

A NATURAL 17Å MONTMORILLONITE-ORGANIC COMPLEX FROM ALLEPPEY, KERALA STATE—INDIA

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Abstract—A black organic-rich alluvial clay from Alleppey, Kerala State, India, gave a well defined 17Å reflection in the natural untreated state. Ethylene glycol and heat treatments showed it to be essentially a smectite. Treatments with H₂O₂ and 0.1 N NaOH contracted the spacing to about 14Å, indicating that sorbed organic matter was responsible for the original enhanced spacing.

In the natural state, the clay was chiefly divalent with respect to the ions on its exchange sites and was at a pH of 6.2. Subsequent attempts to resorb the organic matter (which had been extracted from the clay by repeated NaOH treatments, converted to the H-form, concentrated and freeze-dried) into the interlamellar space of H₂O₂-treated clay proved successful only after the pH was brought down to 3.2 and the clay converted to an essentially monovalent state through repeated 1 N NaCl treatments.

INTRODUCTION

ORGANIC matter exists in soils as discrete particles of woody material, leaf, spores, etc. and as sorbed molecules on the surface of clay minerals. The nature and amount of such organic matter and quite probably the manner in which it is bonded to the clay mineral surfaces are important factors that significantly influence the physical and chemical properties and the biological environment of soils (Grim, 1962).

Although a considerable amount of literature exists on the reactions between pure organic compounds and clay minerals (MacEwan, 1962), relatively little is known about the interactions of clays with naturally occurring soil organic matter (Greenland, 1965 a and b, 1971; Schnitzer and Kodama, 1967). The present work offers X-ray diffractometric evidence of natural sorption of organic matter in the interlamellar space of an organic-rich clay from Alleppey, Kerala State, India. The study forms a part of a comprehensive survey of the effects of soil organic matter on important geotechnical properties of clays.

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§Sample stored in the laboratory for two months before investigation.

EXPERIMENTAL

Material. The clay sample investigated was black in color and came from a depth of 25 m from the surface. It had the following properties§:

< 2µm: about 60%
liquid limit: 108%
plastic limit: 27%
organic matter: 5%
shells: 5-10%
pH: 6.6

Exchangeable Cations (mequiv/100 g)

Na	1.22
K	1.27
Mg	7.81
Ca	21.41

Total 31.71 (CEC 71.71 mequiv/199 g)

Earlier studies (Narain and Ayyar, 1968, 1970; Ayyar and Ramakrishnan, 1969) on clays from the same locality revealed that air drying and sodium hexametaphosphate treatment for dispersing the clay considerably altered the Atterberg limits. Hence in this work the Atterberg limits were determined without any pretreatment.

These clays were considered to be alluvial (King, 1884), deposited by rivers that flowed west from Western Ghats in peninsular India. Their subsequent diagenetic histories are not known.

Methods. The present clay sample was investi-

gated by standard X-ray diffraction procedures (Brindley, 1961) with a General Electric XRD-3 diffractometer situated at the Norwegian Central Institute for Industrial Research. The experimental conditions were as follows: Ni-filtered $\text{CuK}\alpha$ radiation, 40 kV, 17 mA, a scanning speed of $2^\circ 2\theta$ per minute and a slit width of 0.2. Oriented slides were made in all cases by pipetting the clay suspension on glass slides and drying at room temperature. Diffraction patterns were obtained for bulk sample

and $< 2\mu\text{m}$ fraction separately. Patterns were also obtained after glycolation and after heating the slides at different temperatures. The results are presented in Table 1 and the diffractometer traces are shown in Figs. 1-6.

RESULTS AND DISCUSSION

The diffraction patterns for the bulk sample (Fig. 1) in an untreated state indicate the presence of hydromica, kaolinite, quartz, and possibly traces

