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### Research paper

# Hydrogen and oxygen isotope composition of selected Cretaceous and Paleogene/Neogene kaolins from Nigeria: Paleoclimatic inferences



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#### ABSTRACT

The  $<2\,\mu m$  fractions of Cretaceous and Paleogene/Neogene kaolins from Eastern Dahomey and Niger Delta Basins, Nigeria were selected. Oxygen and hydrogen stable isotopic kaolinite geochemistry were used to estimate the paleoclimatic conditions under which they were formed. Nine (9) samples comprising of five (5) Cretaceous and four (4) Paleogene/Neogene kaolins, respectively, were collected. The  $\delta^{18}O$  (19.1 to 21.6%) and  $\delta D$  (-66 to -49%) values for the Cretaceous – Paleogene/Neogene kaolinites suggest equilibration with meteoric waters which support a weathering origin before its sedimentation. The calculated paleotemperature range from 17.0 and 32.2 °C are characteristic of tropical climate. In addition, kaolinisation temperatures during the formation of the Cretaceous kaolins (30.7 °C) were warmer than those for the Paleogene/Neogene kaolins (20.5 °C) based on their respective average paleotemperatures. The isotopic composition of the paleometeoric water in equilibrium with the kaolinites from Cretaceous kaolins were enriched relative to the kaolinites from the Paleogene/Neogene kaolins.

## 1. Introduction

Understanding the dynamic nature of the Earth climatic system in the past along with the knowledge of the present is crucial in predicting and responding to current and future climatic and environmental challenges. Various autonomous parameters such as fossil content, mineralogy, and geochemistry have been applied in paleoclimatic and paleoenvironmental assessment of ancient sedimentary successions. Interpretation of fossils (flora and fauna) paleoecological evidences also provides information regarding depositional environments and paleoclimate (Brenchley and Harper, 1998). Clay minerals in sedimentary basins can be detrital or authigenic in origin (Chamley, 1989; Fagel, 2007). Authigenic clay minerals are formed in situ by post-depositional diagenetic changes and hydrothermal alteration, whereas the detrital clay minerals are weathering products of the initial rocks or the source area which were transported and deposited as detrital grains (Singer, 1984; Chamley, 1989; Weaver, 1989). Clay minerals of detrital origin are useful tools to study provenance of sediments on the hinterland, transport, and paleoenvironment. Only detrital clays can represent important proxy of paleoclimatic and paleoenvironmental conditions. However, post-formational diagenetic changes can obliterate the climatic signal (Girard et al., 2000) and lead to incorrect paleoclimatic interpretations (Lacoviello et al., 2012). In order to constrain the reliability of the paleoclimatic inferences made from detrital clays, an integrated approach based on combined examination of the Oxygen (O) and Hydrogen (H) isotopic compositions is crucial and correlation with documented inferences from other paleoclimatic proxies (if available) (Girard et al., 2000; Baioumy, 2013).

The study of stable isotope of O and H ratios (<sup>18</sup>O/<sup>16</sup>O and D/H) for kaolins in paleoenvironmental and paleoclimatic evaluations date back to 1960s (Savin and Epstein, 1970). Kaolinite has been identified as a useful isotopic indicator of ancient continental climate (Singer, 1984). The isotopic composition of the kaolinite is a function of the following: (i) Isotopic composition of the various waters with which the kaolinite may have interacted with during and after its formation; (ii) Temperature of the environment at any given time during which the kaolinite was subject to isotopic exchange; and (iii) Whether the kaolinite reached isotopic equilibrium with its environment (Savin and Epstein, 1970). The latter is critical for it to be considered as a good paleoclimatic and paleoenvironmental indicator by reaching a state of equilibrium with the contemporaneous environment.

The isotopic O and H compositions of the meteoric waters vary proportionately with climatic variables such as rainfall and temperature. Hence, there exists the likelihood to obtain paleoclimatic information from stable isotopic composition of ancient kaolinite. Thiry (2000) supported the stability of kaolinite over other clay minerals as

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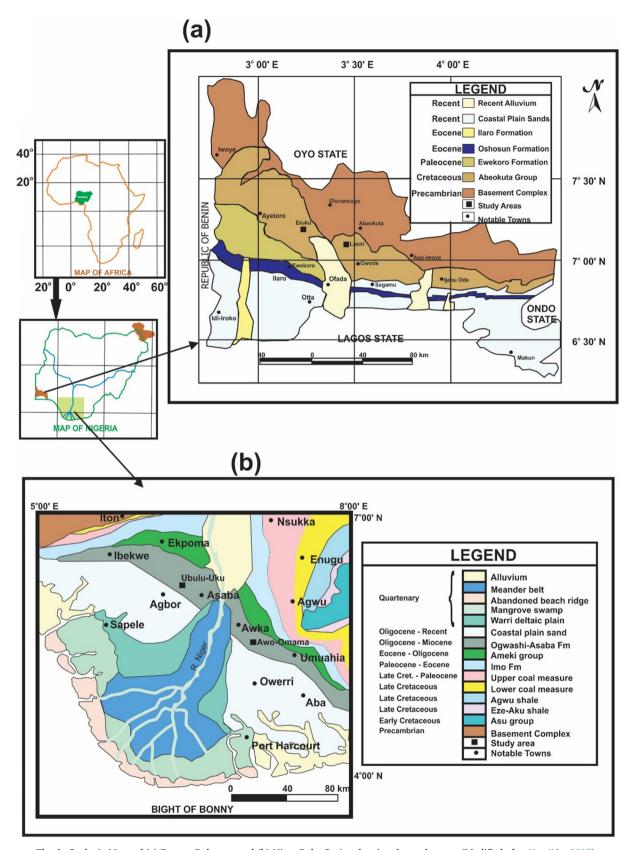


Fig. 1. Geologic Maps of (a) Eastern Dahomey and (b) Niger Delta Basins showing the study areas (Modified after Nwajide, 2013).

paleoclimatic indicators because once formed, they remain stable for a long time. It can retain the original isotopic signatures for over time-scales of 10<sup>8</sup> (Gilg et al., 2013). Post-depositional isotopic exchange between kaolinite and water for oxygen is virtually rare but for

hydrogen isotopic exchange can occur under certain conditions (O'Neil and Kharaka, 1976 and Bird and Chivas, 1988) like recrystallization or increase in temperature above formation temperature even at temperatures as low as 40 °C (Longstaffe and Ayalon, 1990).

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