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GR Letter

Kaolin deposits at Melthonnakkal and Pallipuram within Trivandrum block, southern India

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Abstract

The kaolin deposits at Melthonnakkal and Pallipuram mines form part of the Warkalli Formation belonging to the Tertiary sequence in southern Kerala and occur at the boundary between the Tertiary sequence and Precambrian granulite facies metapelites (khondalites). The sedimentary clays are composed mainly of kaolinite, quartz and gibbsite. XRD and SEM studies have revealed that kaolinite is well-crystallized variety and the platy crystals are scarcely broken in the sedimentary clays. These sedimentary kaolins are considered to have been formed by intense tropical weathering of the khondalites, and subsequently transported and deposited with high organic input into lakes near the weathering crust over the basement rock. Besides, the surficial parts of the sedimentary deposits are extensively lateritized with the formation of goethite and hematite by Quaternary tropical weathering processes.
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Keywords: Kaolin clay deposits; Well-crystallized kaolinite; Weathering; Sedimentation; Khondalite

1. Introduction

Clay deposits constitute one of the important mineral resources, with different types of clays formed under various environments and mined for a variety of applications. Among the important clay deposits in southern India, an integral fragment of the Gondwana supercontinent, a number of clay workings occur surrounding Trivandrum region in southern Kerala. The clays are mostly kaolin and other similar types such as bauxitic clay and dark plastic clay. These clays are considered to be products of tropical weathering. The occurrence of these clay deposits and their general mineralogical features are outlined by Soman (1997), Soman and Machado (1986), and Soman and Slukin (1987), although detailed studies have not yet been carried out. The industrial properties were studied by Chandrasekhar and Ramaswamy (2002), and compared to the kaolin from Kutch, Gujarat.

At Melthonnakkal and Pallipuram in the Trivandrum district, high quality kaolin is mined by the English Indian Clay Mine and Sulaikha Clay Mine, respectively. The kaolin has been designated as china clay and has been used mainly for white paper and sanitary wares. The results from field studies in both these mines and the mineral associations and the properties of kaolinite through laboratory investigations are reported in this paper, together with some genetic considerations.

2. Geology

Southern India comprises a collage of Proterozoic high grade metamorphic rocks of dominantly upper amphibolite to granulite grade which are welded onto an Archean craton in the north (Drury et al., 1984). The southern part of South India comprises a vast supracrustal sequence of granulites termed as the Kerala Khondalite Belt (Chacko et al., 1987) or the Trivandrum Granulite Block (Santosh, 1996). The major lithounits in this block are garnet–sillimanite–cordierite–spinel bearing aluminous granulites (khondalites), garnet–biotite gneisses (leptynites), and orthopyroxene-bearing anhydrous granulites (charnockites) with subordinate pyroxene granulites and calc-silicate rocks (Fig. 1). The latest granulite facies metamorphism in the region is dated

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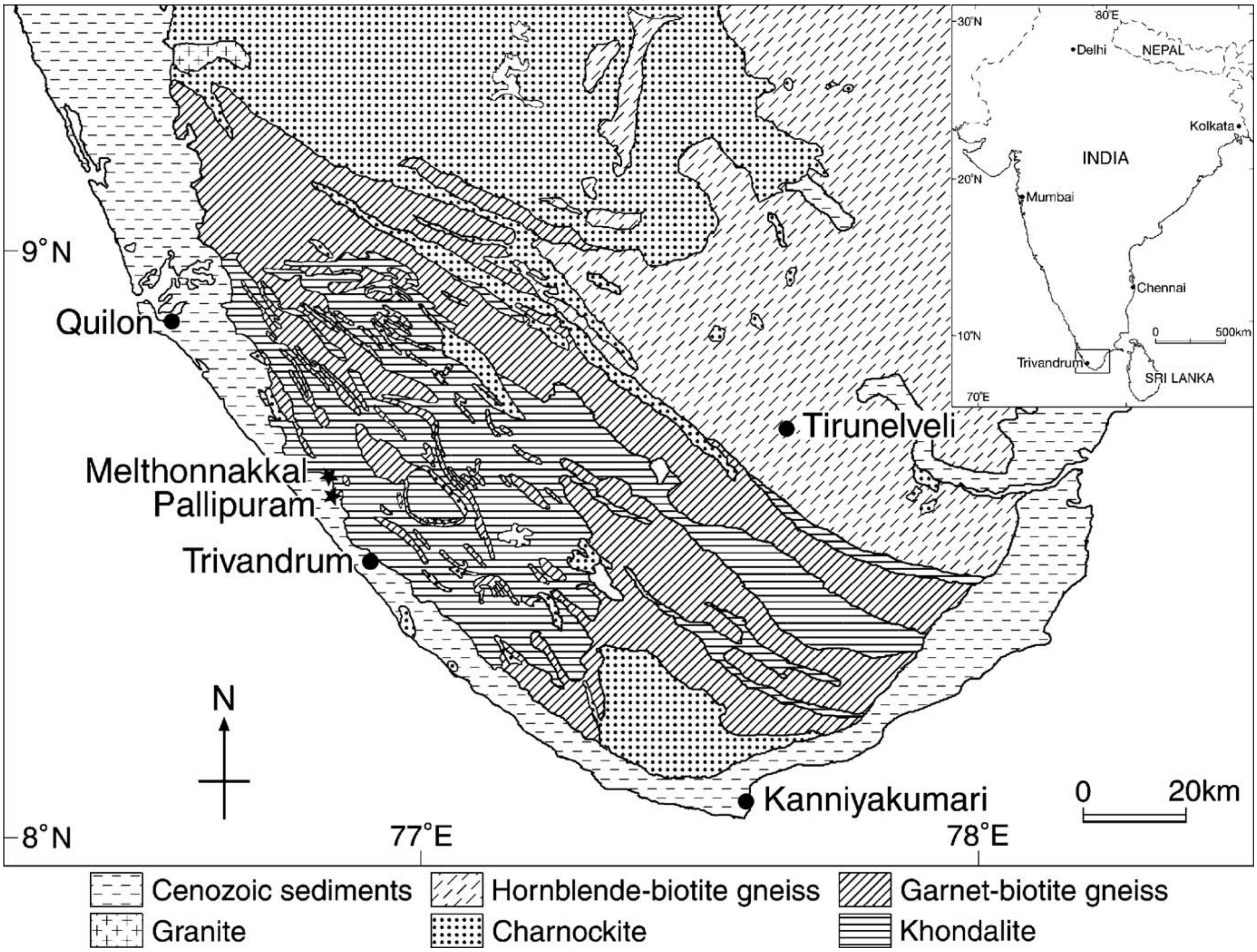

