# MINERALOGY OF CLAY DEPOSITS NEAR BAGH (33° 45′ 30″, 72° 11′ 40″) CAMPBELLPORE DISTRICT, RAWALPINDI DIVISION

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X-ray, DTA, thermobalance and chemical analyses data have shown that Bagh clays are composed of kaolinite with subordinate amounts of diaspore, haematite and rutile (or anatase). The leaching of alkaline earths from ferruginous carbonate rocks resulted in the formation of brown laterites. Further weathering of laterites under restricted conditions gave rise to bleached clays.

## Introduction

The main purpose of this report is to present the mineralogical and chemical data of clay samples collected from village Bagh in Campbelpore District. The clay deposit occurs at the top of the denuded hillock about half a mile south east of the village Bagh. The denuded hillock is one of the spurs of the Kala Chitta Hills. The river Indus flows about a mile northwest of the deposit.

Laterites are well developed in the area. Below the hard laterite layer is a soft clayey material. The laterite and clays outcrop at a number of places.

The folded and denuded anticlines of Kala Chitta Hills expose a series of starta ranging in age from Upper Trias to Siwaliks.[1] The exact age of the clay deposits is not certain. However, they occur in association with limestone of eocene age, and may therefore be of eocene age. They could have formed after the rocks were exposed at the surface, thus during post eocene time. Crookshank[2] has mentioned that the ferruginous bauxite found near Surg occurs above(?) Ranikot shales (Palaeocene) and can be traced for miles. The Bagh laterites and the Surg ferruginous bauxites may be of the same age.

## Materials and Methods

*Samples.*—The clay samples used in the laboratory investigations were obtained from a testpit and outcrops. The testpit was dug by the leasee of the property after removal of the lateritic overburden. The width of the clay seam was estimated between 20′ and 30′. Total depth of the clay is not known. The clay seam outcrops at a number of places. The details of each sample are as follows:

KLN1 Reddish brown ferruginous limestone; occurs at about 20′ S.E. of the pit.

KLN2 Reddish brown laterite, massive, overlying bleached clays.

KLN3 Pit sample, depth 2′ from surface (overburden removed); greyish-white in colour; brown iron oxide mottling, talcose feel.

KLN4 Pit sample, depth 4′ away from surface; similar to KLN3.

KLN5 Pit sample, depth 6′ from surface; similar to KLN3.

KLN6 Same pit 4′ away from KLN3 and KLN4; similar to KLN3.

KLN7 Outcrop sample, about 25′ S.E. of the pit.

KLN8 Outcrop sample, about 75′ S.E. of the pit; brown in colour; soft.

KLN9 Outcrop sample, about 200′ S.E. of the pit; similar to KLN7.

KLN10 Outcrop sample, about 300′ S.E. of the pit; brown in colour; intercalation of white material.

KLN11 Outcrop sample, about 500′ S.E. of the pit; grey in colour; few pisolites; massive.

KLN12 Outcrop sample, about 3 furlong from the pit; seam direction is East-West; intercalation of grey and brown clays.

KLN13 Outcrop sample, about ½ mile from the pit, near the border fencing of the Reserve Forest; grey in colour; iron oxide mottling; few pisolites.

## Experimental

X-ray diffraction photographs were taken with 114.6 mm. diameter Debye-Scherrer Camera using CuK α radiation. DTA was carried out

with a uniform rise of temperature of the furnace (10°C per minute). DTA curve was recorded on a Cambridge recorder with a range of $+1$ to $-1mV$. Brabender thermobalance was used for thermogravimetric analysis. Chemical analyses were made following the classical methods and methods given by Riley.[3]

## Results

*X-ray Diffraction.*—Twelve samples were examined by x-ray diffraction technique. Table 1 shows d spacings and relative intensities, estimated by visual inspection from powder photographs of typical samples KLN2, KLN4, KLN6 and KLN8. Table 2 gives the summary of the minerals identified in each sample. All the samples except KLN2 gave the reflections (d=7.13, 3.57 and 1.48A) of well crystallized kaolinite.

