

**ORIGINAL ARTICLE**

**GEOLOGICAL SETTING AND MINERALOGICAL CHARACTERIZATION OF TERTIARY CLAYS OF TRIVANDRUM AND KOLLAM DISTRICTS, KERALA, INDIA**

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*Article History: Received 20<sup>th</sup> June,2015, Accepted July 30<sup>th</sup> 2015, Published 1<sup>st</sup> August ,2015*

**ABSTRACT**

The study concerns Tertiary clay deposits occurring at Trivandrum and Kollam District, Kerala, India. Most of the major residual and sedimentary deposits including kaolinite deposits are associated with the Tertiary sedimentary formations. This great sedimentary deposit is spread over a major part of the western margin of Kerala. The sequence consists of both marine and non-marine rocks in the on-land part and are distributed in two major basins of deposition 1) between Trivandrum and Ponnani in the south and central Kerala with a maximum width of 16 km between Quilon and Kundara and 2) between Cannanore and Kasargode in north Kerala with a maximum width of 10 km at Cheruvattur. Mineralogical characterization has been carried out by using FTIR analytical technique. Kaolinite is the predominant clay mineral with subordinate illite, montmorillonite, quartz and hematite. The result which reveals that the clay deposits are mostly derived from weathering of Granitic rocks and deposited in a fresh water continental basin.

**Keywords:** FT-IR technique, Tertiary Clays, Trivandrum and Kollam district of Kerala State

**1.INTRODUCTION**

The clay materials possess a layered structure and are considered as host materials. They are classified by the differences in their layered structures. There are several classes of clays such as smectites (Montmorillonite, Saponite), clay mica (illite), Kaolinite, serpentine, pyrophyllite (talc), vermiculite and sepiolite (Shichi and Takagi, 2000). In recent years, there has been an increasing interest in utilizing minerals such as bentonite, kaolinite, diatomite and fullers earth for their capacity to adsorb not only inorganic but also organic molecules. They showed that this naturally occurring material could act as substitute for activated carbon as an adsorbent due to its availability and low cost, and its good sorption properties (Preethi sagar Nayak and Singh, 2007). Kaolinite group of minerals found in two different environments as tropical weathered products of all major rocks rich in alumina and as detrital or residual sedimentary deposits (Grim,1968;Kellar,1956;Millot,1970;). This paper deals with the geological setting and mineralogical characterization of Tertiary clays of Trivandrum and Kollam Districts of Kerala State.

**GEOLOGICAL SETTING**

Clay deposit of southern peninsular India is located in the eastern periphery of the Cenozoic sedimentary basin of South Kerala (Fig.1). Geologically the area is dominated by a thick sequence of white residual clay, formed from Precambrian crystalline rock. The sedimentary Warkallai bed of Upper Tertiary age is found above this primary deposit. These Tertiary sedimentary sequences are extensively lateritised in the uppermost portions and are found to overlie the entire region. The entire sequences of the clay in this deposit have an overall thickness of 55 meters. The clay sequences in the mine profile are divided into three groups: white residual clay, gray carbonaceous clay and hematitic clay for convenience.

The residual white clay is approximately 15 meters thick and sampling from this seam is done at 5 m interval. These clays show the presence of garnet patches, relict foliation and quartz vein of parent rock, the garnetiferous biotite gneiss. In addition, prominent black patches of FeS<sub>2</sub> almost circular in shape of ~ 5-10 cm in diameters are seen in certain portions of the residual clays. These patches are frequent up to a depth of 2-8 meters from the top of the residual clay layer and the frequency of the same decreases with depth. In addition, size of the patches also reduces with depth. Yellow coloured precipitation is found to encrust these occluded