Fig. 1. Geologic map of southern India (after Satish-Kumar et al., 2002; Geological Survey of India, 1995), showing location of the Melthonnakkal and Pallipuram mines (indicated by black stars).

as late Neoproterozoic, at ca. 550 Ma, coinciding with the collision of the East and West Gondwana megacontinents to form the Gondwana supercontinent (Santosh et al., 2003).

Although crystalline rocks constitute the dominant lithounits of the area, the Cenozoic sediments fringe the coastal tract overlying the Precambrian crystallines (Geological Survey of India, 1993, 1995; Soman, 1997). The coastal sedimentary basins also occur, located in the offshore, among which the Kerala–Konkan Basin forms the southernmost segment, the land extension of which is known as the South Kerala Sedimentary Basin (SKSB; Nair et al., 1998). The SKSB comprises both Quaternary sediment fill and ridge–runnel system formed by Holocene sedimentary events (Jayalakshmi et al., 2004). Various clay deposits constitute part of the Cenozoic sediments. Among them, several prominent kaolin deposits including those at Melthonnakkal and Pallipuram mines occur as part of the Tertiary Warkalli Formation near the boundary between the Tertiary formation and the crystalline rocks of the khondalite belt at lat. 8.5–9°N in the western coastal belt. The Melthonnakkal and Pallipuram clay deposits are located at the western periphery of the khondalite and associated gneisses in the area.

3. Lithology of the clay deposits

The Melthonnakkal clay mine is one of the largest kaolin deposits in India. The deposit is stratified nearly horizontally. Clayey sediments ca. 30 m thick belonging to the Warkalli Formation are exposed by open-cut mining. The top to bottom lithostratigraphic profile (Fig. 2a) shows the sequence: brownish laterite soil, lateritized sandy clay, clay containing graphite spots, white clay, sandy clay, carbonaceous clay and sandy clay. The white clay is massive and very fine grained with soapy touch and is the most promising kaolin in this deposit. These pure clay horizons occur as beds or lenses up to 5 m in thickness within sandy clay bed. The carbonaceous clay is dark-colored kaolin clay that contains organic matter. It also occurs as lenses near the white clay bed. The sandy clay is massive and appears to contain many quartz grains cemented with white fine clay. Parallel cross bedding is occasionally present in sandy clay beds. The upper part of the

