

# Technology Section

Pakistan J. Sci. Ind. Res., Vol. 21, No. 1, February 1978

## THE MINERALOGY AND GEOCHEMISTRY OF SOME CLAYS FROM NAGARPARKAR

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(Received January 10, 1977)

**Abstract.** The clays of Parodharo near Nagarparker are exposed in a nala and can be divided into yellow and white clays on the basis of colour. Thirteen samples were collected from these clays for mineralogical, chemical and economic studies. Both types of clay contain dominant kaolinite with traces of illite. Yellow clays contain some goethite and quartz in addition. The mineralogy, chemistry and the behaviour of the clays at high temperatures makes them very suitable for ceramic and refractory use.

### Introduction

The clay deposit in Tharparkar District of Pakistan are exposed near the town of Nagarparker around the Precambrian granite ridges. The clays are well exposed in nala cuttings. The samples for the present investigations were obtained from Parodharo where the clays are exposed along a nala and are about 13 ft thick. The clays lie below a loose thin layer of laterite about 1 ft thick, and can be divided into two groups, yellow and white clays, on the basis of colour. The yellow clays lie just below the laterite and are generally 5 ft thick. The yellow colour is almost certainly due to the leaching of iron oxides from the overlying lateritic bed. The white clays lie below the yellow clays and are about 8 ft thick. The clays show a uniform thickness over an area of about half a square mile and should extend for considerable distances. The clays have originated by the alteration of feldspars in granites and have been deposited in plains around Nagarparker. The stages of the alteration of feldspars to kaolinite can be traced from the plains towards the granite ridges along nala cuttings. Eight samples were obtained from yellow clays and five from white clays at horizontal intervals of about 200 ft for representative mineralogical and chemical analyses. The white clays were not exposed in three localities.

### Methods of Investigations

**Sample Preparation for X-ray Diffraction.** Each sample was finely ground and a random powder X-ray diffractogram obtained. A group of three slides was prepared from the remaining powder on which oriented aggregates of less than  $5 \mu$  e.s.d. were deposited. This fraction was obtained by sampling at a depth of 5 cm from a tube in which the suspension had been standing for 35 min. The slides prepared as above were subjected to the following treatments. Normal slides: diffraction patterns of the air-dried original material were recorded.

Glycolated slides: all slides were treated with ethylene glycol at  $60^\circ\text{C}$  for 1 hr.

Heat treated slides: all slides were heated at  $550^\circ\text{C}$  for 2 hr.

The diffractograms of the samples were obtained using a Philips PW 1010 X-Ray diffractometer.

**Differential Thermal Analysis.** The finely ground samples was analysed on a DuPont 900 (D.T.A.) from  $50$ – $700^\circ\text{C}$ .

**Sample Preparation for Chemical Analysis.** The sample, broken into small pieces, was ground in a Tema disc mill for 15 min to produce a powder of less than 200 mesh particle size (0.05 mm). This was pelleted for X-ray fluorescence spectrometry, using an automatic Philips PW 1212 X.R.F. spectrometer. All the major elements were expressed as percentage by weight of oxides,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . The minor and trace elements were determined as elements in parts per million.

### Results

**X-Ray Diffraction.** The random powder diffractograms of white clays gave all the reflections of well crystallized kaolinite [1,2]. Fig. 1 is a represen-

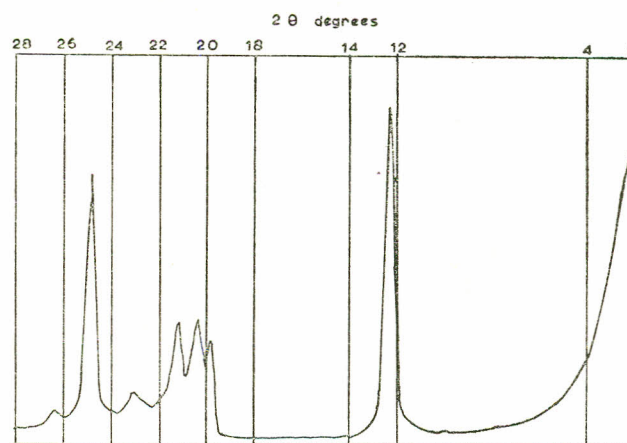


Fig. 1. Random powder data diffractogram of well crystallized kaolinite from white clays.