Samples KLN6 and KLN11 have strong lines at d=3.98A indicating the presence of diaspore. Reflection at d=2.63A in KLN8 and KLN10, the two brown samples, confirms the presence of α iron oxide (haematite). KLN2 has strong lines of both boehmite and diaspore.

*Differential Thermal Analysis.*—Figures 1 and 2 show the differential thermal analysis curves of the 13 samples. The DTA curve of KLN1 is comparable to that of dolomitic limestones. The acid insoluble fraction of KLN1 (curve KLN1a) contains two endothermic peaks, one at 290°C and the other at 340°C. The two endothermic peaks may be due to gibbsite. The DTA curve of KLN2 shows the presence of diaspore or boehmite. It is not possible to distinguish the two minerals by differential thermal analysis. The DTA curves of KLN3, KLN4, KLN5, KLN6, KLN11 and

TABLE 1.—X-RAY DIFFRACTION DATA FOR KLN2, KLN4, KLN6 AND KLN8.

| KLN2 | | KLN4 | | KLN6 | | KLN8 | |
|---|---|---|---|---|---|---|---|
| d(A) | I | d(A) | I | d(A) | I | d(A) | I |
| 6.10 | 80 | 7.12 | 100 | 7.13 | 100 | 7.13 | 100 |
| 3.86 | 100 | 4.71 | 20 | 4.71 | 20 | 3.56 | 80 |
| 3.14 | 100 | 4.41 | 60 | 4.52 | 20 | 2.63 | 100 |
| 2.48 | 70 | 4.15 | 50 | 3.98 | 100 | 2.47 | 60 |
| 2.29 | 60 | 3.57 | 100 | 3.57 | 100 | 2.30 | 60 |
| 2.18 | 10 | 2.77 | 10 | 3.18 | 5 | 2.18 | 30 |
| 2.10 | 60 | 2.46 | 70 | 2.75 | 10 | 1.97 | 30 |
| 2.05 | 60 | 2.30 | 80 | 2.52 | 70 | 1.82 | 80 |
| 1.82 | 80 | 2.12 | 25 | 2.47 | 70 | 1.68 | 80 |
| 1.68 | 90 | 1.96 | 30 | 2.30 | 90 | 1.48 | 80 |
| 1.62 | 80 | 1.88 | 10 | 2.12 | 70 | 1.44 | 80 |
| 1.47 | 90 | 1.83 | 10 | 1.96 | 20 | 1.30 | 60 |
| 1.44 | 40 | 1.78 | 10 | 1.88 | 20 | | |
| 1.42 | 40 | 1.66 | 50 | 1.65 | 80 | | |
| | | 1.62 | 70 | 1.62 | 90 | | |
| | | 1.53 | 20 | 1.48 | 100 | | |
| | | 1.48 | 100 | 1.45 | 50 | | |
| | | 1.45 | 50 | 1.42 | 50 | | |
| | | 1.42 | 30 | 1.39 | 50 | | |
| | | 1.33 | 20 | 1.37 | 40 | | |
| | | 1.30 | 50 | 1.33 | 40 | | |

TABLE 2.—SUMMARY OF MINERALS DETECTED BY X-RAY DIFFRACTION.