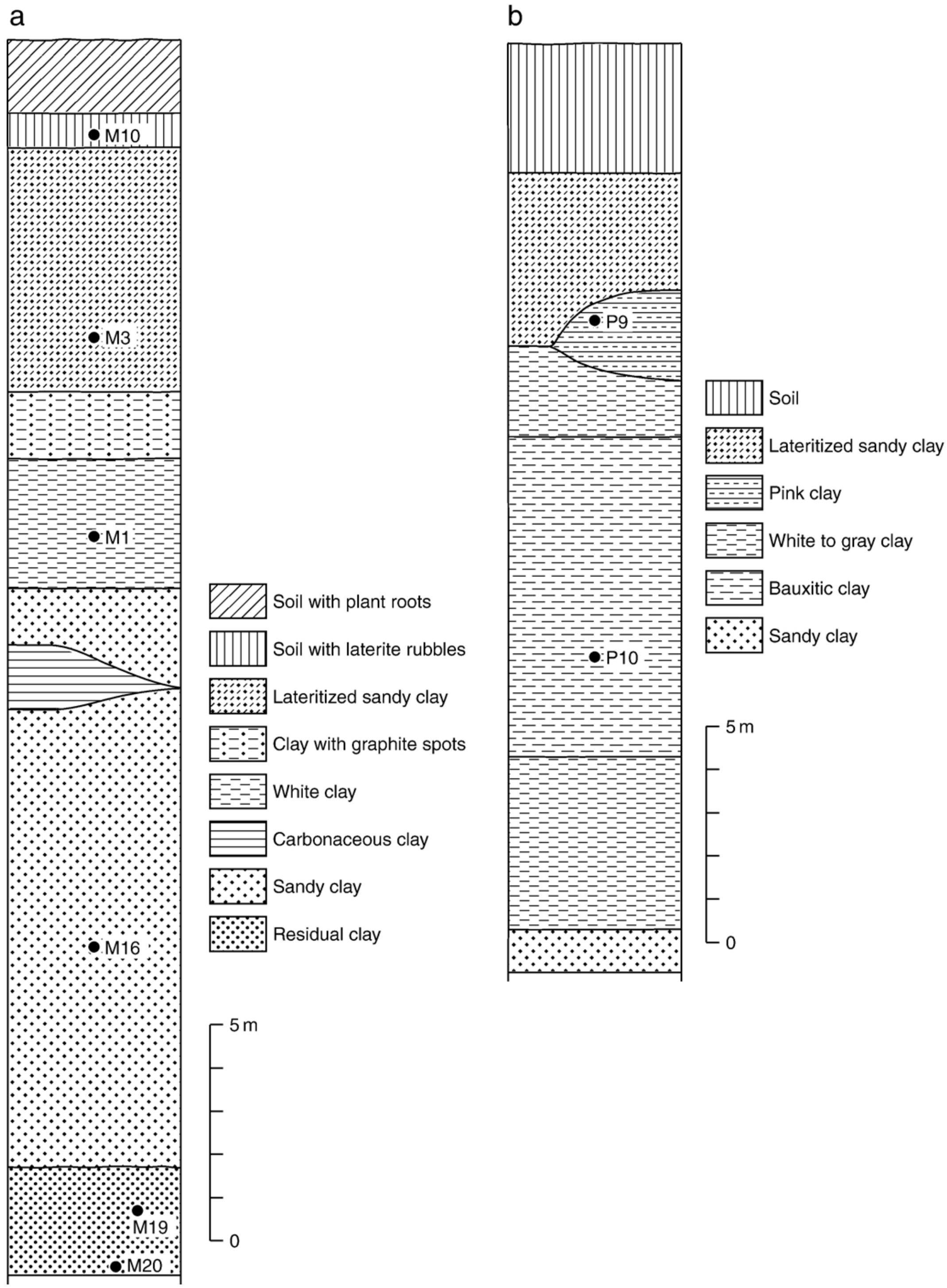

Fig. 2. a: Lithology of the Melthonnakkal mine, with locations of the samples M1, M3, M10, M16, M19, M20. b: Lithology of the Pallipuram mine, with locations of the samples P9, P10.

sandy clay is lateritized. At the lowest part of the mine, residual clay which is the weathered portion of the basement rock occurs below the sedimentary clay sequence. Dark heavy minerals occur scattered in the residual clay.

Kaolin mine at Pallipuram produces high quality kaolin ore and bauxitic ore. About 20 m thick clayey beds of the Warkalli Formation are exposed at the quarry. Its lithostratigraphic profile (Fig. 2b) exhibits from top to bottom sequence of reddish brown to brown laterite soil, lateritized sandy clay, pink clay, white to gray clay, bauxitic clay, white to gray clay and sandy clay. These clay beds are massive and fine grained. The gray clay is stained by organic matter. Nearly horizontal bedding is seen within the lowest sandy clay bed. The upper part of the deposit is lateritized.

4. Analytical methods

Representative kaolin samples were collected from both the clay mines during field investigations. X-ray powder diffraction method was employed to characterize the constituent minerals of kaolin samples, employing a Rigaku Geigerflex 2038 diffractometer using CuKα radiation. The accessory minerals were concentrated by hand-picking or sedimentation method for the X-ray identification. Microscopic observations of thin sections of representative samples were performed. Morphology of kaolinite was also observed with a JEOL-JSM-6100 scanning electron microscope (SEM) using gold-coated samples.

5. Results

5.1. Microscopic observation

Under the microscope, quartz grains cemented with clayey material in sandy clay samples are angular and poorly sorted (Fig. 3). Quartz grains are fringed with ferruginous material in lateritized sandy clay. In general, quartz in the Pallipuram samples are of finer grain size than those in the Melthonnakkal samples, although sandy quartz of varying grain size occur in both deposits. Trace amounts of rutile, graphite, sillimanite and zircon are found in sandy clay and sandy laterite samples in both mines.

5.2. Mineralogy

The representative X-ray powder patterns of the clays from the Melthonnakkal mine are given in Fig. 4. The high quality white clay is composed predominantly of kaolinite and contains a small quantity of quartz (Fig. 4b). The sandy clay is composed of kaolinite and quartz (Fig. 4c). Goethite occurs within laterite soil sample (Fig. 4a). The kaolin from the Pallipuram mine is composed of kaolinite (Fig. 4d), and the bauxitic clay is composed of gibbsite and kaolinite (Fig. 4e). In addition, we also identified several accessory minerals in the clays such as hematite (Fig. 5a), graphite (Fig. 5b), pseudorutile (Fig. 5c), rutile (Fig. 5c), monazite (Fig. 5d), anatase, sillimanite and zircon.

