIC SETTING

The area around Agaria (Fig. 1) is included within the Survey of India topographic sheet No. 64 A/3. The area is located at about 30 kms to the NE of the

township of Jabalpur. It experiences tropical wet-dry climate and receives heavy rains during the period from July to September the mean annual rainfall being 1500 mm. In summer, the temperature may rise upto. 46° C, while it may fall down to 5° C in winter. The region, more or less a flat terrain with a few isolated ENE-WSW trending ridges, is drained by the Hiran river and its tributaries, the most prominent being the Barne river. Southern fringes of the region show rugged hills with steep to moderate slopes.

GEOLOGY OF THE AREA

Northern part of the Jabalpur district of Madhya Pradesh, shows the presence of Vindhyan rocks, while in its southern part are exposed the Upper Gondwana sediments. The north-central portion of the district exposes the Precambrian supra-crustal (Naqvi and Rogers, 1987) rocks which show lateritic capping.

The sandstones and clays of the Jabalpur Formation of Gondwana Supergroup are well developed in the area around Jabalpur.

These rocks are seen to rest upon gneisses schists and granites which occur as a narrow strip extending northeastwards from the township of Jabalpur. The Jabalpur formation is overlain by a thick sedimentary sequence of the Lameta Formation and basaltic lava flows.

In the area around Agaria, Precambrian metasediments comprising of phyllites, quartzites and banded iron formations are exposed. These rocks, at a number of localities, show varying degrees of lateritisation. The ferruginous argillites show maximum lateritisation and are weathered to a considerable depths, sometimes exceeding 20 metres. The upper 1.0 to 1.5 m thick lateritic duricrust is followed downward by a 10 to 20 m thick mottled horizon of lithomarges of variagated colours. This horizon is seen to grade into pallid horizon which overlies the bed rock (Fig. 2). The

lithomargic horizon shows a variety of colours like white, yellowish white, light yellow, pinkish white, pink, etc.

PHYSICO-CHEMICAL PROPERTIES OF CLAYS

Systematic sampling of the lithomarges from the area under study was carried out. Sample locations are shown in Fig. 1. Representative samples of the lithomarges were powdered, coned and quartered for further laboratory studies.

The lithomarges under study have been physically examined. Some important physical properties are presented in Table 1. The lithomarges show relatively high bulk density and specific gravity values, low apparent porosity and low shrinkage characters. This indicates that the clays form a reasonably good refractory material.

TABLE 1

Some physical properties of the Agaria clays, Jabalpur district, Madhya Pradesh

Sr. No.	Name of Clay Deposit	Colour	Specific Gravity	Bulk Density gm/cc	Apparent porosity (%)	Plasticity	Shrinkage (%)
1	Gidurana	Pinkish white	2.55	2.15	16.01	Plastic	11.0
2	Jhiti	White/ Cream	2.51	2.17	13.45	Plastic	9.0
3	Barne	White/ Cream	2.59	2.08	19.80	Plastic	10.0

Table 2 presents pH, electrical conductivity (EC), cation exchange capacity (CEC) and pyrometric cone equivalent (PCE) data for the clays under study. The CEC values of 14.6 to 15.6 meq/100 gram are indicative of poorly ordered kaolins. It has been shown that the CEC has a direct relation-

ship with crystallinity of kaolins. According to Jackson (1958) CEC for kaolins varies between 10 to 15 meq/100 grams. Higher CEC values indicate poorly ordered kaolins as there are more exposed charge-sites for exchange to take place (Murra and Lyons, 1960; Grim, 1968).

TABLE 2

pH, EC, CEC and PCE values for the Agaria clays, Jabalpur district, Madhya Pradesh.

Sr. No.	Name of Clay Deposit	pH	EC (mmhos/cm ²)	CEC (meq/100 grams)	PCE
1	Gidurana	7.3	0.240	15.1	28.0
2	Jhiti	7.2	0.241	15.2	29.0
3	Barne	7.4	0.255	14.6	28.0

EC : Electrical Conductivity

CEC : Cation Exchange Capacity

PCE : Pyrometric Cone Equivalent

The clays have been analysed for major elements using a 1275 Varian Atomic Absorption Spectrophotometer. The chemical data for clays presented in Table 3, have revealed that the clays are highly aluminous. The amount of Al₂O₃ ranges from 28.52 to 34.32 per cent. This suggests that the clays have very good refractory characters. The silica content ranges from 48.10 to 54.20 per cent which is rather little high. This may be partly due to the presence of free silica in the clays. However, it is a relatively inter constituent and acts as diluent in the clay. The presence of iron oxide in the clay is undesirable as it greatly affects the refractory properties. However, the present clays contain relatively lower Fe₂O₃ (2.16 to 3.52 per cent) amount which indicates that the clays may form a good refractory material. The alkalis content of the clays is very low, while TiO₂ content is little higher in the range of 2.32 to 3.04 per cent. However, this does not affect the refractory properties of the clays as alkalis and titanium act as flux.

