

# Kaolinite Occurrence of Kachchh, Gujarat: A Product from Rhyolitic Tuff by Hydrothermal Alteration

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## ABSTRACT

**Kaolinite associated with Mesozoic sediments of Kachchh and alkaline igneous rocks are not well studied in view of its genesis. The petrography, EPMA and DTA studies support that the studied kaolinite samples formed by mature transformation from rhyolitic tuff by hydrothermal alteration in epithermal condition. Such postulation indicates that there was intermittent acid volcanic episode along with alkaline basic igneous magmatism in the Cretaceous of Kachchh basin, western part of India.**

## INTRODUCTION

The Kachchh basin is an east-west trending pericratonic rift basin at the western most periphery of Indian craton (Sukla and Singh, 1990; Biswas, 2005). Mesozoic sediments filled the Kachchh basin prior to a series of magmatic activities during the late Cretaceous period (Maitra and Korakappa, 2012). The mafic alkaline rocks (Bose, 1980; Maitra, 2005; Dey, 1969) and Deccan basalt occurring as plugs and flows are the main magmatic episodes recorded in the Kachchh basin. The Deccan trap lava flows form an interface between Tertiary and Mesozoic sequences (Singh et al., 2006), delimiting the southern part of the basin. The studied clay layer along with sand stones and basalts occur at the northern fringe of Dhruv Donger ( $\Delta$  348), about 52 km south west from Bhuj, Kachchh district of Gujarat. In the east-west trending railway cutting shows sand stone bed is overlain by clay layers which is further overlain by basaltic rocks occurring at the top. A thin ferruginous silica rich band ( $\approx$  8 cm) blankets the clay layers at the contact with the basalt. To the eastern part of the section, a steep westerly dipping fault truncates the sand stone – clay – basalt sequence for which the post magmatic younger sediments of foot wall side comes in contact with the older clay and sand stone sequence across the fault plane.

The sandstone is coarse to very coarse grained, well sorted, massive, brownish to buff coloured and similar to the youngest lithostratigraphic units of Kachchh Mesozoic sediments known as Bhuj sand stone (Bhuj Formation) of lower Cretaceous age (Sukla and Singh, 1991; Biswas, 1983). A set of well defined horizontal pervasive planes are restricted within the clay layers. The basaltic rock hosts lenticular caught up patches of underlying sandstones.

Alteration of the volcanoclastic material largely depends upon chemical composition, texture of the rocks and the physico chemical conditions of the surroundings (Garcia Romero et al., 2005; De La Fuente et al., 2000). Kaolinite, a very common group of clay minerals, formed from felsic tuffs by hydrothermal alteration are known. The physicochemical conditions under which the kaolin mineral form are low temperature and pressure (Ali Sayin, 2007; Yuan et al., 2014; Celik et al. 1999). The most common parent minerals from which kaolin minerals form are K-feldspar and muscovite. Transformations

of K-feldspar into kaolin can be expressed by the equation:



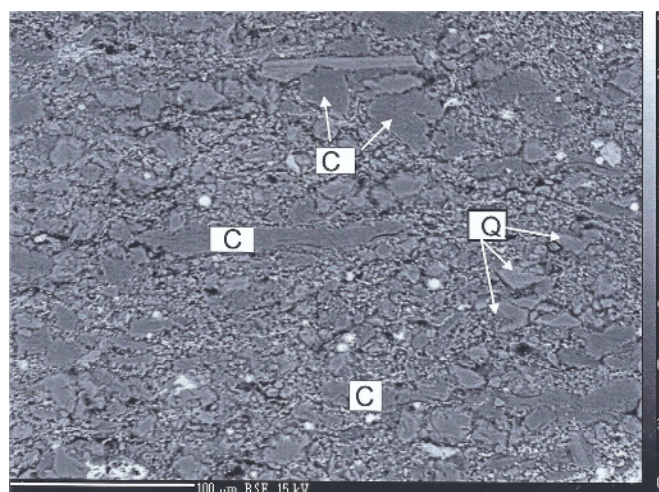
Kaolinite, dickite and nacrite are included within kaolinite group of minerals and have uniform composition corresponding to  $\text{Al}_2\text{Si}_2(\text{OH})_4$  besides its hydrated analogous halloysite ( $\text{Al}_2\text{Si}_2(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ ). Kaolin mineral frequently include Fe, Ti, Cr, K and Mg which frequently substitutes in minor amounts in the structure, mainly depending on bulk rock compositions.

