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Geochemical characterisation of the $< 2\,\mu m$ fractions of cretaceous-tertiary kaolins from eastern dahomey and Niger delta basins, Nigeria: Implications on paleoenvironment, provenance, and tectonic settings



Olaonipekun Oyebanjo^{a,*}, Georges-Ivo Ekosse^b, John Odiyo^a

- ^a School of Environmental Sciences, University of Venda, P/Bag X5050, Thohoyandou, 0950, South Africa
- ^b Directorate of Research and Innovation, University of Venda, P/Bag X5050, Thohoyandou, 0950, South Africa

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ABSTRACT

The geochemistry of the $<2~\mu m$ fractions of Cretaceous-Tertiary Kaolins from Eastern Dahomey and Niger Delta Basins, Nigeria was investigated to infer their paleoenvironment, provenance, and tectonic settings using major, trace, and rare earth elements (REE). Twenty-eight (28) samples comprising of fifteen (15) Cretaceous and thirteen (13) Tertiary kaolins, respectively, were collected. Geochemical compositions of the $<2~\mu m$ fractions were obtained using X-ray fluorescence (XRF) Spectrometry and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) analytical methods. Weathering indices such as chemical index of alteration (CIA, 96.98–99.39) and chemical index of weathering (CIW, 98.95–99.89) suggested intense chemical weathering under a wet tropical climatic condition. Ni/Co, V/Ni ratios and bivariate plot of V versus Ni indicated that they were deposited under marine oxygen-poor environment which is consistent with the horst and graben structural framework model of the Eastern Dahomey and Niger Delta Basins. The major, trace and REE data suggest that these deposits were derived from predominantly felsic source rocks with contributions from intermediate source rocks. The geochemical discrimination plots showed that the Cretaceous and Tertiary kaolins have been deposited in passive margin tectonic settings.

1. Introduction

Geochemical variations of major, trace and rare earth elements (REEs) can be reliable geochemical proxies in paleoclimatic, paleoenvironmental, tectonic settings, and sediment provenance considerations (Bhatia, 1983; Taylor and McLennan, 1985; Roser and Korch, 1986; Nesbitt and Young, 1989; Verma and Armstrong-Altrin, 2016). The geochemistry of sediments can be altered by post-depositional processes such as weathering and diagenesis since some minerals containing calcium (Ca), sodium (Na), magnesium (Mg), Iron (Fe), and manganese (Mn) degrade quickly during weathering to form Al-rich clays such as kaolins (Cox et al., 1995). However, the minerals in which these elements are hosted can as well determine the extent of occasional modifications by effect of weathering, hydraulic sorting, and diagenetic processes on the chemical signature of the source rock (Bock et al., 1998). The REEs are generally believed not to be affected by fractionation during sedimentation processes and are readily insoluble in most natural waters and provide relevant information concerning the provenance of the sediments. The REEs are concentrated in the clay

fraction especially kaolinite as the principal carrier (Prudêncio et al., 1989) but lower in the silt and sand fractions due to the dilution effect of quartz with low REE content (Cullers et al., 1988).

Discrimination plots, functions, indices, and elemental ratios of major and trace elements have been developed (For example by Bhatia, 1983, Nesbitt and Young, 1982; Roser and Korch, 1988; and Hofmann et al., 2001). Dombrowski (1982) and Dombrowski and Murray (1984) in resolving the controversies regarding the origins of the soft (predominantly Cretaceous) and hard (Tertiary) Georgia sedimentary kaolins applied Th and Co trace element geochemistry. The immobility of Th under supergene conditions and its concentration in alteration products is vital in source material analyses. Baioumy (2014) based on the integration of major, trace, and REE geochemistry of clay fractions of the Cretaceous sedimentary kaolins in Red Sea, Egypt concluded that they were from a mixture of mafic (with relatively high TiO2 and Ni content), granitic (with REE pattern with negative Eu anomaly andhigh Zr and Y contents), and alkaline (with abnormally high Nb contents) rocks. The characterisation of two Cretaceous kaolin facies from Ediki, Southwest Cameroon as having low alumina content, CIA, and high

E-mail address: oladayo2004@yahoo.com (O. Oyebanjo).

^{*} Corresponding author.

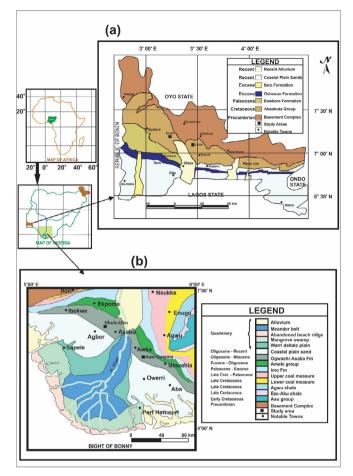


Fig. 1. Geologic Maps of (a) Eastern Dahomey and (b) Niger Delta Basins showing the study areas (Modified after Nwajide, 2013).

