

CHAPTER III

CLAY MINERALS : CHARACTERISATION BY X-RAY DIFFRACTION

Clay, Clay Minerals and their Classification

The term clay is being used as a rock term and also as a particle size term in mechanical analysis of sedimentary rocks, soils etc. for years together. In general the term clay implies a natural, earthy fine grained material which develops plasticity when mixed with water. Chemically, clays are composed essentially of silica, alumina and water. Iron, alkalis, and alkaline earths are nearly always present. The term clay is used for material that has a variety of origin e.g. (i) product of weathering, (ii) formed by hydrothermal action on preexisting rocks or (iii) sedimentary deposition in river or lake or sea. Wentworth (1922) assigned clay grade to material less than 4 microns in size, whereas soil scientists have placed clay grade at 2 microns. It has been observed that most of the clay fraction occurs with size less than 2μ only, so 2μ appears to be a convenient limit.

Because of their wide applications in ceramics and pottery, clays are being studied for thousands of years with the available tools. However, until very recently there were

no adequate analytical tools to determine with any degree of certainty the exact nature of most of the clay minerals.

One of the very old ideas about clay mineral is that it is essentially kaolinite and sometimes other materials occur only as impurity. This idea grew probably because kaolin clays had widest applications in ceramics and art and were relatively more studied. Another concept held mostly by soil scientists, was that the essential component of all clay materials was a colloid complex.

Hadding (1923) working in Sweden and Rinne (1924) working in Germany were the earliest workers to publish X-ray diffraction analyses of clays. With these studies the clays were regarded as independent minerals and not amorphous material or colloids etc. Ross and Shannon (1925, 1926) in United States, studied clays using petrographic microscope and carried out chemical analyses. They suggested that the components of clay materials are essentially crystalline and they may be called as clay minerals and in 1928 Ross proposed a classification of clay minerals.

In the decade 1930-40 the concept of "clay mineral" was widely understood. Works of Ross and Kerr (1931) and

Correns (1936) are particularly responsible for spreading this concept of clay mineral amongst the scientists. According to this concept clays are regarded to be composed of extremely small crystalline particles, the clay minerals which are essentially hydrous aluminium silicates. Alkalis and alkaline earths are present in some clay minerals while in some others magnesium or iron partly replace some of the aluminium. In addition to clay minerals some of the nonclay minerals, organic matter, soluble salts also form important constituents of clays.

Ross and Kerr worked on kaolinite (1931) and halloysite (1934) in detail. Another important clay mineral, montmorillonite was also studied in detail by Ross and Hendricks (1945). Contribution by Hendricks and his coworkers towards study of the physicochemical properties of different clays is highly significant (Hendricks, 1938, 1941, 1942, 1945; Hendricks et al, 1936). Workers from Illinois State Geological Survey and University of Illinois, especially, Grim and Bradley and their coworkers have studied clays from different angles (Grim, 1947, 1948, 1950; Grim et al, 1935, 1937; Bradley, 1945).

The credit of synthesising clay minerals in the laboratory for the first time goes to Noll (1935). OrceI (1933) was the first to apply the differential thermal analysis, as an

important technique in the study of clays.

In later years Brindley and Robinson (1946a, 1946b) studied kaolin minerals and their crystallinity in greater detail. Glaeser (1948), Mering et al (1950) studied adsorption of various ions on clay minerals and their textures using electron microscope.

In the second half of this century the importance of studying clay minerals was accepted and highly useful books describing the nature of clays and the methods of study were published. The important ones include "X-ray identification and crystal structure of clay minerals by Brindley (1951). Its second edition was presented by Brown (1961). Carroll (1970) published a guide to clay mineral identification using X-ray techniques. Grim (1953) published a book "Clay Mineralogy" in the light of new developments. A largely revised edition of this book came in 1968. "Applied Clay Mineralogy" by Grim (1962), "Differential thermal investigations of Clays" edited by Mackenzie (1957); "Geology of clays" by Millot (1970); "Atlas of infrared spectroscopy of clays and their admixtures" by Van der Marrel and Beutelspacher (1976); and "Atlas of electron microscopy of clays and their admixtures (1968) are few other books extremely useful in clay mineralogical studies.