TABLE 3

Chemical data for the Agaria clays, Jabalpur district, Madhya Pradesh.

Oxide	Gidurana clays		Jhiti clays		Barne clays	
SiO ₂	48.50	52.10	49.30	48.10	51.88	54.20
Al ₂ O ₃	34.32	28.52	32.52	33.85	30.74	28.52
Fe ₂ O ₃	2.24	3.52	2.16	2.20	2.24	2.36
TiO ₂	2.32	3.04	2.88	2.76	2.66	2.76
CaO	Traces	Traces	Traces	Traces	Traces	Traces
MgO	0.36	0.38	0.79	0.80	0.34	0.35
Na ₂ O	0.15	0.17	0.16	0.16	0.35	0.35
K ₂ O	0.10	0.12	0.12	0.11	0.05	0.04
LOI	12.00	12.00	12.00	12.00	11.20	11.50
Total	99.98	99.85	99.93	99.98	99.46	100.08

LOI : Loss on ignition

The loss on ignition (LOI) of these clays is in the range of 11 to 12 per cent. The LOI has been considered to be one of the important characteristics of clays. On the basis of this total amount of kaolin minerals present in a clay mixture can be roughly estimated, although it may not be possible to ascertain individual proportion of the different mineral phases in the mixture. The weight loss of pure kaolinitic clay is 13.9 per cent. If this value is taken into consideration, it may be concluded that the amount of kaolin minerals present in the clays is over 70 per cent.

CLAY MINERALOGY

The lithomarges were studied by employing DTA, XRD and IR spectroscopic techniques, in order to know their clay mineral assemblage. The result of these analyses are presented in this section.

The differential thermal analysis (DTA) was carried out using a MOM derivatograph

in the temperature range ambient to 1000° C at a heating rate of 10° C per minute. Representative thermograms of the lithomarges under study are presented in Fig. 3. It is seen that the thermograms have two prominent endothermic peaks at 100°–120° C and 550° C and an exothermic peak at 960°–970° C. The thermogram (Fig 3) of the Barne lithomarge shows an additional endothermic peak at 800° C.

The endothermic peak between the temperature range 100° C and 120° C is generally related to dehydration of water sorbed on the surfaces of the clay particles. However, this peak along with the two other peaks at 550° C and 960°–970° C can also be ascribed to the presence of halloysite (Mackenzie, 1970). The endothermic peak at 550° C and the exothermic peak at 960°–970° C have been ascribed to the presence of fire-clay variety of kaolinite. According to Mackenzie (1970) the endothermic and exothermic peaks of kaolinite respectively lie in the temperature range of 550° C to 700° C and 950° C to 980° C. The exothermic peak has been explained as due to the crystallisation of a spinel phase (Smykatz-Kloss, 1974). The endothermic peak at 550° C has been due to dehydration and decomposition of the mineral structure. An endothermic peak observed at 800° C (Fig. 3) can be ascribed to vermiculite (Smykatz-Kloss, 1974).

The magnitude of these peaks varies with particle size as well as on the degree of disorder in the stacking of structural layers. Small peaks are associated with finer particle size and more disordered structures. In the present case, the peaks are of medium size indicating that the clays are relatively more disordered.

In order to know the structural state of the clays and other minerals that may be present in small quantities, the lithomarges were subjected to X-ray diffraction studies. The XRD studies were carried out on a Philips X-ray diffractometer using FeK α

radiation. From the X-ray spectra, it has been observed that the lithomarges under study are predominated by the minerals of kaolinite group with minor illite, vermiculite and chlorite.