The occurrence of clay in the area and its genetic importance has received a little attention. This write up presents the clue for the formation of clay and its genetic significance to understand the geological processes that had taken place during late Mesozoic period in the area.

## PETROLOGY

The clay sample in studied area is largely white to grey in colour with reddish tint veins. It is cryptocrystalline flaky friable in nature and gives a soapy feeling in hand specimens. Petrographic studies in DMRX microscope and back scattered image in SEM (Fig. 1) shows flakes of elongated to sub-rounded pseudomorph of clay after K-feldspar and fragmentary angular quartz clasts set in glassy matrix showing a typical volcanogenic detrital texture. Some of the elongated grains are slightly  $> 100\mu\text{m}$ . Numerous fine bright metallic oxides grains are seen in the interstitial spaces.

EPMA studies have been carried out (model SX 100 CAMECA) for determining the chemical composition of the constituted minerals of the clay layers. In EPMA studies, low total major element oxide composition of clay indicating  $\approx 16\%$   $\text{H}_2\text{O}$  (Table 1, Sr. no. 2) content in lattice structure, similar to  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  formula of kaolinite,



**Fig.1.** Back scatter image of kaolinite layers in studied area; C – kaolinite; Q – quartz

**Table 1** Major element analyses of Kaolinite

Sr. no.	1	2	3
	KGa - 1	Kaolinite	Cation
SiO <sub>2</sub>	44.2	44.48	Si - 1.97
Al <sub>2</sub> O <sub>3</sub>	39.7	38.09	Al - 1.98
CaO	N.D.	0.18	Ca - 0.01
Na <sub>2</sub> O	0.01	0.07	Na - 0.01
K <sub>2</sub> O	0.05	0.04	K - 0.02
FeO	0.13	0.87	Fe - 0.03
TiO <sub>2</sub>	1.39	0.51	Ti - 0.02
Total	85.48	84.24	4.04/7 oxygen
H <sub>2</sub> O	13.78	≈16 %	

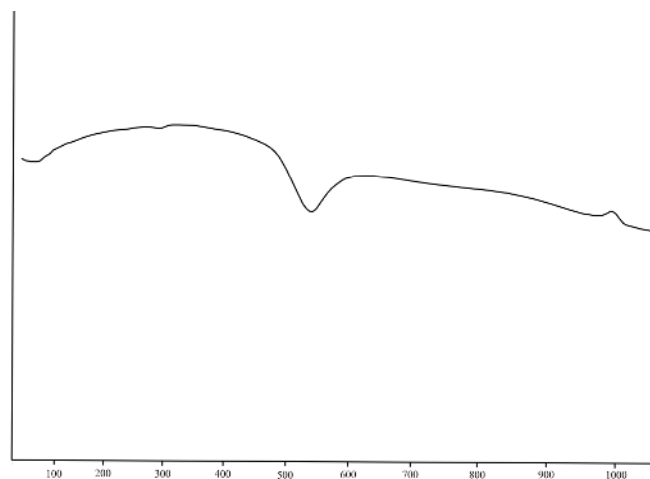
Sr.no. 1, KGa - 1, standard kaolinite for Georgia, USA; Source Clay repository, Clay Minerals Society, N10, USA. (Sanchez et al., 1994); Sr. no. 2, Avg. EPMA of Kaolinite composition of present study (n = 7); Sr. no. 3, Cat ion per 7 oxygen in Kaolinite composition.