Clay minerals are phyllosilicates or layer silicates i.e. they are extended more in two dimensions. They consist of layers with two types of units involved in each layer, the tetrahedral and the octahedral. The tetrahedral unit consists of silica tetrahedra. In each tetrahedron silicon is situated at the centre and four oxygens are at the four corners. Several such tetrahedra form a hexagonal network. Tips of these tetrahedra point in a single direction and their bases lie in a plane. On the other hand six oxygen or hydroxyl ions occupy corners of each octahedron and aluminium, iron or magnesium are situated at their centres.

The present definition as suggested by Brindley and Pedro (1972) states "Clay minerals belong to a family of phyllosilicates and contain continuous two-dimensional tetrahedral sheets of composition T_2O_5 ($T = Si, Al, Be, \dots$) with tetrahedra linked by sharing three corners of each, and with the fourth corner pointing in any direction. The tetrahedral sheets are linked in the unit structure to octahedral sheets, or to groups of coordinated cations, or individual cations".

Several workers have attempted classification of clay minerals, mainly based on the structural characteristics as there is a wide range of chemical composition not only within

a single group, but also within single mineral.

Caillere and Henin (1956) proposed a tabular classification of sheet silicates. This was later modified by Caillere in (1960) (in Millot, 1970). It consists of six tables one for the general classification of hydrated silicates, and kaolinites and serpentinites with real basal spacing of 7 \AA , micas and dioctahedral montmorillonites with basal spacing of 10 \AA , micas and trioctahedral montmorillonites with basal spacing of 10 \AA , chlorites having basal spacing of 14 \AA and for mixed layer complexes having varying basal spacing, are the other five tables classifying major groups of clays.

Deer, Howie and Zussman (1962, 1976) have classified clay minerals into five main groups, again on the basis of characteristic basal spacings.

1. Kandite group (7 \AA) - kaolinite, dickite and nacrite, anauxite, halloysite, metahalloysite and allophane.
2. Illite group (10 \AA) - illite, hydro-micas, phengite, brammallite, glauconite and celadonite.
3. Smectite group (15 \AA) - montmorillonite, nontronite, hectorite, saponite and sauconite
4. Vermiculite (14.5 \AA)
5. Palygorskite group - palygorskite, attapulgite and sepiolite.

The clay minerals attapulgite and sepiolite from the palygorskite group have chain like crystal structures and are less common. However, the mixed layered minerals which occur very commonly in nature have no place in this classification. Though there are few more classifications available, such as those by Franke-kamenetskii (1961); Jasmund (1955); the classification scheme for phyllosilicates proposed by AIPEA etc. The one proposed by Grim (1968) and reproduced below is more useful and takes into account not only structure but shape and also the expandibility.

Classification of the Clay Minerals by Grim (1968)

- I. Amorphous group
 - Allophane group
- II. Crystalline
 - A. Two layer type
 - 1. Equidimensional
kaolinite group - kaolinite, nacrite etc.
 - 2. Elongate
Halloysite group
 - B. Three layer types
 - 1. Expanding lattice
 - a. Equidimensional
Montmorillonite group - montmorillonite,
sauconite etc.
Vermiculite.

b. Elongate

Montmorillonite group - nontronite,
saponite, hectorite

2. Non expanding lattice

Illite group

C. Regular mixed layer types

Chlorite group

D. Chain - structure types

Attapulgitic

Sepiolite

Palygorskite

The important clay mineral groups relevant to the present work are described in brief below.

The kandite group

The kandite group includes a group of minerals characterised by a basal spacing of $7 \overset{\circ}{\text{A}}$. Compared to the clay minerals from other groups the kandites have a very restricted range of chemical composition. Kaolinite, dickite and nacrite and halloysite are described from this group.

Kaolinite : It is chemically a hydrated aluminosilicate

$\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$. Silica tetrahedra are linked with the octahedra with aluminium at their centers by OH^- group, forming a single layer. Several such layers are stacked together with a periodic spacing of 7 \AA . This is clearly reflected in the X-ray diffractograms. On heating to 600°C the structure collapses and the 7 \AA peak is lost in the diffractogram. These two features were also observed in the present study in the clays from Panchgani-Mahabaleshwar area.

Dickite and nacrite : These are rare minerals usually found in hydrothermal deposits. Chemically they are identical with kaolinite, and crystallise in monoclinic system contrast to kaolinite. However their lattice structures are different. They also give an intense peak at 7.1 \AA , but the structure remains stable after heating to 600°C .