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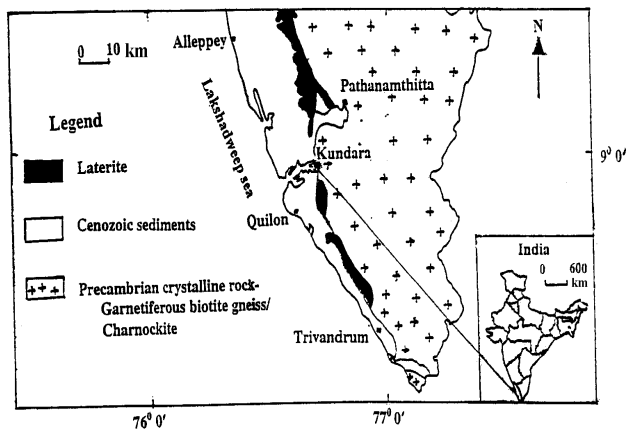


Fig.1 Location map of the study area

patches at some portions as a result of oxidation in areas of intense surface weathering. Numerous fossilised plant roots are preserved at the top 0 - 0.5 meters of the residual clay, indicating an intense growth of vegetation and consequent weathering of the Precambrian rock prior to Tertiary sedimentation.

The Warkallai beds, which overlie the residual clay are horizontally bedded and consist of layers of gray carbonaceous clay and lignite seams together making an approximate thickness of 20 meters followed by layers of ferruginous and variegated clay, sandy clay and lateritised sandy clay having maximum thickness of 1.8, 10.8 and 12.3 meters respectively. The entire Tertiary deposit has a maximum thickness of around 44 meters and the individual bed has varying thickness. The intensity of ongoing weathering under tropical climate of this area is evident from the extent of lateritisation of uppermost Tertiary sandy clay bed.

The entire region is fringed by younger fluvial sediments of Quaternary age towards the northwestern side and the lateritised Precambrian hard rock borders the east. Tertiary sedimentary sequences of Lower Miocene age with hard fossiliferous limestone and marl of Quilon Formation are exposed in the cliff section of Padappakara (towards north west of Kundara mine).

## 2.MATERIALS AND METHODS

Representative clay samples were collected from the Tertiary clays both from surface outcrops, nallas and working mine sites of Trivandrum and Kollam district, Kerala State. Well mixed large samples, which were reduced to about 250 g each by coning and quartering, were taken from clay mines. The samples were crushed in a agate mortar and a fine fraction of clay samples were used for Fourier Transform Infra-red Spectroscopy (FTIR) analysis.

## 3.RESULTS

### FTIR Studies

The major clay minerals identified in the Tertiary clays are Kaolinite together with small amounts of illite and Montmorillonite. The Non-clay minerals are Quartz and

Hematite. The FT-IR Spectra patterns of Tertiary clays are shown in the Figure 2. The important Infrared bands of clay along with their possible assignments are shown in the Table 1.

## CLAY MINERALS

Kaolinite is a major clay mineral which is present in all the samples and has been identified by the strong bands at 3695 cm<sup>-1</sup>, 3676 cm<sup>-1</sup>, 3650 cm<sup>-1</sup>, 3620 cm<sup>-1</sup>, 3546 cm<sup>-1</sup>, 3600 cm<sup>-1</sup>, 3565 cm<sup>-1</sup> in the OH- stretching of inner hydroxyl bonding regions which are characteristic of kaolinite. The characteristic band at 754cm<sup>-1</sup> and 432cm<sup>-1</sup> in the Si-O of mixed vibration and octahedral sheet vibration also reveals the presence of kaolinite. Montmorillonite is identified by the band at 1115cm<sup>-1</sup> in the (Al-O-(OH)<sub>6</sub> stretching regions.

Fig.2 FTIR Spectra of clays of the Trivandrum and Kollam District

### Non clay Mineral

Quartz is identified by the band at 796cm<sup>-1</sup>, 1,793cm<sup>-1</sup>, 1,696cm<sup>-1</sup>, 694cm<sup>-1</sup> and 468cm<sup>-1</sup>. Organic matter is identified by the band at 3546cm<sup>-1</sup> and 3600cm<sup>-1</sup>. Hematite is identified by the band at 537cm<sup>-1</sup> in the Fe-O (Fe<sub>2</sub>O<sub>3</sub>) stretching regions.