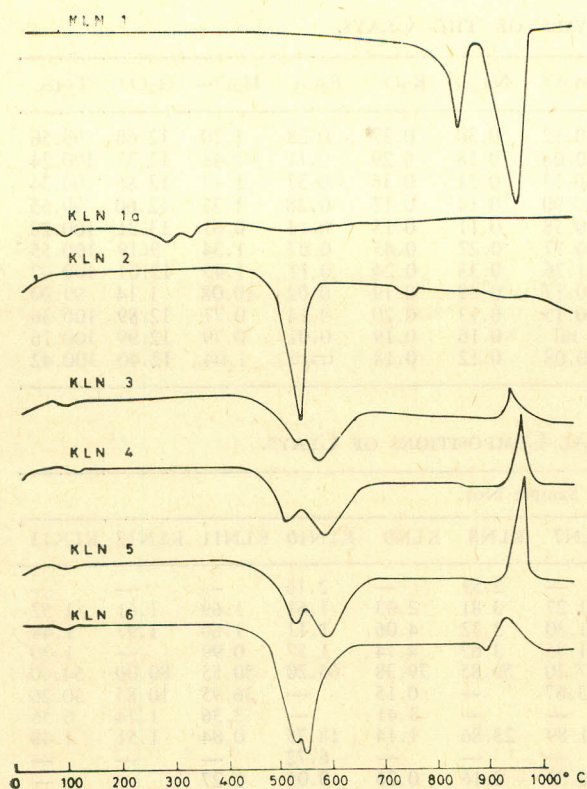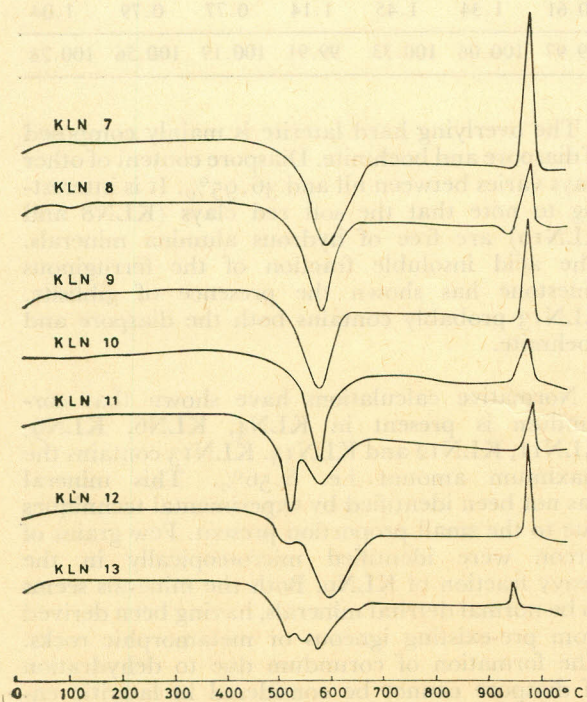| KLN2 Boehmite Diaspore | KLN3 Kaolinite | KLN4 Kaolinite | KLN5 Kaolinite | KLN6 Kaolinite Diaspore | KLN7 Kaolinite |
|---|---|---|---|---|---|
| KLN8 Kaolinite α–$Fe_2O_3$ | KLN9 Kaolinite | KLN10 Kaolinite α–$Fe_2O_3$ | KLN11 Kaolinite Diaspore | KLN12 Kaolinite | KLN13 Kaolinite |

Fig. 1.—DTA curves of the samples.
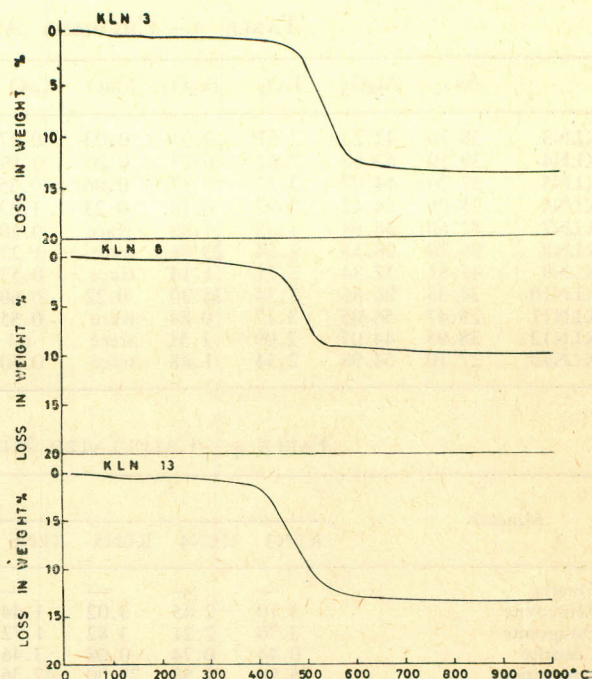


Fig. 2.—DTA curves of the samples.