Halloysite : It is known to occur in two forms with basal spacing 10 \AA and 7 \AA and also with two morphologies viz. elongate tubes and spherical globules. The one with basal spacing 10 \AA is called halloysite and the one showing 7 \AA as metahalloysite. Recently AIPEA (1980) has accepted that instead of calling the hydrated and dehydrated or calling separately as halloysite and endellite they should be termed simply 'halloysite 10 \AA ' and 'halloysite 7 \AA '. A slight

deviation in the structure of halloysite occurs from kaolinite in the fact that a water layer is present separating the kaolinite layers.

Smectite group

A central alumina (or Fe, Mg) octahedral sheet is sandwiched between two tetrahedral sheets (2:1 minerals). Apices of the silica tetrahedra point towards the center of the sheet. Tips of the tetrahedra from each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. Smectites are thus similar to micas in structure but the bonds in between are much weaker and water can enter in variable quantity between the unit layers. The stacking periodicity of the layers is 14 \AA . Water and other polar molecules can easily enter in between the unit layers and cause expansion of lattice in the c direction. The expansion property is reversible. Another characteristic of the smectites is the presence of exchangeable cations. Na^+ and Ca^+ occur as common exchangeable cations between the silica tetrahedra of two layers. The basal spacings along 'c' axis vary with the amount of water molecules, exchangeable cations, and nature of adsorbed organic molecules. Under normal conditions when the exchange ion is Na^+ the basal 'd' spacing is 12.5 \AA and

monomolecular water layer. The basal 'd' spacing is 14.5 to 15.5 Å when the exchange ion is Ca^{++} and in this case usually two molecular water layers are present. Homann et al (1956) have shown that intercrystalline swelling is absent when there is no charge on the lattice. Hight et al (1962) found that in dilute aqueous suspensions, sodium montmorillonites occurred in independent layers 10 Å thick.

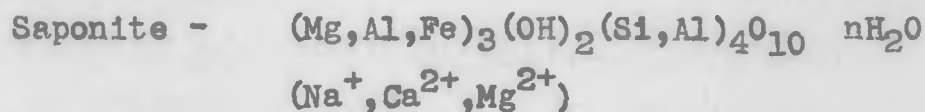
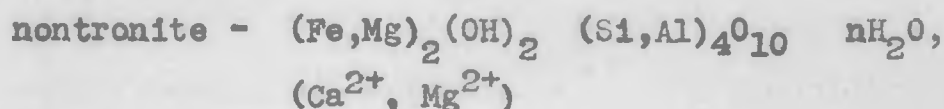
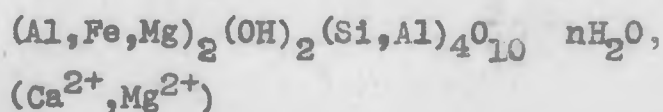
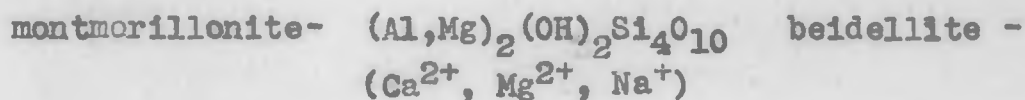
The nomenclature of the smectite group depends on the substitution within the lattice. Accordingly, smectites have been divided into -

- (a) dioctahedral series - 1/3 or nearly 1/3 octahedral positions are empty.
- (b) trioctahedral series - all or nearly all positions are occupied by cations.

In the trioctahedral smectites there is a complete substitution of magnesia for alumina.

The important clay minerals from this group are described in brief below. Water and other polar molecules that may occur in between the silicate layers are omitted from the formula.

Montmorillonite is a high alumina endmember of the montmorillonite group with some slight replacement of Al^{+3} by Mg^{+2} and without any substantial replacement of Si^{+4} by Al^{+3} . At the beidellite end of the montmorillonite-beidellite dioctahedral series, aluminium replaces silicon in the tetrahedral sheets. When ferric iron replaces aluminium the dioctahedral nontronite-beidellite series results. Saponite, the octahedral mineral from this group contains Mg and Na occurring as interlayer cation.



Illite Group : Illite is the most common clay mineral group occurring in nature. Minerals from the illite group have structures that are similar to those of micas differing only in

the content of potassium ion which is less and is replaced by water. Illites and montmorillonite both have same unit layer configuration, however, some of the silicons in illite are always replaced by aluminium and the resulting excessive negative charge is balanced by potassium in interlayer positions.