dickite or nacrite minerals of kaolin group. Chemical composition of clays shows that higher Al<sub>2</sub>O<sub>3</sub> content varies between 37 to 39.5% (x = 38.1%) indicating higher degree of kaolinitization. The studied kaoline shows similar composition while compared with pure well-ordered crystallised kaolinite (Table 1, Sr.no. 1). A differential thermal analysis (DTA) of the clay mineral shows conspicuous endothermic peak at 520°C and exothermic peak at 990°C (Fig. 2). An ideal well synthesized kaolinite is characterised by endothermic peak at 500-600°C and exothermic peak at 900-1000°C (Karakas and Kadir, 2000) which also confirms the studied sample is kaolinite. Presence of heavy element oxides like TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, FeO bears the signature of igneous influence in the detritus (Brindley et al., 1986). Traces of Na<sub>2</sub>O (≈0.07%) and CaO (≈0.18%) in kaolinite composition (Table 1, sr.no. 2) indicates absence of plagioclase. Trace element content of kaolinite depends on bulk composition of precursor rock. Low but consistent presence of TiO<sub>2</sub> (≈0.51%) and FeO (≈0.87%) in clay composition attributed to its volcanogenic signature (Buie, 1963). Consistently higher FeO (≈0.31%) in detrital quartz associated clay mineral preferring incorporation of other element in its open structure form at higher temperature.

## DISCUSSION

Volcanic ash is not stable and is more susceptible to transform into secondary phases (Yuan et al., 2014) in shallow low temperature condition. Rhyolite ash transform to halloysite and kaolinite that are more thermodynamically stable (Harvey and Murray, 1993; Yuan et al., 2014.)

In the studied clay samples comprises mainly of kaolinite, quartz



**Fig. 2.** Differential thermal analyses (DTA) of clay mineral showing endothermic (528°C) and exothermic (990°C) peaks.

and traces of very fine particles of Fe, Ti oxides. DTA studies indicate a prominent endothermic and exothermic peak at 528°C and 990°C respectively so complete expulsion of the structure water is at 990°. The higher range of endothermic and exothermic temperature implicates higher temperature/pressure alteration of pristine minerals in favourable conditions where the hydrothermal fluid possibly played an important role for higher degree of kaolinitization process. Kaolinite mineral often forms by hydrothermal alteration of strong acid condition (Celik et al. 1999). At lower temperature (< 80°C) halloysite may be preferred stable phase (Yuan, 2014) whereas pyrophyllite formation is observed > 260°C (Tzuzuki and Mizutani, 1971; Hamley, 1959). At temperature > 100°C kaolinite is the preferred stable phase whereas pyrophyllite formation is generally observed at the temperature > 200 - 260°C, therefore the upper thermal limit of kaolinite formation is restricted below 200 - 260°C.

The field evidences reveal the clay layer is sandwiched between early Cretaceous Bhuj sand stone and late Cretaceous magmatic rock in a normal sequence so it also belongs to Cretaceous age. The presence of steeply dipping fault which truncates the sand stone - clay - basalt sequence in the studied area is possibly syn- to post magmatic and may have developed due to sagging or by any neotectonic adjustment. Convection of hydrothermal fluid through such fault planes could have facilitated the transformation of acid volcanic detritus to form kaolinite of present study. The overlying silica rich band above the kaolinite layers could be formed by hydrothermal silicification process wherein dissolved silica migrated upward forming a silica rich zone above the kaolinite deposit (Sayin, 2007). Meteoric water may be heated by contact with hot rocks adjacent to magma chamber or heated by vapour coming from magma. Kaolinite formation from rhyolitic tuff by hydrothermal alteration is widely reported during late Mesozoic from the different parts of the world (Celik et al., 1999; Yuan et al., 2014). So from the present study it can be summarised that

- The texture and petrochemistry of the altered kaolinite and the associated detrital quartz indicate acid volcanogenic character.
- Kaolinite of the studied sample shows very mature transformation and pyrophyllite is significantly absent in the sample. Therefore, observed secondary mineral, reflects a classic low temperature (≤ 200°C) hydrothermal alteration condition indicating a shallow epithermal system.
- O- and H- stable isotope composition study in future may reveal the nature of the hydrothermal fluid responsible for kaolinitization process which could not be constrained by the present study.
- The kaolinite of the area owes their origin from hydrothermal alteration of acid volcanic rock by the action of post-volcanic acidic solution. The rhyolitic ash deposit is indicating the volcanogenic activity along with predominant alkaline basic igneous magmatism in the area during late Cretaceous in Kachchh basin.

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