On X-ray spectra Kaolinite has been identified at d-spacing values of 7.17, 4.186, 3.579, 3.376, 2.338, 2.064, 1.81 and 1.489°A. The presence of halloysite has been indicated by d-spacing at 3.34, 2.36, 2.06 and 1.481°A. Dickite and nacrite respectively have d-spacings of 7.15, 3.58, 3.099, 1.805 and 1.49°A, and 7.18, 4.13, 3.59, 2.32 and 2.03°A. The d-spacing values 4.29, 3.36, 2.39 and 1.42°A can be ascribed to the presence of illite, while vermiculite can be identified at 7.14, 4.25, 2.36, 2.06 and 1.82°A d-spacings (JCPDS, 1974a, b). The intensity and d-spacing of the peaks reflect the degree of crystallinity of clays. According to Patterson and Hosterman (1960) the degree of crystallinity of kaolinite varies with the proportion of other minerals present in a clay mixture. In the present case, the low peaks indicate that the kaolinite is poorly crystallised. Quartz, the only non-clay mineral, is identified on the X-ray spectra at d-spacing values of 4.26, 3.34, 2.817 and 1.453°A. This accounts for the presence of free silica in the lithomarges.

In order to supplement the DTA and XRD data and to identify other minerals that may be present in very small quantities, the clays were also studied with the help of infrared technique. The IR spectra of a mineral is one of the most characteristic properties and provides a fingerprint for identification of the minerals. The IR spectra of clays were obtained on a Perkin-Elmer Infrared Spectrometer 221, using Nujol as medium. The IR spectra of the representative samples are presented in Fig. 4. The IR analysis has revealed that the lithomarges are predominated by the presence of minerals of kaolinite group.

The minerals of smectite and chlorite groups, iron and aluminium minerals occur in very small quantities. The different mineral phases have been identified by comparing the wavenumbers for the mineral as given by Van der Marel and Beutelspacher (1976).

The kaolinite samples show wide variation in their intensities at higher wave numbers between 3695 and 3620 Cm^{-1} . Kaolinite has been identified by absorption bands of large intensity at 3685, 3675, 3635, 3610, 530, 471 Cm^{-1} . It also shows less intense absorption bands at 1032, 935, 828, 750, 690, 605, 535 and 470 Cm^{-1} . Fire-clay typically shows absorption bands of large intensities at 3695, 3621, 1101, 1031, 1008, 539 and 471 Cm^{-1} . Some bands of kaolinite overlap the bands of halloysite which, however, has characteristic bands at 3623, 1033, 1012, 540 Cm^{-1} . The absorption bands at 3708, 3655, 3622, 1035, 1002, 538, 469 Cm^{-1} and 3701, 3628, 1038, 1002, 535, 470 Cm^{-1} have been respectively ascribed to the presence of dickite and nacrite. Aluminium minerals like gibbsite (3455, 1020 Cm^{-1}), bayerite (3520, 3462, 3448, 1020, 764 Cm^{-1}) and nordstrandite (3558, 3490, 1060, 1030, 1000 Cm^{-1}) have also been identified with the help of IR spectra. The presence of illite has been indicated by absorption bands at 3622, 1022 and 523 Cm^{-1} . The absorption bands at 1172, 1084, 798, 780, 512, 478 and 462 Cm^{-1} indicate the presence of silica in the form of quartz and chert.

DISCUSSION

The lithomarges from the area around Agaria are the result of chemical weathering of rock of various lithologies under tropical wet-dry climate which is characterised by alternating wet and dry spells. Lateritic product is resulted due to the weathering of rocks under high temperature and high seasonal rainfall. Rainfall has been considered as one of the most important components of climate in the development of a lateritic profile. The rainfall commonly

affects the trend of chemical weathering. On the other hand, temperature affects only the rate of transformation (Pickering, 1962). It is possible to visualise the environment of transformation of parent rock into clay and related minerals, from a study of abrasion pH of the constituent minerals of the parent rock. The abrasion of pH of the fresh rock has been in the range of 9.0 to 10.0, while that of completely weathered rock (forming clays), is commonly between 5.0 and 6.0 (Stevens and Carron, 1948). The weathering of silicate minerals commences due to the action of meteoritic waters which have an initial pH in the range 5.5 to 6.5 and which may be subsequently lowered to 3.5 by incorporation of CO_2 (Norton, 1973). At pH 5.5 to 6.5, the silicate minerals from the parent rock breakdown and Ca, Mg, K and Na are taken into solution. As a result water becomes alkaline in the near surface environment. Under alkaline condition silica is mobilised compared to iron and aluminium (Cawsey and Mellon, 1983). Aluminium and iron have relatively low solubility over a wide range of pH, however, acidic conditions with pH 3.5 favour their mobility (Petersen, 1971, Cawsey and Mellon, 1983). The Na, K, Ca and Mg, major exchangeable cations, are highly soluble, hence they are removed from the weathered product by percolating waters. Fe^{+2} being highly unstable, is converted into Fe^{+3} which is relatively immobile and therefore, retained in the weathered product (Birkeland, 1984).