In illites the characteristic $10 \overset{\circ}{\text{A}}$ diffraction line in X-ray diffraction is often modified into a band because of the small particle size, variation in the interlayer cation, and interlayer hydration. This band tails off towards the low angle region. Polymorphs of illites are also known to occur. They may be distinguished from each other by the manner in which sheets stack together in the 'C' direction. They are indicated by a number and a letter. The numbers 1,2,3 indicate layers in a unit cell and letters M or T suggest the crystal system monoclinic or triclinic.

Chlorite Group

These are the foliated micaceous minerals rich in ferrous iron. Because of the substitutions in tetrahedral, octahedral, as well as brucite layers a great variety of minerals are observed in this group. They are characterised by $14 \overset{\circ}{\text{A}}$ basal spacing. However, when present in small quantities in clay

minerals, one cannot identify them to the mineral level and only it may be said that a "non-expanding" mineral with 14 Å basal spacing is present. The clay mineral chlorites differ from true chlorites i.e. the chlorites in schists and gneisses in somewhat random stacking of layers and perhaps in some hydration.

Celadonite : Celadonite has been defined as a dioctahedral mica with an ideal composition $\text{KMgFe}^{3+}\text{Si}_4\text{O}_{10}(\text{OH})_2$ but allowing a tetrahedral Al (or Fe^{3+}) range of 0.0 to about 0.2 atoms per formula unit by the AIPEA Nomenclature Committee (1978).

Further important characteristics to define celadonite include $d(060)$ less than 1.510 Å and sharp infrared spectra as against the similar mineral glauconite has $d(060)$ greater than 1.510 Å and a broader infrared spectra (Buckley *et al.* 1978).

Vermiculite Group

Vermiculite is very much similar to mica, but when heated it becomes worm like. It consists of mica layers separated by water molecules and to balance the charge Mg and at times Ca are present as interlayer ions. Millot (1970) has defined the "clay vermiculites" as the dioctahedral or trioctahedral micaceous structures in which bonding between the layers is weaker than in micas and chlorites, but stronger than

that in montmorillonites. When heated to 500 °C, water between mica layers is lost but the mineral quickly rehydrates on exposure to moisture. The lattice expansion in vermiculite is about two water molecules or 4.98 Å. On heating to 700 °C, it does not show any further expansion and gives a typical diffractogram in which 14 Å line is lost, and new 9.3 Å line of mica is introduced. The basal spacings of vermiculite vary with the interlayer cation. However, most of the Mg saturated vermiculites give a basal spacing 14.3 Å under glycerol, which helps as a criterion to distinguish them from the smectites.

Mixed layer clay minerals

Mixed layer minerals are highly complex in their structure and composition and are very difficult to study, though their occurrence is quite frequent in soils, sediments and alteration products.

Three types of mixed layer structures have been shown by MacEwan (1949). Regular mixed layer structures are those in which layers of different types, regularly alternate with each other following a certain law. Some such minerals have been given specific names, such as allevardite, rectorite, and corrensite. In irregular interstratification, the alternation of layers is not governed by any law and they are randomly

distributed. They are very common but it is very difficult to identify the components. Still more difficult to analyse are the structures with segregation of alternating pockets of clay layers, which themselves are interlayered at times.

Millot (1970) has shown that by interstratification of illite, chlorite, montmorillonite and vermiculite layers two by two, six types of interstratifications are possible. If along with the above standard minerals the swelling chlorite and 12 Å⁰ montmorillonite are also considered several more varieties result.

X-ray Diffraction of Clays

X-ray diffractometry is the best possible and primary technique used for the identification of clay minerals. Other techniques of infrared absorption, thermal analysis, electron microscopy, stain tests etc. are either supplementary or confirmatory to XRD.

Clay minerals are layer silicates in which sheets of atoms, of the general composition $(Si, Al)_4O_{10}(OH)_2$ are stacked one above another in various ways with different kinds of atoms lying between the layers and holding them together. As they have planar structures the 'd' spacings corresponding to 001

reflections get an importance in the identification. The common method of sample packing in a window randomises all the reflections. It was observed that if by some means the clay particles are allowed to lie flat on the substrate then in the X-ray diffractogram only the 001 reflections characteristic of the individual mineral would be enhanced. Variations in these 001 reflections also help in the study of interstratification, if any.

The XRD work of the representative samples was done on two diffractometers at different times. A part of the work was carried out on the Phillips X-ray diffractometer in the Tata Institute of Fundamental Research, Bombay and a part on Phillips X-ray diffractometer in the Atomic Minerals Division Laboratory, Hyderabad. CuK_α radiations were used for diffraction in most of the samples, however, a few were scanned with CoK_α radiations.