tative diffractogram of the random powder of white clays which shows the kaolinite reflections. Reflections due to other minerals were not detected. The oriented slides of the white clays of less than  $5\mu$  fraction gave strong basal reflections of kaolinite at 7.13 and 3.57Å. These reflections were not affected on glycolation, but disappeared on heat treatment due to the destruction of the kaolinite structure (Fig 2). Weak reflections of illite were also observed at 10Å in oriented slides. The reflections of illite did not show any change on glycolation and heat treatment (Fig. 2). The mineral illite is present only in traces. Figure 2 shows a representative diffractogram of the oriented slides of white clays for normal, glycolated and heated slides. The random powder diffractograms of yellow clays also gave the reflections of a well crystallized kaolinite. In addition to kaolinite weak reflections of quartz and goethite were also detected. The yellow colour of the clays is probably due to the presence of goethite. The oriented slides of yellow clays also gave the strong basal reflections of kaolinite, and very weak reflections of illite (10Å) and goethite (4.14Å).

**Differential Thermal Analysis.** The differential thermal analyses of white and yellow clay samples were carried out to confirm the results obtained by X-Ray diffraction. Figures 3 shows representative curves of white and yellow clays. An endothermic peak appears at about 575°C, and confirms the presence of kaolinite. No other peaks were noted below this temperature in white clays (Fig. 3), but yellow clays gave a broad peak at 350°C due to the presence of goethite [5].

**Chemical Analyses.** Chemical analyses of the white clays (average of five samples) and the yellow clays (average of eight samples) are shown in columns 1 and 2 respectively of Table 1. Columns 3-5 show the kaolinite analyses obtained by other workers [3]. The white clays contain relatively high amount of alumina when compared with the other analyses. Hence the silica/alumina ratio (0.801) is lower. The high alumina content of white clays may be due to the presence of some amorphous oxides of aluminium which do not give discrete X-ray diffraction peaks. A systematic sampling of the white clays from other parts of Nagarparkar area might reveal the presence of aluminium oxides or aluminium ores (bauxites). White clays also contain more titanium than the other analyses. The low quantities of potassium confirm the existence of only traces of illite. In the yellow clays, the silica/alumina ratio is higher than the white clays, but still lower than the other kaolinitic clays (Table 1). The yellow clays contain more iron than the other analyses. Although goethite has been detected by X-ray diffraction, it is possible that some of the iron is also present as amorphous material, not detected by X-ray.

Table 2 reports the minor elements in parts per million for white and yellow clays in columns 1 and 2 respectively. The comparative study of minor element analyses of white and yellow clays does not indicate much variation in these elements, except

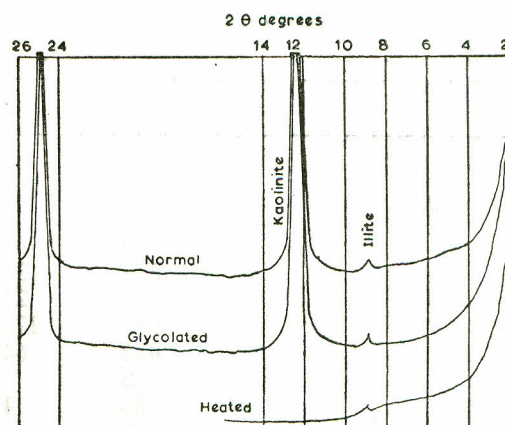


Fig. 2. Reflections given by kaolinite and illite from white clays in oriented slides.