Under acidic conditions with the presence of organic matter and impeded groundwater circulation silica, obtained from the breakdown of primary silicates, if retained at the site for a longer time, recombines with aluminium hydroxide to form clay minerals. In deeper environment, the pH of percolating waters is towards acidic side which can be attributed to the decay of organic matter and incorporation of CO_2 . If the waters remain in voids in lithorelicts, in that case, the pH of such waters may not

be the same as that of original percolating waters. The rate of weathering is governed by the pH of percolating waters as well as by the length of time the solutions are in contact with the rock particle surfaces. As soon as the equilibrium pH is reached, further alteration takes place at this pH. The equilibrium pH has been also shown to be a function of the rate of renewal of percolating waters. If the renewal rate is fast, the pH will tend to be on the acid side of the equilibrium pH (Eswaran and Coninck, 1971). Thus, microenvironment controls the alteration of rock fragments into different products.

The rate of leaching during chemical weathering is shown to be controlled by the amount of rainfall and type of topography, that in turn, defines both internal and external drainage conditions. Experimental studies carried out by Wollast (1967) and Berner (1971) have shown that the rate of chemical reaction is a direct function of pH of solution which again is controlled by the rate of flow of water. Berner (1971, p. 173) has recorded the chemical and mineralogical changes that took place in the experimental chemical weathering of albite under various conditions of flow of water. He has observed that at higher rate of flow of water chemical weathering of albite led to the formation of gibbsite, while at lower flow rate, kaolinite was formed. When the flow rate conditions approached stagnation, formation of montmorillonite took place. In the present case, the lithomarges are predominated by the minerals of kaolinite group indicating that they must have formed under free drainage conditions.

In order to explain the genesis of kaolinite in lateritic profile, it is necessary to know the different horizons of a typical lateritic profile. A typical lateritic profile has an upper ferrillitic soil, a ferricrete—the laterite duricrust, an alucrete—the bauxitic horizon, a saprolite—the kaolinitic zone, and a pallid zone of partly weathered rock over-

lying unweathered parent material (Valeton, 1983). In order to explain the genesis of lithomarges (saprolite) which constitute the lower horizon of the lateritic profile, it is necessary to explain the development of lateritic profile into different horizons. It has been observed that iron is concentrated in the top layer to form ferricrete and aluminium in the lower horizon to form lithomarges. The effective separation of Fe and Al into respective upper and lower horizons can be explained by two mechanisms namely, the absolute accumulation and the relative accumulation. Absolute accumulation means concentration of an element increases by addition of more of the element, while relative accumulation takes place by the removal of other elements. Most ferricretes are formed by absolute accumulation. However, some ferricretes may be residual.

Under acidic environment silica obtained from the breakdown of primary silicate minerals recombines with aluminium hydroxides giving rise to kaolinite and related clay minerals under free drainage conditions. Iron in deeper environment is in a ferrous state and is soluble over a wide range of pH. Iron in weathering profile may produce complex organic molecules with combined ferrous and ferric hydroxides in solution or in colloidal suspension.

Once the parent rock is kaolinised, the particle size becomes more finer. This promotes capillary action. Molecules of ferrous and ferric hydroxides migrate upward towards more aerated near surface oxidising environment by capillary action during dry season. On oxidation, iron gets precipitated as ferric hydroxide in the top layers. The ferric hydroxide on dehydration gets hardened to form ferricrete. Thus, this process leads to the accumulation of iron in top horizon on one hand and depletion of it from lower horizon on the other. Aluminium is insoluble over a wide range of pH and can get relatively enriched in the lower horizon to form lithomarges.