Finely ground samples were scanned by powder pack method and the clay separates were scanned by oriented mount method followed by ethylene glycol saturation and heating to 600°C for one hour.

Sample preparation and methodology

Rock powders finely ground in agate mortar to a size less than 200 mesh were used as starting material. These powders were scanned by powder pack method to give the general mineralogical composition. Clay separates were also made and scanned by oriented mount method largely following the procedures given by Brown (1961) and Hutchison (1974).

The powder pack method : In this method an aluminium plate with a rectangular hole inside, backed with a glass slide is used to place the sample. Powder is filled in the cavity and is smoothed off. Though this method might have introduced some preferred orientation in the sample it was not much harmful in the present study and special precautions for obtaining perfect random orientations were not necessary. The powder packs thus prepared were directly placed in the sample-holder and scanned at a rate of 1° per minute in the scanning range of 2θ values between 5° to 50° .

The clays were separated from the rock powders in the following manner and then they were used to prepare oriented mounts.

Clay separation : About 50 gms of ground rock powder was

placed in 1000 ml capacity cylinder and distilled water was added till the mark. The mixture was stirred vigorously and allowed to stand overnight. The clay flocculated and a clear water column remained above. This water was siphoned off and cylinder was refilled with fresh distilled water. The process was repeated for about 8 days. Finally the clays were disaggregated in an ultrasonic vibrator for about 10 minutes, then put back in the cylinder. The cylinder was then filled in with fresh distilled water and about 10 drops of ammonia were added. The mixture was stirred and allowed to stand for 10 hours. This standing period allowed only the clay fraction ($< 2\mu$) to be in suspension whereas all higher size fractions settled down. Upper 200 ml liquid containing clay matter was siphoned off. This was repeated several times. Clays present in this liquid were concentrated by centrifuging and the clay slurry thus obtained was stored in small bottles for further analysis.

The oriented mount method : Microscope glass slides were cut into half (25 x 35 mm) so as to fit well in the sample holder of the Phillips X-ray diffractometer. A few drops of the clay slurry were placed on the glass slide using an eye dropper and allowed to dry at room temperature. This gave a thin, uniform,

and well oriented layer of clay on the glass slide. Duplicate mounts of each sample were prepared. Part of slide that goes in the clip was wiped clear before mounting the slide on goniometer shaft.

X-ray diffractograms of the oriented mounts of the clays yield maximum information. Brown (1961) has recommended a preferential order for running samples on a diffractometer.

- (1) Well oriented specimen of each clay at low relative humidity (10-20 %),
- (2) ethylene glycol treated specimen,
- (3) heat treatment at 550 °C to 600 °C,
- (4) heat treatment at 110 °C.

In the present study first three recommended steps were carried out. Relative humidity was only under partial control in an air conditioned room (relative humidity - 55 to 60 %). Thus any error in the reflections due to change in humidity was avoided.

After recording a diffractogram all slides were placed in a dessicator containing ethylene glycol for 24 hours. The diffractograms of the glycolated samples were made in order to see any change in the 001 reflection, expansion of which is

a characteristic of clays having expandible lattice i.e. montmorillonites. The other batch of oriented mounts was heated in a muffle furnace to 600 °C for one hour, cooled and a diffractogram upto $2\theta = 24^\circ$ was recorded for each sample. Difference in the diffractogram from the corresponding untreated one indicated destruction of lattice and probable presence of kaolinite.

The results of the X-ray diffraction work are detailed in Table 3.1. It may be mentioned here that while interpreting the X-ray diffractograms it was observed that due to poor crystallinity and impure nature of the study material a certain amount of variation from the JCPDS standard data was observed and the interpretations were not so obvious. Secondly, certain samples were scanned only for the clay separates. Thus escaping the probable detection of minerals like plagioclase feldspars or gibbsite. A high proportion of glass in the samples from the interflow zones has made the detection of other minerals difficult.