Table 1. Basal spacings obtained from X-ray diffractometer traces

Sample	Treatments (D spacings)			Mineral name
	Untreated	Glycolated	550°C	
Fig. 1.				
Bulk sample $< 60\mu\text{m}$	17.66†	17.66	14.02	?
	10.16	10.04	10.04	hydrousmica
†broad	7.69	—	—	? amphibole
†shoulder on the high angle side	7.19	7.08	—	kaolinite + chlorite
enhanced	4.98			hydrousmica
	4.87			gibbsite?
	4.74			chlorite
	4.27			quartz
	3.59			kaolinite
	3.56†			chlorite
	3.36			hydrousmica + quartz
	1.99			hydrousmica
Fig. 2.				
	17.66	17.66 Δ		
Clay separate	10.16	10.16 $^{++}$	10.16	
$< 2\mu\text{m}$ fraction	9.4†	7.19	—	
†shoulder on the high angle side	5.06-4.79†		5.06 $^{++}$	
	3.59			
	3.35			
†broad reflection sharpened and enhanced	1.99			
Δ Broader and reduced				
$^{++}$ trace				
Fig. 3.				
Bulk - $60\mu\text{m}$ fraction H_2O_2 treated	14.48	16.98†-15.49		
	10.27	10.04		
	7.19	9.30		Interstratification?
	5.03	8.04		
**Shoulder on the low angle side	4.87	7.00		
	4.76			
	4.27			
	3.59			
	3.2			feldspar
Fig. 4.				
	14.24	17.66	14.24 $^{++}$	
Clay separate	10.39 $^{++}$	10.04	10.04	
treated with H_2O_2	7.19	7.19		
	5.06-4.79†			

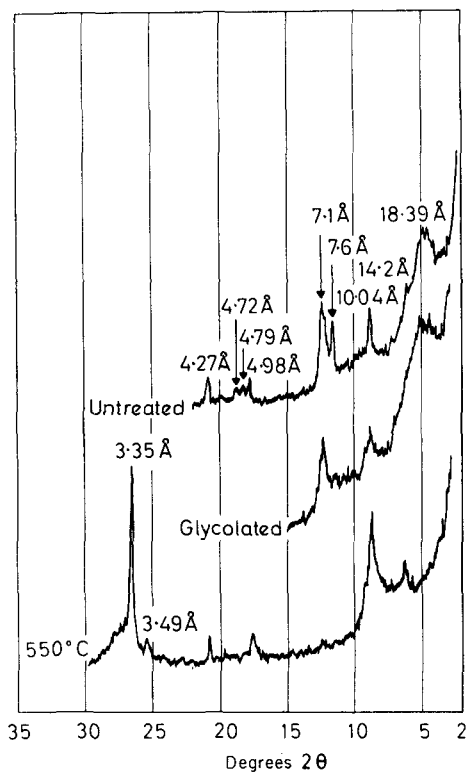


Fig. 1. Diffraction patterns of the bulk ($< 60\mu\text{m}$) fraction.

of gibbsite (4.87\AA), chlorite (4.7\AA), feldspar (3.2\AA), and amphibole (7.7\AA). In addition there is a broad spacing at 18.4\AA which shows no expansion on treatment with ethylene glycol. On heating the slide at 550°C for an hour, the 18.4\AA spacing collapsed to 10\AA , leaving a trace at 14\AA region. The peak at 7\AA completely disappeared.

Figure 2 (clay fraction, $< 2\mu\text{m}$) shows similar behavior. The largest spacing is now 17.7\AA in the untreated fraction, but this peak is sharper and more enhanced than in the bulk sample. Glycolation again had no effect. Heat treatment at 550°C for an hour completely collapsed the peak to 10\AA .

The question arises as to the nature of this mineral which, in an untreated state, has a well defined diffraction maximum in the 17\AA region. To the knowledge of the authors, none of the different combinations of mixed layer clay minerals so far reported in the literature (MacEwan, Amil and Brown, 1961) shows any reflections in the 17\AA region. On the possibility that sorbed organic matter may have caused the 17\AA reflection, the bulk sample and the clay fraction ($< 2\mu\text{m}$) were treated with 35 per cent hydrogen peroxide mixed with an equal amount of water. After the initial reaction ceased, the mixture was heated at 75°C

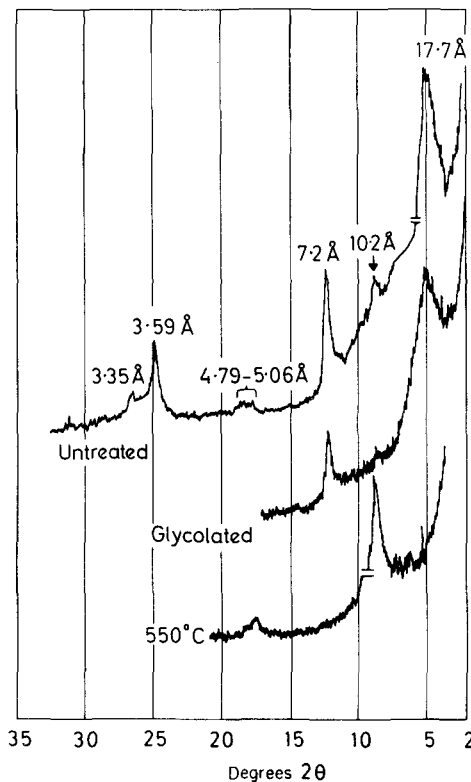


Fig. 2. Diffraction patterns of the clay ($< 2\mu\text{m}$) fraction.