CONCLUSIONS

The lithomarges in the area around Agaria, are residual in nature having been found to form from the decomposition of the argillitic rocks under tropical wet-dry climatic conditions. They are essentially composed of kaolinite, halloysite, dickite, etc. minerals. Kaolinite constitutes major portion of the clays. Clay mineralogical studies have shown that the kaolins are moderately stacked and fall within the clay group broadly distinguished as 'fire clays'. The kaolins are fine grained and poorly crystalline which make them suitable for use in paper industry, as thin flakes of kaolin readily orient parallel to the sheet and form smooth surface imparting better gloss to the paper. The kaolins with lower degree of crystallinity, have higher plastic and bounding properties (Grim, 1968).

This along with their low iron and titanium oxides and alkalies content make them suitable for use as best quality refractory material, foundry molds, etc.

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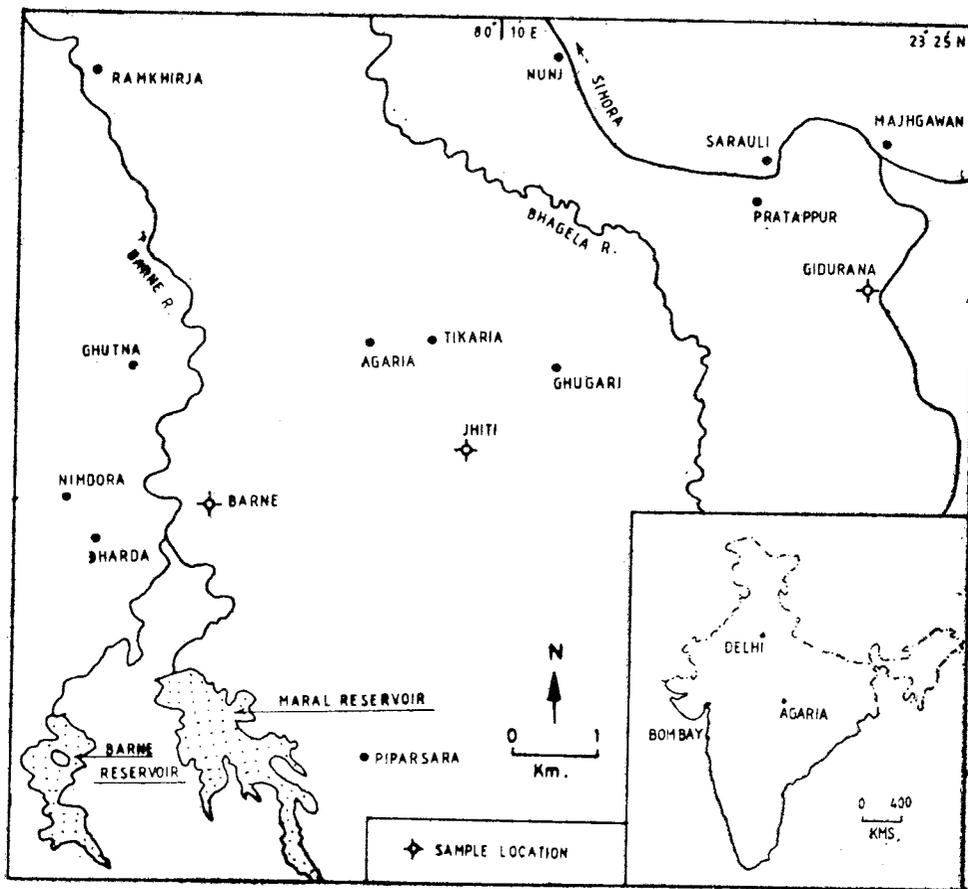


Fig. 1 : Location map of the Agaria clay deposit, Jabalpur district, Madhya Pradesh.