Si₂O₃/Al₂O₃ ratio with relative K enrichment over the alkali was interpreted to represent partial kaolinisation processes, low to moderate degrees of crystallinity and significant quartz contamination in both facies (Diko and Ekosse, 2013).

Nigeria is endowed with abundant clay mineral deposits and widespread distribution of kaolin. Data from the Federal Ministry of Solid Minerals Development shows that an estimated reserve of 3 billion tonnes of good kaolinitic clay have been identified in many localities within the basement complex and sedimentary basins in Nigeria (Onyemaobi, 2002). Kaolin characteristics depend on the environment of formation, geological origin, and tectonic settings (Murray and Kogel, 2005). This research regarding kaolin in Nigeria is to decipher the paleoenvironmental conditions and tectonic settings under which they were formed by exploring new geochemical data since they are valuable indicators of past climates and environment.

2. Geology of the study areas

The study areas fall within the peri-oceanic Dahomey and Niger Delta Basins formed at the periphery of and marginal to the West African Craton in the southern part of Nigeria (Fig. 1). The Dahomey Basin, also called the Dahomey Embayment, Benin Basin, or West Nigerian Basin in older literature, extends from southeastern Ghana in the West, through Southern Togo and southern Benin Republic (formerly Dahomey) to Southwest Nigeria (The western flank of the Niger Delta). The Dahomey Basin (together with other West African coastal sedimentary basins) formed during the Mesozoic in response to the separation of the African – South American land masses and the subsequent opening of the Atlantic Ocean. Deposition was initiated in fault-

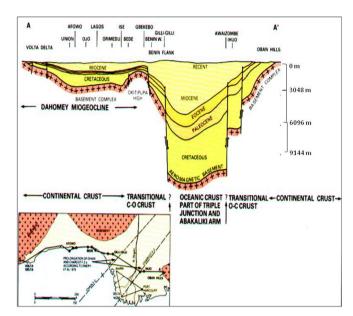


Fig. 2. East-West Geological Section showing the Dahomey and Niger Delta Basins (After Whiteman, 1982).

controlled depressions on the crystalline Basement Complex.

The depressions were a result of rift-generated basement subsidence during the Early Cretaceous (Neocomian) (Billman, 1976; Omatsola and Adegoke, 1981). The axis of the basin and the thickest sediments occur west of the border between Nigeria and Benin Republic. The basin is bounded on the west by faults and other tectonic structures. Its eastern limit is marked by the Benin Hinge line, a major fault structure marking the western limit of the Niger Delta Basin. To the west of the Benin Hinge line is the Okitipupa Ridge (Adegoke, 1969). The Tertiary sediments of the Dahomey Basin thin out and are partially cut off from the sediments of the Niger Delta Basin against this ridge of basement rocks. The basin's offshore limit is not well defined (Fig. 2).

The Niger Delta is the most important sedimentary basin in Nigeria from the point of view, both in size and thickness of sediments. It is also the most important, from the economic point of view as its petroleum reserves provide a large part of the country's foreign exchange earnings. The delta covers a land area in excess of 105,000 km² (Avbovbo, 1978). To this must be added a larger offshore part. It extends in an East-West direction from SW Cameroon to the Okitipupa Ridge. Its apex is situated southeast of the confluent of the Niger and Benue Rivers. It lies in the Gulf of Guinea to the Southwest of the Benue Trough and makes up the most important Cenozoic construction in the South Atlantic. It is agreed that the modern Niger delta is built on an oceanic crust. Supporting arguments come from the pre-continental drift reconstructions (Carey, 1958; Stoneley, 1966) – which shows an important overlap of the NE Brazil with the present Niger delta (Burke et al., 1971).

3. Materials and methods

3.1. Materials

The studied samples were collected from four (4) kaolin deposits comprising of two (2) sites (Eruku and Lakiri) from Cretaceous Units from the Eastern Dahomey Basin and two (2) sites (Awo-Omama and Ubulu-Uku) from the Tertiary Units from the Niger Delta Basin in Nigeria (Fig. 1). To avoid contaminations from recent weathering products, the outcrop faces were dug back to at least 60 cm to gain access to fresh surface for proper description and sampling of the kaolins (Deepthy, 2008). Nine (9) and six (6) samples were collected from Eruku (EP) and Lakiri (LP) deposits at 2 m interval, respectively; whereas six (6) and seven (7) samples were collected from Awo-Omama

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