The mineral constituents of the clays in the Melthonnakkal and Pallipuram deposits examined by X-ray diffraction are summarized in Tables 1 and 2. Sandy clay which is composed of kaolinite and quartz is the major component at the Melthonnakkal deposit. The high quality white clay which is composed purely of kaolinite frequently occurs with small quantities of quartz as beds or lenses within sandy clay beds. The bauxitic clay containing gibbsite is mainly distributed in the Pallipuram deposit. Goethite, hematite and gibbsite are found in laterite soil and lateritized sandy clay in the upper parts of the deposits. Trace amounts of rutile, graphite, sillimanite and zircon which are considered to be the residual products from the weathering of the original rock are locally found in the sandy clay beds. Pseudorutile, rutile, monazite and anatase are contained in the residual clay at the lowest part of the Melthonnakkal mine.

5.3. Properties of kaolinite

X-ray powder patterns of kaolinites from the two mines show sharp diffractions (Fig. 4), namely, 00*l* basal reflections near 12.4°, 24.9° and 37.8° (2θ), and 02*l*, 11*l*, 13*l* and 20*l* reflections in the range of 19.5–43° (2θ). This X-ray property is characteristic of well-ordered triclinic kaolinites. The kaolinites in the sedimentary clays of the two mines are always well-ordered kaolinites. The sample

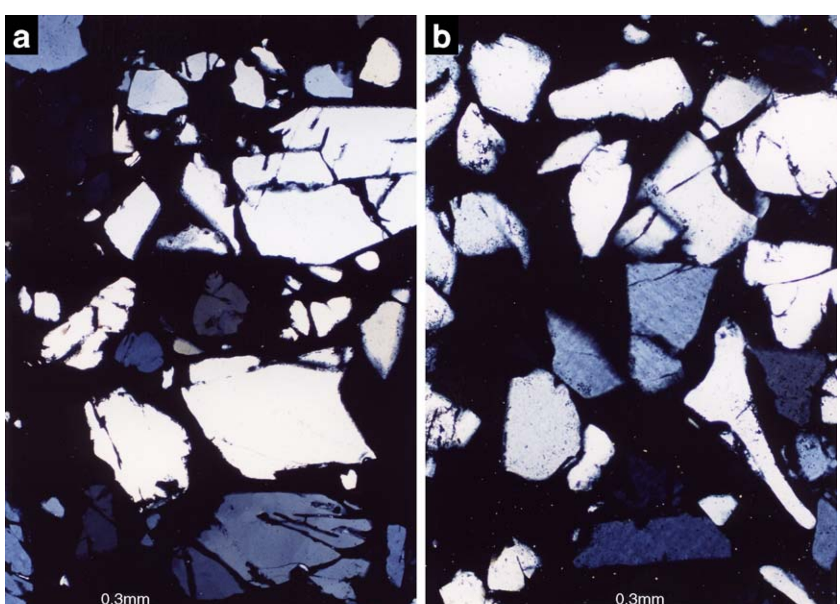

Fig. 3. Photomicrographs of sandy clays of the Melthonnakkal mine. Crossed polars. Scale bars are 0.3 mm in length. a: Lateritized sandy clay (M3). b: Sandy clay of the lower part of the deposit (M16).

shown in Fig. 4d is a typical example of very well-ordered kaolinite.

Scanning electron micrographs of kaolinite are shown in Fig. 6. Good crystals of pseudo-hexagonal plates are observed in the above very well-ordered sample (Fig. 6b). A few stacks of kaolinite plates are observed (Fig. 6a). The stacks are broken pieces of large vermicular kaolinite books such as those found as authigenic materials in Cretaceous Georgia kaolin of the United States (Murray and Keller, 1993) and in situ kaolin of Cornwall–Devon region, southwest England (Bristow, 1993). These platy grains of kaolinite are little broken in the sedimentary clays.

6. Discussion

Kaolin of the Melthonnakkal and Pallipuram mines are considered to be secondary (sedimentary) accumulations derived from weathered primary source. The process of formation of the deposits is schematically shown in Fig. 7 and summarized below.

Sedimentary and residual clays of the mines are mostly composed of kaolinite and quartz. The kaolin clay containing organic matter occurs in the mines. The top portions of the profiles are extensively lateritized. Graphite and sillimanite are contained in the sandy clay in these mines. Khondalites which form the major rock type in the inland of the kaolin deposit area commonly contain both graphite and sillimanite. Therefore, it is considered that primary kaolin (residual clay) was formed by chemical weathering of the basement rock which is khondalite or associated peraluminous gneiss. This weathering seems to have involved very intense kaolinization at high temperature and heavy rainfall during pre-Tertiary time. Vegetation might have provided organic acids intensifying the chemical weathering. The