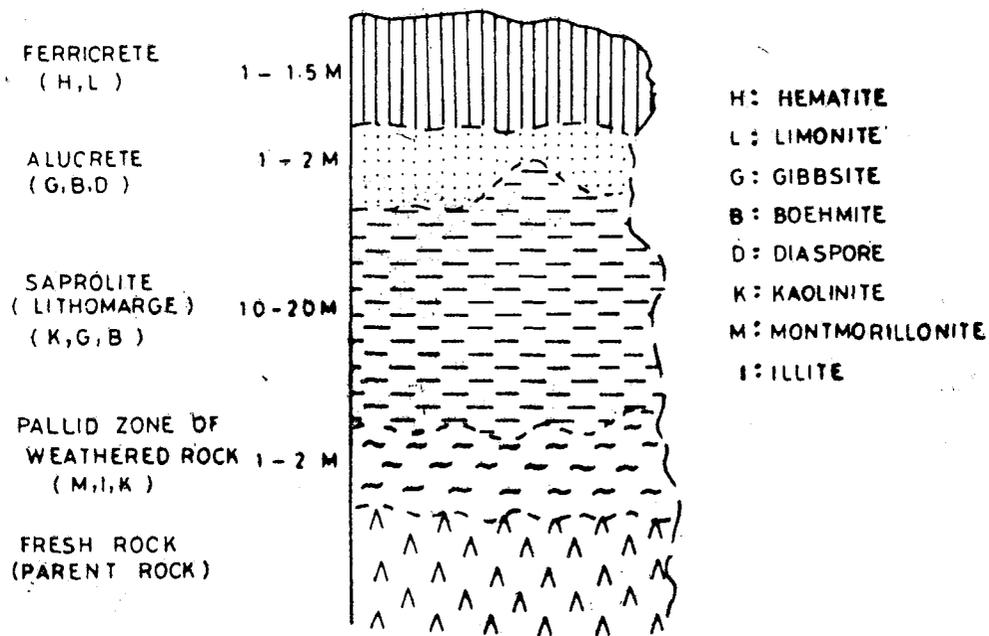


Fig. 2 : Generalised section showing lateritic profile in the area around Agaria.

