Contents lists available at ScienceDirect

Comptes Rendus Geoscience

www.sciencedirect.com

Paleoclimatic implications of hydrogen and oxygen isotopic compositions of Cretaceous–Tertiary kaolins in the Douala Sub-Basin, Cameroon[☆]

Nenita Bukalo [a,*], Georges-Ivo Ekosse [b], John Odiyo [a], Jason Ogola [a]

[a] School of Environmental Sciences, University of Venda, Private Bag X5050, 0950 Thohoyandou, Limpopo Province, South Africa
[b] Directorate of Research and Innovation, University of Venda, Private Bag X5050, 0950 Thohoyandou, Limpopo Province, South Africa

ARTICLE INFO

ABSTRACT

Increased interest in paleoenvironmental studies is a result of climatic changes occurring at present and predicted for the future. Such studies could be done using the stable isotope compositions (δ^2H and δ^{18}O) of kaolins, which provide knowledge on the paleoenvironmental conditions prevailing during the time of kaolinisation. In this study, the stable isotopic compositions of clay-size fraction of kaolins occurring in Cretaceous and Tertiary Formations of the Douala Sub-Basin in Cameroon are presented, with the aim of reconstructing the paleoenvironmental conditions of the Sub-Basin. To achieve this, the clay-size fraction ($< 2\ \mu$m fraction) of 8 kaolinite-rich samples were analysed for their δ^2H and δ^{18}O compositions, and results were reported as part per mil (‰) relative to the SMOW standard. The δ^{18}O values of kaolins found in the Cretaceous–Tertiary Formations of the Douala Sub-Basin varied between +18.2 and +21.0‰, whereas the δ^2H values varied between –69 and –53‰. Nine of the eleven samples plotted on the right of the supergene–hypogene line. Five of these nine samples plotted very close to the kaolinite line, which represents the composition of kaolinite in equilibrium with meteoric water at 20 °C; suggesting a supergene weathering origin of these kaolins. The determination of the temperature of kaolinisation yielded mean formation temperatures of 22 ± 2 °C and 27 ± 6 °C for Cretaceous and Tertiary kaolins, respectively. Excluding the two samples falling in the hypogene field, averages of kaolinisation temperatures were 20 and 25 °C during the Cretaceous and Tertiary periods, respectively. These temperatures are slightly below the present mean annual temperature in Douala (27 °C), thereby suggesting that the climate was becoming warmer from the Cretaceous to the Present. Therefore, Douala had a cooler and rainy climate during the Cretaceous, and the climate is gradually becoming hotter and more humid, favouring the refinement of existing kaolins and the kaolinisation of kaolin-forming minerals in the Sub-Basin.

1. Introduction

Environmental changes occurring at present and predicted for the future have increased interest in paleoclimatic and paleoenvironmental studies (Becker et al., 2006). Records on paleoenvironments may elucidate the causes of climate change (Stern et al., 1997), which could be retained in stable isotopes. The oxygen and hydrogen isotopic signatures of naturally occurring kaolin minerals (kaolinite, halloysite, nacrite, and dickite) carry information about the climatic conditions under which these minerals formed (Savin and Hsieh, 1998).

Kaolinite is correlated with climatic factors, such as temperature and water availability in the soil, because these factors strongly affect the amount and effectiveness of chemical weathering from which they result (Sheldon and Tabor, 2009). Due to its small particle size and large surface area, kaolinite is essentially affected by the duration of weathering, the slope, the water–rock ratio, and the hydrochemistry (Fagel and Boës, 2007; Fürsich et al., 2005; Heckroodt, 1991; Moriarty, 1977). In addition, continental weathering rates and runoff are controlled by climatic changes, which also affect sediment formation and transport of these sediments into a Basin (Das et al., 2013). Hence, the stable isotopic compositions of kaolinite are potentially powerful proxies of paleoenvironmental and paleoclimatic conditions (Ortega et al., 1998; Tabor et al., 2002). However, some conditions need to be taken into consideration when using stable isotopic compositions of kaolinite as paleoenvironmental and paleoclimatic proxies. These include: known kaolinite–water equilibrium isotope fractionation factors, closed system conditions since mineral formation, water dominated environments of crystallisation, and information on the behaviour of the specific isotope in kaolinite and water (Sheldon and Tabor, 2009).