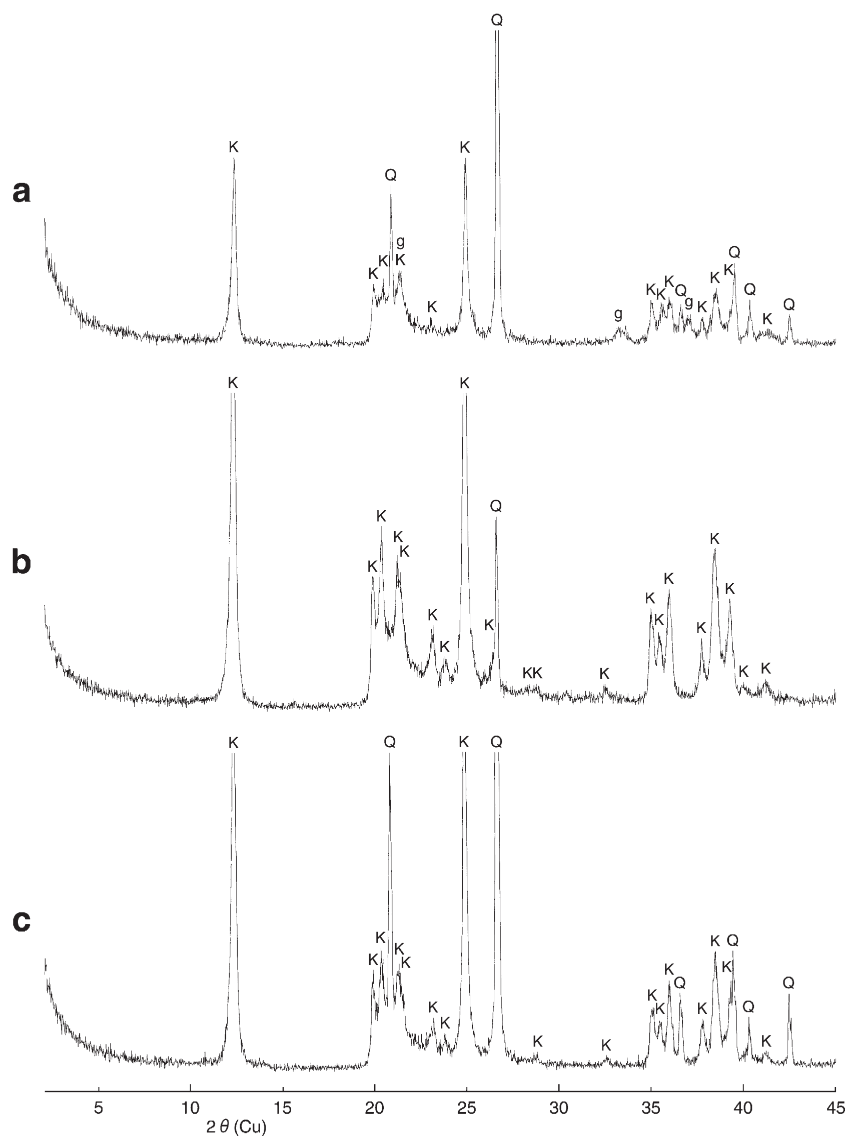

Fig. 4. X-ray powder patterns of the Melthonnakkal and Pallipuram kaolin. a: Laterite of the Melthonnakkal mine (M10). b: White clay of the Melthonnakkal mine (M1). c: Sandy clay of the Melthonnakkal mine (M16). d: Kaolin clay of the Pallipuram mine (P9). e: Bauxitic clay of the Pallipuram mine (P10). K: Kaolinite. G: Gibbsite. g: Goethite. Q: Quartz.

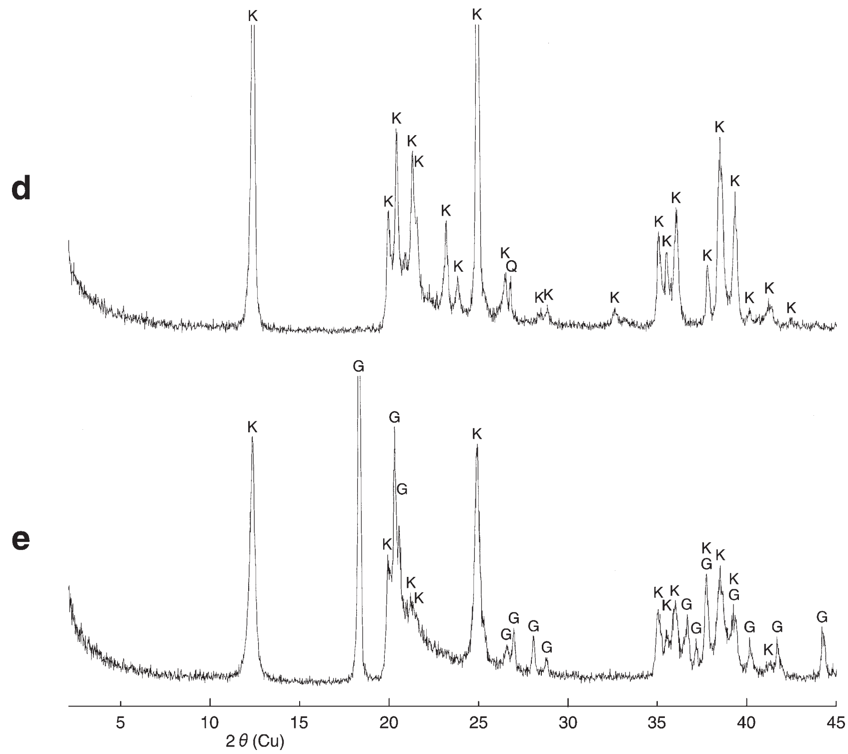

Fig. 4 (*continued*).

constituent alumina-bearing minerals of the khondalite such as feldspar, garnet, sillimanite, cordierite, biotite and spinel were disintegrated by this process yielding kaolinite and gibbsite and releasing alkalis and silica. Sillimanite might have resisted the kaolinization, leaving small amount of sillimanite in the sandy clay layer of the deposits. Most of quartz remained unaltered. Ilmenite is considered to have been altered to pseudorutile. Anatase is assumed to be derived by leaching from the titanium-bearing minerals. Graphite, rutile, monazite and zircon which are all common accessory minerals of khondalite also remained unaltered in the residual weathering products. These residual clays that developed over the basement rock were transported and deposited as the Tertiary Warkalli Formation, finally generating the sedimentary kaolin deposits including thick layers of pure kaolinite. The sandy clay of the upper part of the deposits is considered to have been lateritized forming goethite, hematite and gibbsite by post-Tertiary tropical weathering.