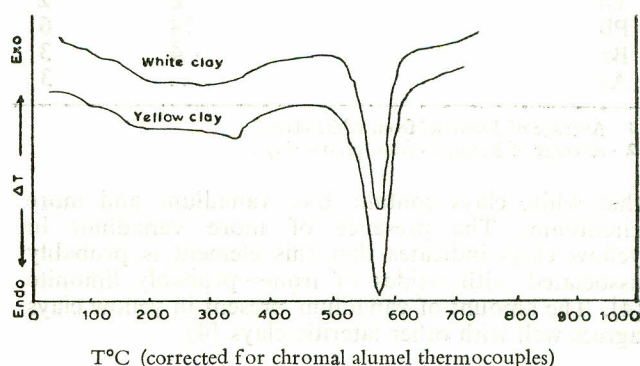


Fig. 3. DTA of white and yellow clays.

TABLE 1. COMPARISON OF PARODHARO CLAYS WITH THE CHEMICAL COMPOSITION OF KAOLINITE FROM OTHER REGIONS.

	1	2	3	4	5
SiO <sub>2</sub>	41.04	41.68	45.80	46.07	45.48
TiO <sub>2</sub>	2.32	1.44	—	0.50	0.86
Al <sub>2</sub> O <sub>3</sub>	45.27	38.50	39.55	38.07	38.84
Fe <sub>2</sub> O <sub>3</sub>	1.83	10.45	0.75	0.33	0.19
MgO	0.18	0.16	0.14	0.01	0.17
CaO	0.03	0.03	0.41	0.38	0.24
Na <sub>2</sub> O	0.67	0.40	—	0.27	0.24
K <sub>2</sub> O	0.27	0.14	0.03	0.43	0.42
Si/Al	0.801	0.958	1.025	1.07	1.035

- 1 Average of 5 samples from white clays.
- 2 Average of 8 samples from yellow clays
- 3 Hypogene kaolinite, hydrothermal veins of Cu-Pb-Zn ore, Mikawo mine, Niigate, Japan (Nagasawa, 1953, quoted in [3]).
- 4 Kaolinite, Mesa Alta, New Mexico, containing 3.61% impurities (Keer *et al.*, 1950, quoted in [3]).
- 5 Kaolinite, Murfreesboro, Arkansas, containing 2.81% impurities (Keer *et al.*, 1950, quoted in [3]).



TABLE 2. MEAN ANALYSES OF THE MINOR ELEMENTS (ppm) FOR PARODHARO CLAYS.

	1	2
Ga	41	37
Zn	25	26
Cu	..	33
Ni	48	53
P	236	320
S	124	238
Cl	3555	1720
V	412	643
Rb	5	5
Sr	84	15
U	2	4
Zr	364	68
Y	77	118
Nb	8	6
Th	2	2
Pb	14	6
Br	4	3
As	..	3

1 Average of 5 samples from white clays.

2 Average of 8 samples from yellow clays.

that white clays contain less vanadium and more zirconium. The presence of more vanadium in yellow clays indicates that this element is probably associated with oxides of iron—probably limonite [4]. The amount of vanadium present in yellow clays agrees well with other lateritic clays [4].

### Discussion

The clay minerals in white and yellow clays are very similar, the only difference being the occurrence of quartz and goethite in the latter. This difference may be due to the greater leaching of white clays than yellow clays, and hence the removal of quartz and goethite. It is also possible that goethite and quartz have been introduced into the yellow clays recently due to the action of leaching solutions from the overlying laterites. In geochemical terms, the white clays contain more aluminium, titanium (Table 1) and

zirconium (Table 2), and less iron and vanadium than yellow clays. This also indicates the same fact that white clays have been subjected to comparatively more leaching as compared to yellow clays. The leaching processes tend to concentrate aluminium, titanium and zirconium and remove iron and vanadium.

### Industrial Uses

The yellow and white clays do not give any reaction with HCl, and show medium plasticity. The white clays, after firing at 1200°C, are a dirty white colour and do not show much shrinkage. The yellow clays after firing are a brownish colour, and also do not show much shrinkage. Both types of clays do not show any cracks or disintegration after firing at high temperatures. The presence of high alumina and their strength after high temperature treatment make them the desirable clays for ceramic and refractory purposes.

**Acknowledgement.** I am very grateful to Professor F. Hodson, Department of Geology, University of Southampton, England, for his permission to use the Departmental facilities and his constant advice and encouragement.

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