Fig. 3.—Thermogravimetric curves.

KLN12 show that kaolinite with subordinate amount of diaspore is present. KLN7, KLN8, KLN9 and KLN10 contain only kaolinite. The DTA curve of KLN13 is interesting. The endothermic peak at 575°C is due to the dehydroxylation of kaolinite mineral. The endothermic peaks at 550°C and 515°C may be due to diaspore and boehmite respectively.

*Thermogravimetric Analysis.*—Fig. 3 reproduces the thermogravimetric curves for samples KLN3, KLN8 and KLN13. These curves resemble those of the kaolinite.

*Chemical Analysis.*—The chemical analysis of the 11 samples are given in table 3 and the calculated norms in table 4.

The calculated composition have been worked out on the assumption that phosphorous is located in apatite, $Ca_3(PO_4)_3$, OH. The lime left over after forming the apatite is combined with magnesia to form chlorite $(Mg, Ca)_{12} Si_8O_{20} (OH)_{16}$. The soda and potash are present as paragonite, $Na_2Al_4(Si_6Al_2)O_{20}(OH)$ and muscovite $K_2Al_4(Si_6Al_2) O_{20}(OH)_4$ respectively. The alumina left over after forming the micas are distributed between kaolinite, $Al_4Si_4O_{10}(OH)_8$ and diaspore, $H_2Al_2O_4$). Whenever sufficient structural water is not present to form kaolinite and diaspore, then the alumina is distributed between kaolinite, diaspore and corundum. In cases (KLN8 and KLN10) where excess silica is left over after forming kaolinite, the excess silica

### Table 3.—Chemical Analyses of the Clays.

| | $SiO_2$ | $Al_2O_3$ | $TiO_2$ | $Fe_2O_3$ | MnO | CaO | MgO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $H_2O-$ | $H_2O+$ | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| KLN3 | 38.76 | 42.23 | 2.57 | 0.55 | 0.03 | 0.47 | 0.12 | 0.30 | 0.37* | 0.28 | 1.20 | 12.68 | 99.56 |
| KLN4 | 39.50 | 42.62 | 2.62 | 0.27 | 0.20 | 0.59 | 0.08 | 0.18 | 0.29 | 0.11 | 1.41 | 12.37 | 100.24 |
| KLN5 | 37.20 | 44.07 | 3.33 | 0.17 | 0.06 | 0.35 | 0.13 | 0.31 | 0.36 | 0.37 | 1.13 | 12.86 | 100.34 |
| KLN6 | 25.00 | 54.42 | 3.07 | 0.18 | 0.25 | 1.23 | 0.90 | 0.14 | 0.17 | 0.28 | 1.31 | 12.60 | 99.55 |
| KLN7 | 42.60 | 38.64 | 1.85 | 1.89 | trace | 0.50 | 0.58 | 0.11 | 0.15 | 0.14 | 0.61 | 13.21 | 100.28 |
| KLN8 | 35.30 | 26.53 | 1.54 | 23.86 | trace | 1.23 | 0.77 | 0.27 | 0.45 | 0.07 | 1.34 | 9.19 | 100.55 |
| KLN9 | 41.81 | 37.34 | 3.71 | 1.14 | trace | 0.57 | 1.76 | 0.33 | 0.24 | 0.11 | 1.45 | 12.01 | 100.47 |
| KLN10 | 34.35 | 26.86 | 1.38 | 24.80 | 0.22 | 0.60 | 0.17 | 0.09 | 0.19 | 0.02 | 10.08 | 1.14 | 99.90 |
| KLN11 | 25.47 | 56.05 | 3.17 | 0.84 | trace | 0.55 | 0.15 | 0.13 | 0.20 | 0.14 | 0.77 | 12.89 | 100.36 |
| KLN12 | 38.95 | 44.07 | 2.09 | 1.51 | trace | nil | nil | 0.16 | 0.19 | 0.01 | 0.79 | 12.99 | 100.76 |
| KLN13 | 27.10 | 54.98 | 2.54 | 1.48 | trace | 0.50 | 0.08 | 0.12 | 0.18 | trace | 1.04 | 12.40 | 100.42 |