Kaolinite occurs with varying degrees of stacking disorder revealed by X-ray powder patterns. In general, the kaolinite formed by higher temperature hydrothermal alteration is well-crystallized one, whereas the kaolinite formed by lower temperature hydrothermal alteration and weathering is lower-crystallized one. Kaolinites of the Melthonnakkal and Pallipuram deposits are characterized as the well-crystallized variety (Fig. 4), despite their derivation as weathering products. The SEM observation of good platy crystals (Fig. 6) is in accord with the result of X-ray diffraction. This well-crystallized kaolinite is considered to have formed in the primary kaolin through intense and prolonged tropical weathering.

The Melthonnakkal and Pallipuram deposits occur at the boundary between the basement khondalite and the Tertiary sediments. Quartz grains in the sandy clay of these deposits are angular and poorly sorted, which is also noted as a common feature of the Warkalli Formation and considered to indicate shallow water shoreline littoral sediments with heavy rainfall (Soman, 1997). Platy crystals of kaolinite are little broken in the sedimentary clay. Such features concerning the locations of the deposits and the morphology of quartz and kaolinite suggest the proximity of the sedimentary basin to the original weathering crust. It is inferred that the kaolin was transported and deposited into two small basins on the basement of khondalite, perhaps within shallow lakes near the original weathering crust.

Organic matter is occasionally present in kaolin clays of both deposits. This suggests that organic acids might have contributed to the accumulation of almost pure kaolin clay by flocculating and settling of kaolinite suspension in freshwater lake. Such lacustrine environment of deposition is similar to those of ball clays of southwest England (Manning, 1995) and Kibushi–Gairome clays of Japan (Nagasawa, 1978).

As compared to the Melthonnakkal deposit, the Pallipuram deposit has some distinct features as follows. At Pallipuram, both the kaolin clay composed nearly of kaolinite and the bauxitic clay containing gibbsite are abundant. The crystallinity of kaolinite revealed by XRD is slightly higher in this locality