Table No. 3.1 : X-ray diffraction results

Sample No.	Method	dA° / I/I ₁												Inference	
Ch 5	oriented mount	dA°	11.40	11.024	10.039	9.0175	3.3236	3.1617	2.7859	2.4111	2.0018	1.90	1.76	montmorillonite-chlorite, illite-montmorillonite, mix layered minerals with expandible lattice	
		I/I ₁	50	50	100	50	75	50	50	25	25	25	25		
	glycolated	dA°	18.018	10.039	6.9642	3.34	3.20								
		I/I ₁	100	50	50	50	50								
Sg 1	random packing	dA°	7.75	4.59	4.37	3.69	3.44	3.34	3.3	3.25	3.23	2.7	2.52	2.45	labradorite, montmorillonite
		I/I ₁	12.5	15.63	28.13	9.38	9.38	100	15.63	12.5	12.5	2.5	18.75	9.38	
	dA°	2.28	2.13	1.79	1.69	1.54	1.45	1.37							
	I/I ₁	6.25	9.38	12.5	12.5	9.38	9.38	9.38							
Sg ₂	random packing	dA°	6.99	4.63	3.79	3.53	3.41	3.28	3.12	3.07	2.94	2.82	2.75	2.56	labradorite, heulandite, montmorillonite
		I/I ₁	100	92.3	26.92	23.1	26.92	34.62	23.1	30.8	19.23	19.23	30.8	65.38	
Sg ₅	oriented	dA°	12.267	10.567	9.1103	7.155	4.3922	4.3161	4.0259	3.6021	3.1883	2.7443		irregular illite-montmorillonite mix layer showing some expansion, hematite, kaolinite(?), baidellite(?)	
		I/I ₁	100	100	100	50	100	100	100	100	100	100			
	dA°	2.668	2.5155	2.1641		8.0364									
	I/I ₁	100	100	50		100									
	glycolated	dA°	17.312	11.324	9.7096										
		I/I ₁	50	100	100										
Sg ₆	random packing	dA°	15.3567	12.6172	11.1815	9.3016	6.0006	4.4357	3.6895	3.5941	3.2406	2.9760		montmorillonite-chlorite mix layer, illite-montmorillonite mix layer, hematite, kaolinite (?)	
		I/I ₁	20	20	40	20	20	100	40	40	20	60			
	dA°	2.6922	2.5060	2.3569	2.1493	1.6851	1.5382	1.4977	1.4890						
	I/I ₁	40	80	40	20	40	20	40	40						
	dA°	1.4784													
	I/I ₁	40													

Th. 6535

Th. 6535

Th. 6535

Th. 6535

Contd..

Table No. 3.1 (Contd.)

Sample No.	Method	dA ⁰ / I/I ₁												Inference	
Sg 6	oriented mount	dA ⁰	11.84	7.0415	6.0209	4.4666	4.2954	3.9481	3.0153	2.4687	1.5887			montmorillonite-chlorite, montmorillonite-illite mix layer minerals	
		I/I ₁	100	40	40	20	20	40	20	20	20				
	glycolated	dA ⁰	20.065	16.064	10.039	4.45									
		I/I ₁	40	100	40	40									
Sh ₄	oriented mount	dA ⁰	12.617	11.383	5.133	4.39	4.401	4.0008	3.735	3.622	3.229	2.976	1.641	montmorillonite-chlorite, irregular mix layer, illite-montmorillonite with little expansion	
		I/I ₁	100	83.33	33.33	50	16.67	33.33	33.33	16.67	16.67	16.67	16.67		
	glycolated	dA ⁰	14.966	12.267	10.039	8.8376	4.5025							montmorillonite and labradorite, magnetite	
		I/I ₁	100	50	100	100	100								
	random packet	dA ⁰	4.60	3.77	3.31	3.035	2.74	2.56	2.11	1.714					
		I/I ₁	100	41.67	25.0	33.33	41.67	58.33	16.67	25					
PSN ₁	oriented	dA ⁰	10.039	9.0544	4.9238	4.4577	4.0919	3.2995	2.6572	2.4792	2.0212			on heating certain peaks show increase in intensity, montmorillonite-chlorite mix layer, illite, illite-montmorillonite mix layer	
		I/I ₁	100	26.32	15.79	10.53	10.53	57.89	10.53	10.53	15.79				
	dA ⁰	1.6542	1.6337												
	I/I ₁	10.53	10.53												
	glycolated	dA ⁰	9.8172	5.5690	5.2852	4.9238	4.48								
		I/I ₁	100	14.29	14.29	14.29	21.43								
heated oriented mount	dA ⁰	9.93	4.9238	4.50	3.34	3.21									
	I/I ₁	100	9.7	6.45	29.03	19.35									
PB 1	random packing	dA ⁰	9.35	8.88	8.38	7.89	5.20	5.06	4.79	4.28	3.86	3.78	3.54	chlorite, montmorillonite nontronite(?) - calcite illite-montmorillonite mix layer	
		I/I ₁	13.79	17.24	20.69	86.21	24.1	24.1	17.24	27.60	62	62	20.69		
	dA ⁰	3.076	3.025	2.69	2.59	2.44									
Psr 1	random packing	dA ⁰	12.90	10.69	10.26	8.38	7.90	5.85	5.53	4.58	4.34			laboradorite, montmorillonite-chlorite mix layer, illite, kaolinite (?)	
		I/I ₁	18.18	27.27	27.27	36.36	27.27	18.18	27.27	63.63	45.45				
	dA ⁰	3.93	3.86	3.75	3.39	3.31	3.27	2.73	2.53						
	I/I ₁	27.27	45.45	45.45	36.36	45.45	100	100	54.54						