for an hour until all the hydrogen peroxide was expelled. The clay was then washed with distilled water and sedimented on glass slides. The diffractograms, given in Figs. 3 and 4, now show that the 17\AA reflection has shifted to 14.5\AA . On glycolation the clay expands to 17\AA , a behavior typical of montmorillonite.

A similar experiment was performed after treating the clay with 0.1 N NaOH , a procedure employed to extract the organic matter from soils (Mortensen, 1965). The NaOH treatment was repeated a number of times until the supernatant liquid was colourless after centrifugation. Fig. 6 (a-c) demonstrates that the NaOH -treatment also reduced the 17\AA spacing to about 14\AA . On heating to successively higher temperatures, the clay behaved essentially like a montmorillonite (Fig. 5). The shift of the 17\AA peak towards the 10\AA region was effected in two stages. Soon after heating at 100°C for an hour, the 17\AA spacing collapsed to 14\AA leaving only a shoulder on the low angle side of the 14\AA peak. At 200°C , the 14\AA spacing became more dominant and symmetrical. At 300°C the peak finally shifted to 10\AA leaving only a trace at 14\AA while at 400°C the peak showed a total collapse to 10\AA .

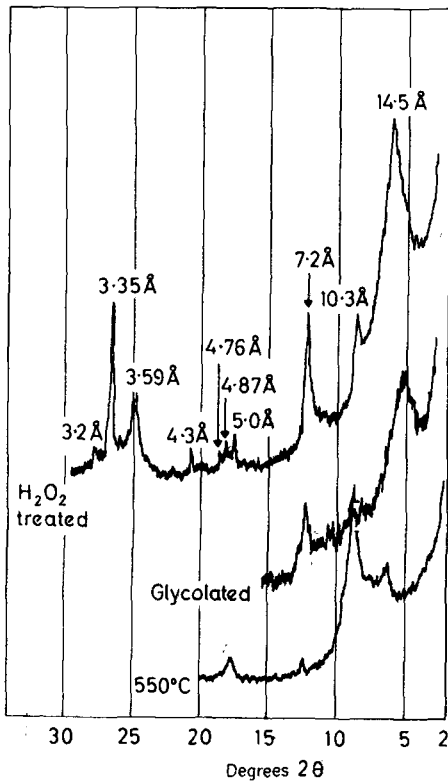


Fig. 3. Diffraction patterns of the H_2O_2 -treated bulk ($< 60\mu\text{m}$) fraction.

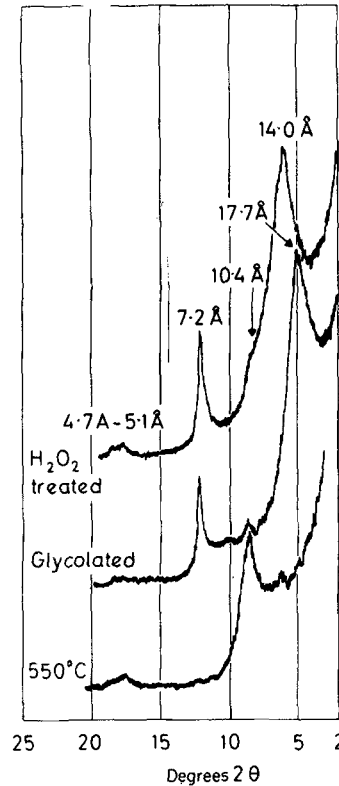


Fig. 4. Diffraction patterns of the H_2O_2 -treated clay ($< 2\mu\text{m}$) fraction

Apparently at 100–200°C the organic matter in the interlamellar space has been oxidized with a concomitant reduction of the 17 peak to 14 Å, and thereafter the behavior of the 14 Å spacing is essentially like that of a normal montmorillonite on further heating to elevated temperatures. Incidentally, the 060 spacing at 1.51 Å suggests the mineral to be essentially dioctahedral in nature (Warshaw and Roy, 1961).