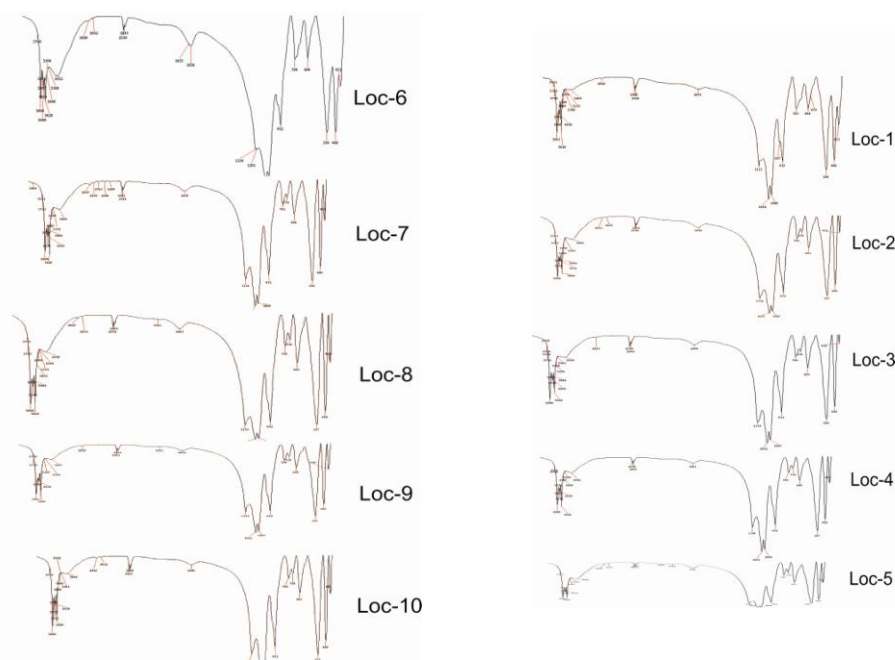
## 4.DISCUSSION AND CONCLUSION

It is well established that the infrared absorption bands in the 3800-3600cm<sup>-1</sup> region in the spectra of clay minerals are due absorption bands in the 3700-3600cm<sup>-1</sup> region. A comparison of these spectra with the spectra of Ramasamy et al. (2000) indicates that all these correspond to well order kaolinite structure. It has been pointed out that the bands at 3695cm<sup>-1</sup> and 3620cm<sup>-1</sup> are attributed to outer and inner hydroxyl groups and that the 3695cm<sup>-1</sup> has a maximum intensity in well-ordered Kaolinite structure while 3620cm<sup>-1</sup> does not change in intensity (Ramasamy et al.,1992). The weak bands around 2900cm<sup>-1</sup> and 2810cm<sup>-1</sup> occur in C-H stretching region (Colthup et al., 1990). The weak intensities of these bands could be an indication of traces of organic matter in Kaolinite from studied clay mines. It should be mentioned that the weak bands at 796,754 and 694cm<sup>-1</sup> may also be considered as lattice vibrations of Quartz (Wilson et al.,1994). This means that there is a possibility that Quartz may be present in kaolinite. However, the weak intensities of these bands may indicate that it occurs in very small amount. The weak bands at 796 and 754 cm<sup>-1</sup> are superimposed in Kaolinite and Quartz. All these samples show very strong absorption band around 535cm<sup>-1</sup>, they are due to hematite (Fe<sub>2</sub>O<sub>3</sub>). This band shows that the crystalline hematite is present in all samples (Ghosh et al., 1978). The bands at 469cm<sup>-1</sup> and 430cm<sup>-1</sup> have been assigned to Si-O of asymmetric bending vibrations and Si-O of mixed vibration respectively.