Th. 6535

Th. 6535

Th. 6535

Th. 6535

Contd...

Table No. 3.1 (contd.)

Sample No.	Method	dA° / I/I ₁												Inference	
Cl 1	oriented mount	dA°	12.62	11.62	10.96	8.466	7.308	5.1332	4.766	3.767	3.184	2.938		illite-montmorillonite mix layer, with expandible lattice, labradorite illite (?), montmorillonite sepiolite (?)	
		I/I ₁	33.33	66.67	100	50	33.33	16.67	16.67	33.33	50	16.67			
	dA°	2.90	2.79	2.12	2.065	1.789									
	I/I ₁	16.67	33.33	16.67	33.33	16.67									
DW 1	oriented mount	dA°	16.54	8.09	7.29	5.11	4.53	4.3	4.06	3.57	3.37	3.23	3.02	montmorillonite, montmorillonite-chlorite with irregular mix layers, illite, sepiolite (?), kaolinite.	
		I/I ₁	100	7.35	5.88	5.88	2.94	1.47	1.47	8.82	2.94	2.94	1.47		
	glycolated	dA°	17.53	8.70	7.34	5.72	4.49								
	I/I ₁	100	11.11	7.41	7.41	5.55									
DW 3	oriented mount	dA°	16.28	10.8	8.22	7.29	5.49	4.97	3.59	3.37	3.23	3.04		montmorillonite-chlorite irregular mix layer, illite-montmorillonite mix layer, illite, montmorillonite, kaolinite calcite.	
		I/I ₁	100	8	2.67	9.33	6.67	9.33	9.33	8	9.3	16			
	glycolated	dA°	17.38	11.4	8.56	7.34	5.56	5.05							
	I/I ₁	100	3.57	10.71	14.29	14.29	7.14								
DW 4	random packing	dA°	15.77	10.91	8.56	3.70								labradorite, montmorillonite, kaolinite, quartz, calcite	
		I/I ₁	100	33.3	33.3	33.3									
	oriented mount	dA°	16.02	7.2	4.80	4.67	3.95	3.55	3.35	3.22	3.04				
		I/I ₁	100	10.53	7.89	7.89	2.63	5.26	5.26	5.26	15.79				
Mtr 1	glycolated	dA°	17.68	12.21	10.80	8.93	5.62							quartz, heulandite mix layer mineral (?)	
		I/I ₁	100	27.27	18.18	31.82	13.62								
	random	dA°	4.2269	3.9656	3.8969	3.6895	3.5172	3.3359	2.9664	2.7944	2.7362				
		I/I ₁	34.38	3.75	2.5	3.13	1.88	100	3.13	1.88	1.88				
		dA°	2.4596	2.2794	2.2360	2.1300	1.9835	1.8192	1.6598	1.5312					
		I/I ₁	10	8.13	4.38	5.63	3.75	13.13	4.38	7.5					
		dA°	1.4435	1.3721	1.3703	1.3668	1.3634	1.2799	1.2483						
	I/I ₁	1.88	3.75	3.75	7.5	8.13	2.5	3.13							

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Table No. 3.1 (contd.)