From the above experiments it seems obvious that organic matter, the nature of which is not clear at present, is sorbed in the interlamellar spaces of the mineral. So long as it is present, ethylene glycol treatment has no effect on the basal spacing. However, when the organic matter is removed by hydrogen peroxide or NaOH treatment, the interlayer space is left vacant for subsequent glycol penetration. This natural sorption of organic matter seems common (Perez-Rodriguez and Wilson, 1969), but is seldom reported, probably because of routine pretreatment of samples for removal of organic matter before irradiation.

Schnitzer and Kodama (1966, 1967); Kodama and Schnitzer (1968) and Schnitzer (1969) had to convert their Ca-bentonite into a monovalent Na-

bentonite before successfully sorbing fulvic acid in the interlamellar space. Their observations show that pH of the medium is also one of the critical factors. The present case is similar. No significant resorption of the mixed fulvic humic acids (the probable nature of the material extracted from the clay by repeated treatment with 0.1 N NaOH) could be observed with the clay in the divalent state. So, in order to resorb the organic extract into H_2O_2 treated clay, the clay was converted into the Na-state by three treatments with 1 N NaCl solution. After removal of the excess salt by repeated washing with distilled water, the clay was dried in air.

Procedures were adopted identical to those given by King (1967) and Rashid and King (1969, 1970) for extraction and purification of humic and fulvic acid fractions from clay. 100 mg of freeze-dried organic extract were weighed into a centrifuge tube and dissolved in 8 ml of distilled water. 40 mg of the dried clay were then added and the volume made up to 15 ml. The pH of the suspension, initially 2.2, was adjusted to 3.2 by addition of 0.1 N NaOH in order to facilitate the complete solution of the organic extract. The tube and con-

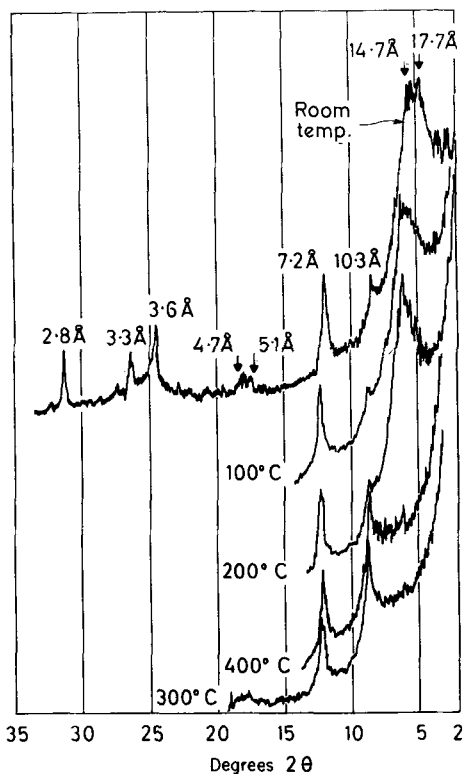


Fig. 5. Diffraction patterns of the clay ($< 2\mu\text{m}$) fraction at successively elevated temperatures.

tents were shaken for 20 hr at room temperature and then centrifuged at 3000 rpm for half an hour. The supernatant liquid was decanted and the residue suspended in 2 ml of distilled water. One ml of this suspension was pipetted onto a porous ceramic plate, because a suspension on a glass plate was observed to curl on drying. The diffractogram (Fig. 6d) of this oriented aggregate shows that some organic matter had been resorbed in the interlamellar space, and given rise to a broad reflection in the 17Å region.

Here, apparently, is a contradiction. In the natural state, the clay has organic matter sorbed in the interlamellar space at a pH of 6.2 and with the exchange sites chiefly occupied by divalent cations. But, laboratory attempts to resorb the organic matter into the H_2O_2 -treated clay proved unsuccessful until the clay was converted to a monovalent Na-state and the sorption conducted at a pH of 3.2.