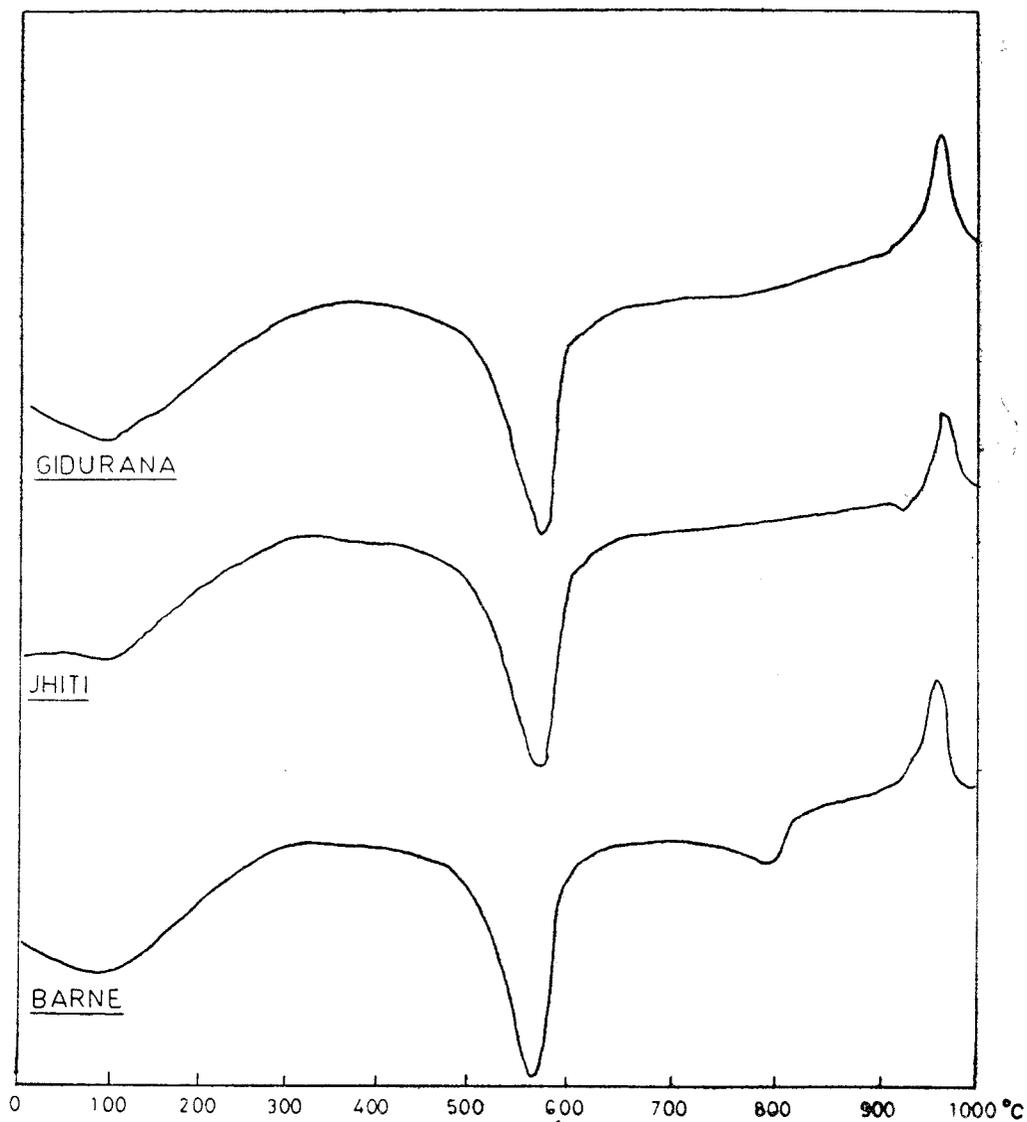


Fig. 3 : Thermograms of the Gidurana, Jhiti and Barne clays.

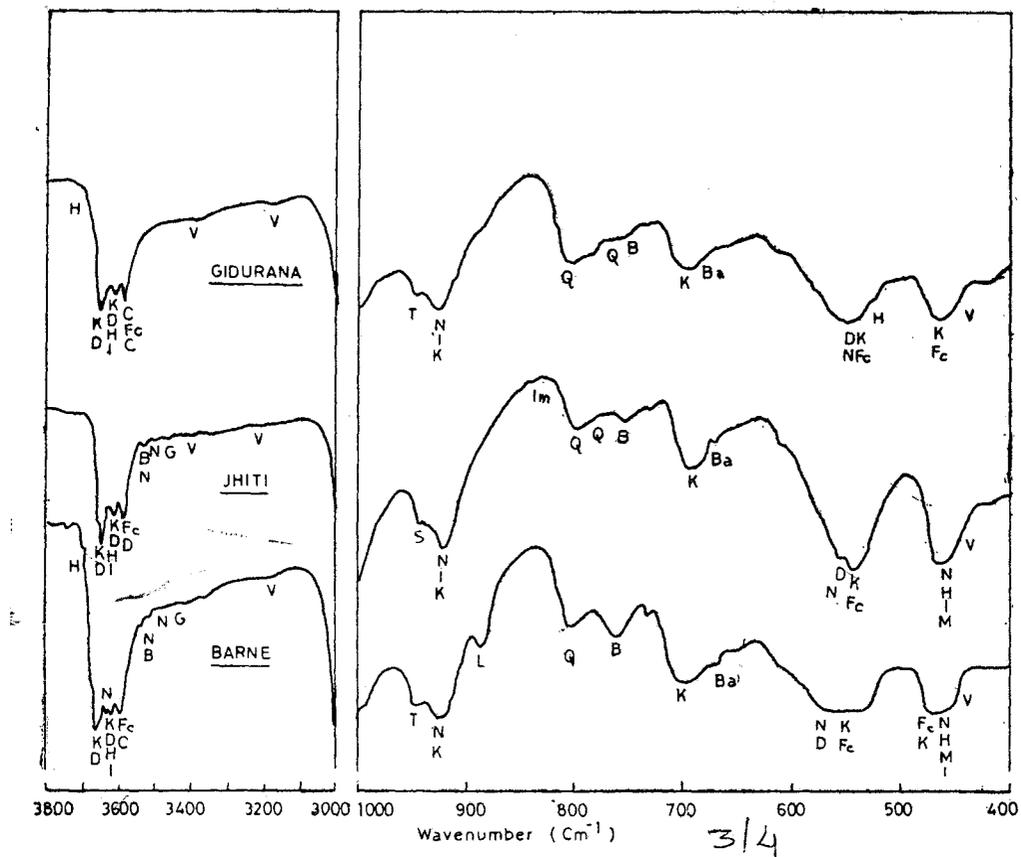


Fig. 4 : IR spectra of the Gidurana, Jhiti and Barne clays.

G : Gibbsite,	Ba : Bayerite,	L : Limonite,
N : Nacrite,	K : Kaolinite,	D : Dickite,
H : Halloysite,	Fc : Fire-clay	I : Illite,
M : Montmorillonite,	Im : Illite-montmorillonite,	V : Vermiculite,
B : Biotite,	S : Sericite,	
T : Talc,	Q : Quartz.	