### Table 4.—Calculated Mineral Compositions of Clays.

| Minerals | Sample Nos. | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | KLN3 | KLN4 | KLN5 | KLN6 | KLN7 | KLN8 | KLN9 | KLN10 | KLN11 | KLN12 | KLN13 |
| Quartz | — | — | — | — | — | 2.51 | — | 2.16 | — | — | — |
| Muscovite | 3.10 | 2.45 | 3.02 | 1.44 | 1.27 | 3.81 | 2.03 | 1.61 | 1.69 | 1.61 | 1.52 |
| Paragonite | 3.70 | 2.21 | 3.82 | 1.72 | 1.30 | 3.32 | 4.06 | 1.11 | 1.60 | 1.97 | 1.48 |
| Chlorite | 0.44 | 0.74 | 0.08 | 3.46 | 1.85 | 3.67 | 4.74 | 1.57 | 0.99 | — | 1.00 |
| Kaolinite | 75.90 | 79.58 | 73.00 | 47.36 | 87.20 | 59.85 | 79.38 | 65.20 | 50.55 | 80.00 | 54.40 |
| Diaspore | 11.22 | 6.02 | 14.66 | 35.90 | 3.67 | — | 0.15 | — | 36.95 | 10.85 | 30.26 |
| Corundum | — | 4.23 | — | 3.96 | — | — | 3.41 | — | 3.36 | 1.74 | 6.56 |
| Haematite | 0.55 | 0.27 | 0.17 | 0.18 | 1.89 | 23.86 | 1.14 | 18.75 | 0.84 | 1.51 | 1.48 |
| Limonite | — | — | — | — | — | — | — | 6.72 | — | — | — |
| Apatite | 0.66 | 0.26 | 0.87 | 0.66 | 0.33 | 0.16 | 0.26 | 0.05 | 0.27 | — | — |
| Rutile or Anatase | 2.57 | 2.62 | 3.33 | 3.07 | 1.85 | 1.54 | 3.71 | 1.38 | 3.17 | 2.09 | 2.54 |
| MnO | 0.03 | 0.20 | 0.06 | 0.25 | trace | trace | trace | 0.22 | trace | trace | trace |
| $H_2O$ | 1.20 | 1.41 | 1.13 | 1.31 | 0.61 | 1.34 | 1.45 | 1.14 | 0.77 | 0.79 | 1.04 |
| Total | 99.37 | 99.99 | 100.14 | 99.31 | 99.97 | 100.06 | 100.33 | 99.91 | 100.19 | 100.56 | 100.28 |

is reported as quartz. Iron occurs as haematite and limonite. Titania is assumed to be present as rutile or anatase.

### Discussion

There is a great lateral variation in the composition of the laterites and clays. The composition of individual profile in the bleached clay-zone is relatively constant, though variation in a single deposit is common.

The x-ray diffraction data and DTA have shown the specimens are composed of kaolinite, diaspore and haematite. The mineralogy deduced from the chemical analysis show excellent agreement in respect of major components.