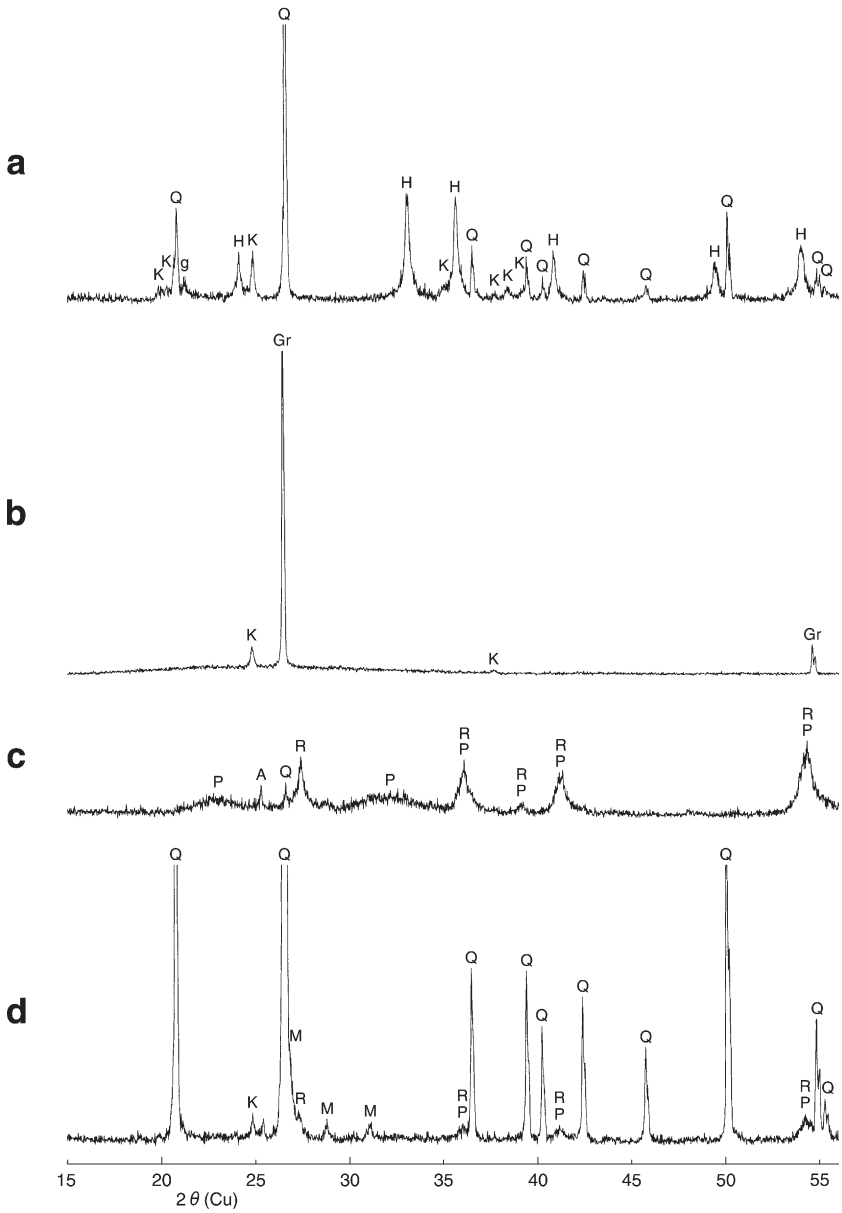

Fig. 5. X-ray powder patterns of accessory minerals in the Melthonnakkal kaolin. a: Reddish brown substance in lateritized sandy clay (M3). b: Black microcrystals in lower sandy clay (M16). c: Black to dark brown microcrystals in residual clay (M20). d: Coarse-grained fraction of residual clay (M19). H: Hematite. g: Goethite. Gr: Graphite. P: Pseudorutile. R: Rutile. M: Monazite. A: Anatase. Q: Quartz. K: Kaolinite.

(Fig. 4). SEM shows relatively thicker crystals of pseudo-hexagonal plates in this sample (Fig. 6b). Therefore, it is inferred that the Pallipuram clay might have been derived from the more intensely altered portion of the weathering crust near the ground surface. There is also a possibility that a part of the kaolinite crystals underwent secondary growth after the deposition.

Table 1
Mineral constituents of various lithologies at the Melthonnakkal mine

Lithology	Main constituent	Minor constituent
Soil with laterite rubbles	Quartz, Kaolinite	Goethite, Hematite, Gibbsite
Lateritized sandy clay	Kaolinite, Quartz	Hematite
Clay with graphite spots	Kaolinite	Graphite, Quartz
White clay	Kaolinite	Quartz
Sandy clay	Kaolinite, Quartz	
Carbonaceous clay	Kaolinite	Quartz, Anatase
Sandy clay	Kaolinite, Quartz	Graphite, Rutile
Residual clay	Kaolinite, Quartz	Pseudorutile, Rutile, Monazite, Anatase, Graphite

Table 2
Mineral constituents of various lithologies at the Pallipuram mine

Lithology	Main constituent	Minor constituent
Soil	Quartz, Kaolinite	Goethite, Hematite
Lateritized sandy clay	Kaolinite, Quartz	Goethite, Sillimanite, Rutile, Zircon, Anatase, Graphite
Pink clay	Kaolinite	Quartz, Hematite, Goethite, Rutile, Anatase
White to gray clay	Kaolinite	Quartz
Bauxitic clay	Gibbsite, Kaolinite	
White to gray clay	Kaolinite	
Sandy clay	Kaolinite, Quartz	Graphite

7. Summary and conclusions

The Melthonnakkal and Pallipuram kaolin deposits occur at the boundary between the Tertiary Warkalli Formation and Precambrian aluminous granulites (khondalites) in the Trivandrum region. The deposits form part of the Warkalli Formation and the sedimentary kaolin clay sequences consist of pure kaolin clay, sandy clay, carbonaceous clay, etc. These clays are composed mainly of kaolinite and quartz. The quartz grains in the sandy clay are angular and poorly sorted. Trace amounts of graphite, sillimanite, rutile etc. are locally found in the sandy clay beds. X-ray powder patterns of kaolinites show sharp diffractions, which are characteristic of well-ordered kaolinites. SEM shows good platy crystals of kaolinite. The platy crystals are scarcely broken in the sedimentary clays.

The kaolin of these deposits is considered to have been derived from the primary kaolin which was formed with the formation of well-crystallized kaolinite by intense and prolonged weathering of the khondalites. From the morphological features of quartz and kaolinite in the sedimentary clays, it is inferred that the primary kaolin was transported and deposited into lakes near the weathering crust.

Additionally, the overburden of the kaolin deposits are extensively lateritized with the formation of goethite, hematite and gibbsite by tropical weathering during post-Tertiary time.

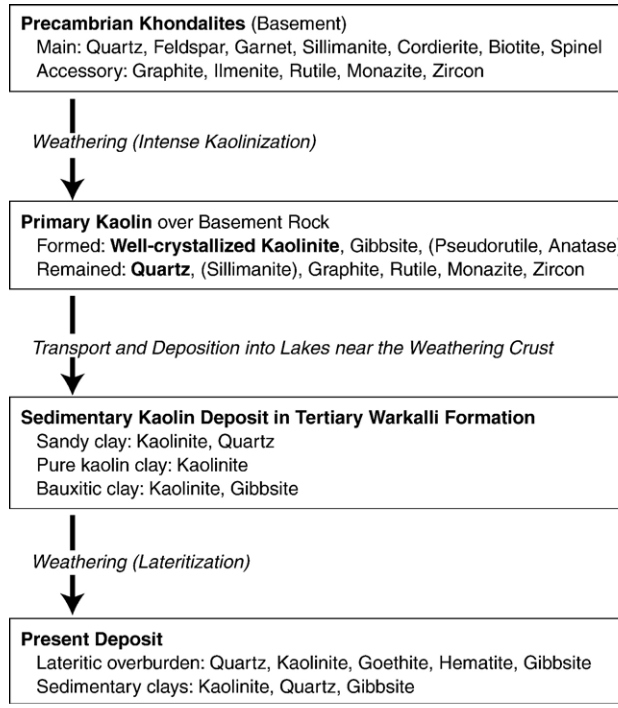

Fig. 7. Formational process of kaolin clays at the Melthonnakkal and Pallipuram deposits.