The results of the mineralogical characterization carried out by IR studies reveal that Kaolinite is the predominant clay mineral together with small amounts of illite, and montmorillonite. The non-clay mineral impurities are quartz and hematite. Bahl (1964) studied the sedimentary clay beds within the upper Gondwana (Jabalpur series) in the Jabalpur

**Table.1 Infrared absorption frequencies (Cm<sup>-1</sup>) of Study area clays**

T-1 Freq.	T-2 Freq.	T-3 Freq.	T-4 Freq.	T-5 Freq.	K-6 Freq.	K-7 Freq.	K-8 Freq.	K-9 Freq.	K-10 Freq.	Tentative Assignment	Minerals Name
3695	3696	3696	3696	3696	3696	3696	3696	3695	3696	OH- stretching of inner hydroxyl bonding	kaolinite
3676	3673	3674	3674	3674	3674	3676	3676		3674	OH- stretching of inner hydroxyl bonding	kaolinite
3669	3668	3668	3668	3668	3667	3669	3669	3669	3668	Degenerate internal Surface free OH anti symmetric stretching mode stretch (Al2O-H)	kaolinite
	3654	3654	3654	3654	3654	3655			3655	OH stretching	kaolinite
3650	3648	3649	3650	3650	3649	3650		3650	3650	OH- stretching of inner hydroxyl bonding	kaolinite
								3568		OH- stretching of inner hydroxyl bonding	kaolinite
3620	3620		3620	3620	3620	3620	3620	3546	3620	H-bands, OH-groups	Soil organic
			3600	3600			3601		3600	OH stretching of inner hydroxyl bonding	kaolinite
										H-bands, OH-groups	kaolinite
3588	3599	3599								OH- stretching of inner hydroxyl bonding	kaolinite
3579	3586	3586	3587							OH- stretching of inner hydroxyl bonding	kaolinite
3568	3565	3565	3566	3567	3566				3556	OH- stretching of inner hydroxyl bonding	kaolinite
3553							3553	3553	3552	OH- stretching of inner hydroxyl bonding	kaolinite
				3545				3546	3545	OH- stretching of inner hydroxyl bonding	kaolinite
3463	3459									OH- stretching of inner hydroxyl bonding	kaolinite
	3446		3446	3446		3448	3448	3447	3446	OH- stretching of inner hydroxyl bonding	kaolinite
2926	2925	2925		2924	2926	2924	2927	2929	2925	Organic matter	Kaolinite
	2854			2853	2852	2853	285			Organic carbon	Soil organic
						2765					kaolinite
						2666				Organic matter	Kaolinite
2362	2359	2359	2359	2360	2359	2363	2362	2361	2361	Organic matter	Kaolinite
2344	2342	2342	2343	2343	2343	2344	2344	2343	2343	Organic matter	Kaolinite
								1825		Organic matter	Kaolinite
1115	1114	1113	1114	1115	1114	1114	1115	1115	1114	(Al-O-(OH)) <sub>6</sub>	Montmorillonite
					1101						kaolinite
1032	1031	1032	1031	1031	1032	1031	1032	1031	1031	OH deformation of inner surface hydroxyl groups	Kaolinite
1008	1006	1007	1006	1006	1007	1006	1006	1007	1006	Al2 OH bending	kaolinite
937										OH deformation	kaolinite
913	912	913		912	912	912	912	912	913	Si-O symmetrical stretching	Quartz
795	794	794	793	793	796	792	793	794	793	Si-O of Quartz	Quartz
	754	754	754	753		754	754	754	754	Si-O, perpendicular	Kaolinite
694	695	695	696	695	694	694	695	696	695	OH deformation	kaolinite
670										Si-O of Quartz	Quartz
538	537	538	537	536	538	536	537	537	537	Fe-O (Fe2O3)	Hematite
469	468	468	468	468	468	468	468	468	468	SiO deformation	Montmorillonite



**Fig.2 FTIR Spectra of clays of the Trivandrum and Kollam District**

area of the Satpura basin and observed that the clay fraction are essentially kaolinite together with traces of Montmorillonite and illite. The kaolinite is originated from the weathering of crystalline rocks in the source area and deposited in a freshwater of the basin. Kaolinite is possibly derived from pre-existing igneous rocks (Granitic rocks) as a product of weathering in acidic environment (Das et al., 1998). Kaolinite is considered to be abundant in regions of intense weathering under tropical (low pH and warm temperature) conditions (Biscaye, 1965, Suraj, 1996). According to Murray (1954) acidic to neutral pH conditions are more suitable for the formation of kaolinite. Presence of kaolinite is indicative of a continental or near shore environment of deposition (Parhem, 1966).