Sample No.	Method	dA ⁰ / I/I ₁													Inference			
S 1	oriented mount	dA ⁰	7.2249	4.3496	4.1390	3.5784	2.4993	2.3779	1.7872						kaolinite, a smectite mineral gibbsite (?)			
		I/I ₁	100	6.56	8.2	70.50	3.28	8.2	3.28									
	heated	dA ⁰	10.3935	5.2111	3.4968													
		I/I ₁	100	100	75													
S 3	oriented mount	dA ⁰	7.155	4.4357	4.1295	3.5728	2.0877	1.7415	1.4912						pure kaolinite			
		I/I ₁	100	7.40	11.11	44.44	3.70	3.70	3.70									
	heated	curve is flat without any recognisable peaks																
Kfm I	random packing	dA ⁰	7.5	4.6	4.48	4.41	4.29	3.95	3.73	3.62	3.55	3.44	2.60	2.57	kaolinite, dehydrated halloysite, labradorite (?)			
		I/I ₁	100	43	68	39	53	25	93	50	22	18	29	20.4				
		dA ⁰	2.54	Th. 6535					Th. 6535									
		I/I ₁	36															
Kfm IV	oriented mount	dA ⁰	7.1897	4.33	4.156	3.82	3.56	2.712	2.55	2.38	2.32	2.29	1.98	1.84	1.78	kaolinite		
		I/I ₁	100	13.79	10.34	6.9	62.1	6.9	10.34	10.34	10.34	6.9	3.5	3.5	3.5			
		dA ⁰	1.67	1.54	1.48													
			I/I ₁	3.5	3.5	3.5												
		heated	curve is flat without any recognisable peaks															
		random packing	dA ⁰	7.5	4.58	4.47	4.28	3.94	3.62	3.44	2.79	2.75						
		I/I ₁	100	51.85	70.37	51.85	18.52	81.48	14.81	40.74	25.93							
DG 4	random packing	dA ⁰	10.39	8.62	8.26	7.46	6.65	6.08	4.51	4.44	4.31	4.25	4.02	kaolinite, halloysite hydrated, halloysite dehydrated, labradorite magnetite quartz (?) boehmite (?) montmorillonite (?)				
		I/I ₁	16.67	10.42	12.5	100	18.75	12.5	60.42	54.17	35.42	39.58	12.5					
		dA ⁰	3.78	3.70	3.41	3.36	3.15	2.98	2.77	2.58	2.54	2.42	2.37					
			I/I ₁	10.42	52.08	12.5	10.42	10.42	10.42	12.5	41.67	43.75	14.58	39.58				
			dA ⁰	2.30	2.103	2.01	1.86	1.68	1.61									
			I/I ₁	20.83	12.5	14.6	12.5	20.83	10.42									

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Table No. 3.1 (contd.)

Sample No.	Method	dA ⁰ / I/I ₁												Inference	
Soil/ Litho- marge a	oriented mount	dA ⁰	11.04	10.393	8.665	7.1897	3.87	3.55	2.74	1.85	1.54			kaolinite, a smectite mineral, dickite (?)	
		I/I ₁	14.3	14.3	21.43	100	14.3	50	14.3	14.3	21.43				
	glycolated	dA ⁰	16.659	8.8376	7.1897	4.1876									
		I/I ₁	16.7	16.7	100	25									
M 2	oriented mount	dA ⁰	16.05	9.817										kaolinite, an illite group mineral	
		I/I ₁	50	100											
	heated	dA ⁰	10.3935	7.2131	5.1214	4.3793	4.1678	3.5643	2.3718	1.4847					
		I/I ₁	20	100	20	40	30	70	20	20					
	heated	curve is without appreciable peaks													
TN 1	oriented mount	dA ⁰	7.1897	4.18	3.56	2.55	2.38							kaolinite	
		I/I ₁	100	20	70	10	10								
	heated	curve is flat without any recognisable peaks													
Kaoli- nised Trap a	random packing	dA ⁰	7.5	6.90	6.63	4.61	4.51	4.30	4.08	3.67	3.60	3.46	3.02	kaolinite, labradorite	
		I/I ₁	100	36.84	36.84	47.37	42.11	36.84	21.1	52.63	15.79	31.58	26.32		
Pr 2	oriented mount	dA ⁰	13.38	12.62	9.3	7.17	4.98	3.58	3.68	2.999	4.437	4.287		kaolinite (?), halloysite (?) illite, illite-montmorillonite mix layer, some expansion is seen	
		I/I ₁	100	82.0	18.2	54.5	100	36.4	18.2	63.6	9.1	9.1			
	glycolated	dA ⁰	6.98	11.383	8.4179	7.18	5.53								
		I/I ₁	9.1	27.3	45.45	45.45	100								
	heated	dA ⁰	10.04	4.75	3.17										
		I/I ₁	25	40	72										

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