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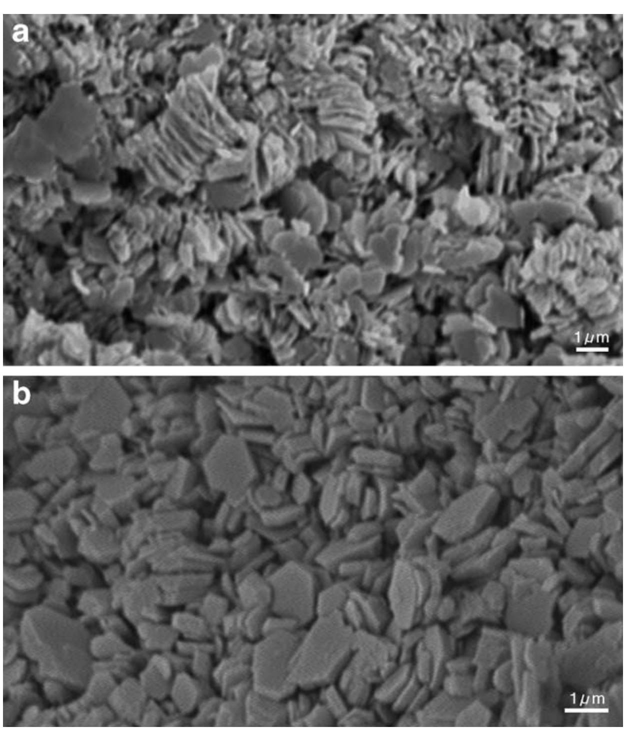

Fig. 6. Scanning electron micrographs of kaolin clays. Scale bars are 1 μm in length. a: Kaolinite of the Melthonnakkal mine (M1, Fig. 4b). b: Kaolinite of the Pallipuram mine (P9, Fig. 4d).

References

Bristow, C.M., 1993. The genesis of the china clays of South-West England — a multistage story. In: Murray, H.H., Bundy, W.M., Harvey, C.C. (Eds.), Kaolin Genesis and Utilization. The Clay Minerals Society, Colorado, pp. 171–203.

Chacko, T., Ravindra Kumar, G.R., Newton, R.C., 1987. Metamorphic *P–T* conditions of the Kerala (South India) Khondalite Belt, a granulite facies supracrustal terrain. Journal of Geology 95, 343–358.

Chandrasekhar, S., Ramaswamy, S., 2002. Influence of mineral impurities on the properties of kaolin and its thermally treated products. Applied Clay Science 21, 133–142.

Drury, S.A., Harris, N.B.W., Reeves-Smith, G.J., Wightman, R.T., 1984. Precambrian tectonics and crustal evolution in South India. Journal of Geology 92, 3–20.

Geological Survey of India, 1993. 1 : 5000000 Geological map of India. Geological Survey of India, Calcutta.

Geological Survey of India, 1995. 1 : 500000 Geological and mineral map of Kerala. Geological Survey of India, Calcutta.

Jayalakshmi, K., Nair, K.M., Kumai, H., Santosh, M., 2004. Late Pleistocene–Holocene paleoclimatic history of the southern Kerala Basin, Southwest India. Gondwana Research 7, 585–594.

Manning, D.A.C., 1995. Introduction to Industrial Minerals. Chapman and Hall, pp. 35–71.

Murray, H.H., Keller, W.D., 1993. Kaolins, kaolins, and kaolins. In: Murray, H. H., Bundy, W.M., Harvey, C.C. (Eds.), Kaolin Genesis and Utilization. The Clay Minerals Society, Colorado, pp. 1–24.

Nagasawa, K., 1978. Kaolin minerals. In: Sudo, T., Shimoda, S. (Eds.), Clays and Clay Minerals of Japan. Kodansha, Tokyo, pp. 189–219.

Nair, K.M., Padmalal, D., Sajikumar, S., 1998. Silting up of a Holocene megalagoon along Kerala coast. Nat. Sem. on Coastal Evolution: Processes and Products. CUSAT, Cochin. Abstract, 12.

Santosh, M., 1996. The Trivandrum and Nagercoil granulite blocks. In: Santosh, M., Yoshida, M. (Eds.), The Archean and Proterozoic terrains of southern India within East Gondwana. Gondwana Res. Group Mem., vol. 3, pp. 243–277.

Santosh, M., Yokoyama, K., Biju-Sekhar, S., Rogers, J.J.W., 2003. Multiple tectonothermal events in the granulite blocks of southern India revealed from EPMA dating: implications on the history of supercontinents. Gondwana Research 6, 29–63.

Satish-Kumar, M., Wada, H., Santosh, M., 2002. Constraints on the application of carbon isotope thermometry in high- to ultrahigh-temperature metamorphic terranes. Journal of Metamorphic Geology 20, 335–350.

Soman, K., 1997. Geology of Kerala. Geological Society of India, Bangalore.

Soman, K., Machado, T., 1986. Origin and depositional environment of the china clay deposits of south Kerala. Proceedings of the Indian Academy Sciences (Earth and Planetary Sciences) 95, 285–292.

Soman, K., Slukin, A.D., 1987. Lateritization cycles and their relation to the formation and quality of kaolin deposits in south Kerala, India. Chemical Geology 60, 273–280.