## 5.ACKNOWLEDGEMENT

Thanks are extended to the Head and the Technician in Centralised Instrumentation services laboratory (CISL), Annamalai University for arranging facilities to take FTIR Spectra.

## 6.REFERENCES

- Bahl, D.P. (1964). Origin and significance of the upper Gondwana Kaolinite beds of Jabalpur, Madhyapradesh, India. International Geological Congress part IX, Proc.Sec.9,Gondwanas, NewDelhi, General Editor R.K.Sundaram,pp.283-289.
- Biscaye,P.E.(1965). Mineralogy and sedimentation of recent deep sea clay in the Atlantic Ocean and adjacent seas and ocean. Geol.Soc.Amer.Bull., Vol.76,pp 803-832.
- Colthup, N.B, Daly, L.H. and Wiberley, S.E., (1990).Introduction to infrared and Raman spectroscopy, Academic press, Oxford.
- Das, D.N., Singh, L.J.C and Das, P.K. (1998). XRD investigation on clay minerals of the Barail sandstones around Sonapur, Jaintia Hills, Meghalaya. Jour. Geo. Sci., Vol.3,pp.27-32.
- Ghosh, S.N., (1978). Infrared Spectra of some selected minerals, rocks and products. Journal of Material Science,29.
- Grim, R.E. (1968). Clay mineralogy, McGraw Hill, Newyork, p.560.
- Iman, M.B. and Shaw, H.F. (1985). The diagenesis of Neogene clastic sediments from the Bangladesh. Jour.Sed.Pet.,Vol.25,pp.665-671.
- Kellar,W.D., (1964). Diagenesis in clay minerals. pro.Eleventh conf.clays and clay minerals, Newyok,pp.3-76.
- Kesler, T.K.(1956). Environment and origin of the Cretaceous Kaolin deposits of Georgia and south Carolina. Eco.Geol. Vol.51;pp541-554.
- Khoshroo, A. and Devaraju, T.C.(1990). A study of the rare illite deposits around Majjur,near Gadag,Karnataka State. Jour.Geol.Soc.India,Vol.35,pp.91-98.
- Millot, G. (1970). Geology of clays, Springer-verlag,New York,p.429.
- Murray, H.H.(1954). Genesis of clay minerals in some Pennsylvanian shales of Indiana and Illinois. In Swinford, A (Ed), Proc.2nd Nat.Conf.on clay and clay minerals. Nat.Aca.Sci.Vol.327,pp.47-67.
- Parhem, W. (1966). Lateral variations of clay mineral assemblage in modern and ancient sediments. Proc. Intern. Clay Confer.Jerusalem,Vol.1,pp.135-145.
- Preethi Sagar Nayak and Singh, B.K.,(2007). Instrumental characterization of Clay by XRF, XRD, and FTIR. Bull. Mater.sci. Vol.30,No.3 pp 235-238.
- Ramasamy, K. and, Venkatachalapathy, R., (1992) Infrared spectroscopic analysis of sedimentary formation of Neyveli Lignite minecut-1. Indian J. Pure and Appl. Phys.,Vol.30,171-179.
- Ramasamy, K., Venkatachalapathy, R., and Sajeev, S.V.,(2000). Proc. Nat. conf. on spectro-physics Chennai,India,p.318.
- Shichi and Takagi, (2000) Jour. Photochem. photobiol.C: Photochem. Rev. vol.1,pp 113.
- Suraj, G., Lalithambika, M. and Iyer, C.S.P.(1996). Clay minerals of Periyar river sediments and their role in the uptake of Cadmium and Nickel. Indian.Jour.Mar.Sci., Vol.25,pp.5-11.
- Wilson, M.J.(1994). Infrared methods in a Handbook of determinative methods in clay mineralogy, pp.133-173,Blackie and Son Ltd., London.

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