These clays are further characterized by appreciable seasonal changes in their strength characteristics. Samples collected in September just after the monsoon rains (pH 4.2) have low shear strength ($\phi' = 26^\circ$) while those collected in March (pH 7.5) show higher strength ($\phi' = 29^\circ$) (Ayyar and Rama-

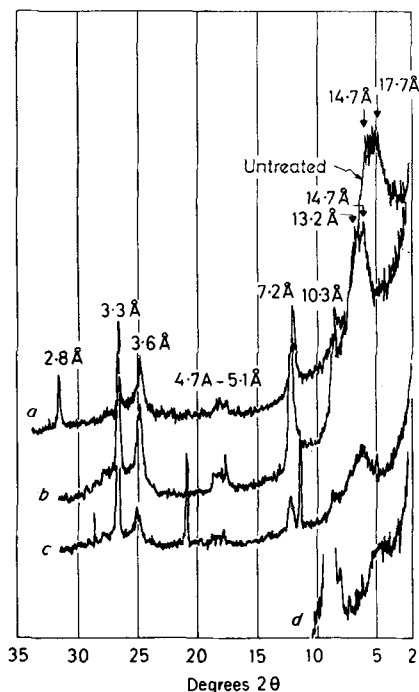


Fig. 6. Diffraction patterns of the clay ($< 2\mu\text{m}$) fraction under various treatments: (a) untreated, (b) NaOH-treated, (c) H_2O_2 -treated, (d) H_2O_2 -treated clay treated with organic extract.

krishnan, 1969). Considerable sorption of organic matter due to low pH and perhaps to a change in the valency state of the exchangeable ions after rains may in part explain this observation.

Further work on the nature of this organic matter and its influence on the geotechnical properties is in progress.

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Résumé— Une argile alluviale noire riche en matière organique, provenant de Alleppey, Etat de Kerala, Indes, a donné une réflexion bien définie à 17 Å, à l'état naturel non traité. Le glycol éthylique et les traitements thermiques ont montré qu'il s'agissait essentiellement d'une smectite. Les traitements à H₂O₂ et Na OH 0,1 N ont ramené l'espacement à 14 Å environ, ce qui indique que la matière organique fixée était responsable de l'espacement originel élevé pour un tel minéral.

A l'état naturel, l'argile était à pH 6,2 et ses sites d'échange étaient principalement saturés par des ions divalents. Les tentatives ultérieures destinées à fixer à nouveau la matière organique (qui avait été extraite de l'argile par des traitements répétés avec Na OH, puis convertie sous forme H, puis concentrée et lyophilisée) dans l'espace interfeuillet de l'argile traitée par H₂O₂, n'ont réussi qu'avec une argile amenée à pH 3,2 et convertie en une forme saturée essentiellement par des ions monovalents au moyen de traitements répétés par Cl Na 1 N.

Kurzreferat— Eine schwarzer, an organischer Substanz reicher, alluvialer Ton aus Alleppey, Staat Kerala, Indien, ergab im natürlichen, unbehandelten Zustand einen gut definierten 17 Å-Reflex. Äthylenglykol- und Wärmebehandlung zeigten, daß es sich im wesentlichen um einen Smectit handelt. Behandlungen mit H₂O₂ und 0,1 n NaOH verringern den Abstand auf 14 Å. Dies zeigt, daß sorbierte organische Substanz für den ursprünglich erhöhten Basisebenenabstand verantwortlich war.

Im natürlichen Zustand waren die Austauschplätze vorwiegend mit zweiwertigen Ionen abgesättigt. Der pH-Wert betrug 6,2. Anschließend Versuche, die organische Substanz (die vom Ton durch wiederholte Behandlung mit NaOH extrahiert, in die H-Form überführt, konzentriert und der Gefrier-trocknung unterworfen worden war) wieder in die Zwischenschichten des H₂O₂-behandelten Tones einzulagern, erwiesen sich nur dann als erfolgreich, wenn zuvor der pH-Wert auf 3,2 herabgesetzt und der Ton durch wiederholte Behandlung mit 1 n NaCl im wesentlichen mit einwertigen Ionen belegt worden war.

Резюме— В природном необработанном состоянии черная богатая органическими веществами наносная глина из Аллеппи, Штат Кэрала в Индии, дала отчетливое отражение 17 Å. Обработка этиленгликолем и термообработка показали, что эта глина по существу является смектитом. Обработка H₂O₂ и 0,1 N NaOH сузило межслоевые промежутки до приблизи-

тельно 14 Å, что указывает на то, что первоначальные большие межслоевые промежутки были вызваны сорбированным органическим веществом. В природном состоянии глина является, главным образом, двухвалентной относительно ионного обмена и ее рН — 6,2. Дальнейшие попытки сорбировать органическое вещество (экстрагированное из глины обработкой NaOH и превращенное в форму-H; концентрированную глину высушивали при температуре ниже 0°C) в межслоевой промежуток глины обработанной H₂O₂ увенчалось успехом только после понижения рН до 3,2 и превращения глины в одновалентное состояние посредством повторных обработок с NaCl.