Kaolinite is the most abundant mineral present. In a profile the kaolinite content varies between 73.00 and 79.58%; kaolinite content falls to 47.3% in the same pit. The overlying hard laterite and ferruginous limestone are free of kaolinite.

The overlying hard laterite is mainly composed of diaspore and boehmite. Diaspore content of other clays varies between nil and 36.95%. It is interesting to note that the soft red clays (KLN8 and KLN10) are free of hydrous alumina minerals. The acid insoluble fraction of the ferruginous limestone has shown the presence of gibbsite. KLN13 probably contains both the diaspore and boehmite.

Normative calculations have shown that corundum is present in KLN4, KLN6, KLN9, KLN11, KLN12 and KLN13. KLN13 contains the maximum amount i.e. 6.56%. This mineral has not been identified by experimental techniques due to the small proportion present. Few grains of zircon were identified microscopically in the heavy fraction of KLN9. Both the minerals seems to be normal detrital minerals, having been derived from pre-existing igneous or metamorphic rocks. The formation of corundum due to dehydration of diaspore cannot be considered in lateritic environment.

X-ray data have shown the presence of haematite in KLN8 and KLN10. The haematite content is fairly high in both the samples. KLN10 also contains 6.72% limonite. The amount of haematite falls systematically with depth in the bleached profile. The haematite mineral of the laterites must be regarded as a detrital mineral formed by subaerial weathering.

The titanium in the clays may be in the form of rutile and anatase. The $TiO_2$ content varies between 1.38 and 3.71%. There is a systematic rise in $TiO_2$ content with depth (KLN3, 4 and 5) and has an antipathetic relationship with the haematite content. Quartz, muscovite, paragonite, chlorite and apatite are present in subordinate amounts and have not been identified by experimental techniques.

The presence of gibbsite in the acid insoluble fraction of the ferruginous limestone and diaspore (and/or boehmite) in the overlying hard laterite suggest that the limestone may be the immediate source of the laterite. The laterite on further weathering gave rise to kaolinitic clays.

The leaching of alkaline earths from the limestone must have occurred under aggressive condition below the pH of 7.8. The pH must have remained above 7, otherwise the haematite content would have been lost. The fall in pH might have occurred due to the increase of $CO_2$ in the circulating water. The presence of haematite in the red clays and hard laterite suggests that the Eh remained positive during leaching of the carbonate fraction of the rock.

Dehydration of gibbsite results in the formation of diaspore (or boehmite). Dehydration may be accomplished by increase of temperature or decrease of suspension pH.[4] Either of the two reasons may be attributed to the diagenesis of gibbsite of the residual rock to diaspore (or boehmite).

The leaching of haematite from the laterite necessitates a condition of oxygen deficiency, which would lower the Eh, thus increasing tremendously the amount of iron that could be removed. Garrels[5] has shown that below the water table the environment can be assumed to be alkaline and reduceing, except in local instances of high rates of water flow. It seems that the fluctuating water table has been responsible for the removal of iron. This is substantiated by the fact that the bleached clays are found underlying the hard laterite. Bleaching occurs upto the upper limit of the water table. The systematic fall of iron content with depth in the bleached profile also suggest a similar mechanism.

The kaolinite in the clays seems to have formed by the resilication of diaspore. Gorden and Tracey[6] have suggested a similar mechanism for the resilication of bauxite in Arkansas. Silica was supplied by the overlying swampy water. The reaction bauxite+silica=kaolinite is reversible under geologic conditions going to the right when the silica content of water is typical of that of swamp water, and to the left at some lower value. Garrels[7] has suggested that monohydrate seem to be more easily kaolinized than the trihydrate. He has also suggested that a reasonable estimate of equlibrium condition would be kaolinization of gibbsite at a dissolved silica content of 10 ppm at 25°C. Tropical streams carry about three times this amount, average stream a little less.[8] Assumnig the dissolved silica content in the underground water of the clays at least 10 ppm, silication of diaspore would have occurred with the formation of kaolinite.

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