Several studies have applied stable isotope geochemistry of clay minerals to various disciplines, such as geothermometry; provenance of clays, diagenetic processes, origin and evolution of upper crustal fluids, hydrothermal systems, water-rock interaction and paleoclimates (Sheppard and Gilg, 1996). The application of the stable isotopes of oxygen and hydrogen to reconstruct paleoenvironments of formation of kaolins have also been used by several authors (Das et al., 2013; Ekosse, 2007; Elliot et al., 1997; Gilg et al., 1999, 2013; Gilg, 2000; Horbe, 2011; Martinez-Ruiz et al., 2014; Roseneau and Tabor, 2013; Savin and Hsieh, 1998; Tabor and Montanez, 2005; Tabor et al., 2002; Turc et al., 2013; Westermann et al., 2013).

Sheppard et al. (1969) developed the hypogene–supergene line, which is equivalent to kaolinite in equilibrium with meteoric waters at about 35 °C. This line allows the distinction between a supergene and a hypogene environment of formation of a kaolin deposit. Later studies by Savin and Epstein (1970) led to the development of the kaolinite line, which represents the location of isotopic data points for pure kaolinites from weathering zones formed in approximate equilibrium with meteoric water at about 20 °C.

On the one hand, knowledge on the environment of formation of kaolins can provide crucial information for their exploration; on the other hand, African paleoclimates have not been substantially addressed. This paper, therefore, provides information on the environment of formation of Cretaceous–Tertiary kaolins of the Douala Sub-Basin and it presents evidence of the Cretaceous–Tertiary climate in Douala and its environs, using the stable isotope composition of Cretaceous–Tertiary kaolins found in the Douala Sub-Basin.

2. Study area

2.1. Geology of the Douala Sub-Basin

The studied Cretaceous–Tertiary kaolins of the Douala Sub-Basin are found in five localities, namely, Bomkoul, Dibamba, Logbaba, Missole, and Yatchika kaolins (Fig. 1). The Douala Sub-Basin stretches on the southern coast of Cameroon, covering a total surface area of 19,000 km^2 (Mbesse et al., 2012), and is subdivided into seven formations (Logmo et al., 2013).

The kaolin occurrences belong to four Cretaceous–Tertiary Formations of the Douala Sub-Basin: the Early Cretaceous Mundeck Formation made up of sandstones; the Late Cretaceous Logbaba Formation, made up of sandstones and clays with intercalations of sands and rare occurrence of limestones; the Paleocene to Middle Eocene Nkapa Formation composed of marls, shales, and calcareous sandstones; the Upper Eocene to Oligocene Souellaba Formation, composed of sandstones and marls, shales, clayey sands, sands, and gravels (Effoudou-Priso et al., 2014). The lithostratigraphy of the Douala Sub-Basin is shown in Fig. 2.

Sedimentation in the Sub-Basin was marked by (Kenfack et al., 2012a, 2012b): Jurassic continental sediments, which were deposited in an Afro-Brazilian depression; a listric faulting during the Jurassic–Barremian; an intensive erosion activity of the highlands and deposition in the previously formed graben; a salt deposition and transform direction resulting in a series of cross-faults that have segmented the rift(s structure during the Mid-Late Aptian; a marginal clastic sedimentation, with sporadic build-ups between the Albian and the Paleocene.

2.2. General description of studied kaolins

A general description of the studied kaolins is given in Table S1 (Ngon Ngon et al., 2012; Blackwatch, 2016).

2.3. Climate

The Douala Sub-Basin has the Guinean type of the equatorial climate, resulting from the combined effect of convergence of the tropical oceanic low-pressure zone and the inter-tropical front within the continent. There are two main seasons: namely, a long rainy season that lasts from April to September, and a short dry season, which generally stretches from October to March. Between these two seasons are transitional seasons: the wet-dry season (September to November) and the dry-wet season (March to May). As shown in Fig. 3, annual precipitation since 2006 is above 2500 mm, and annual temperatures fluctuate between 27 and 28 °C (IAEA/WMO, 2017).

The IAEA/WMO (2017) recorded the stable isotope composition of meteoric water in Douala. It is shown in Table S2.

3. Materials and methods

Kaolins from five localities in the Douala Sub-Basin were studied: namely, Bomkoul, Dibamba, Logbaba, Missole II, and Yatchika (Table S1). In these localities, kaolin is generally hosted in sandstone deposits and occurs as beds less than 5 m in thickness. Samples were collected and were 1 to 5 m apart, depending on the extent of kaolin beds. Due to the low probability of obtaining a pure
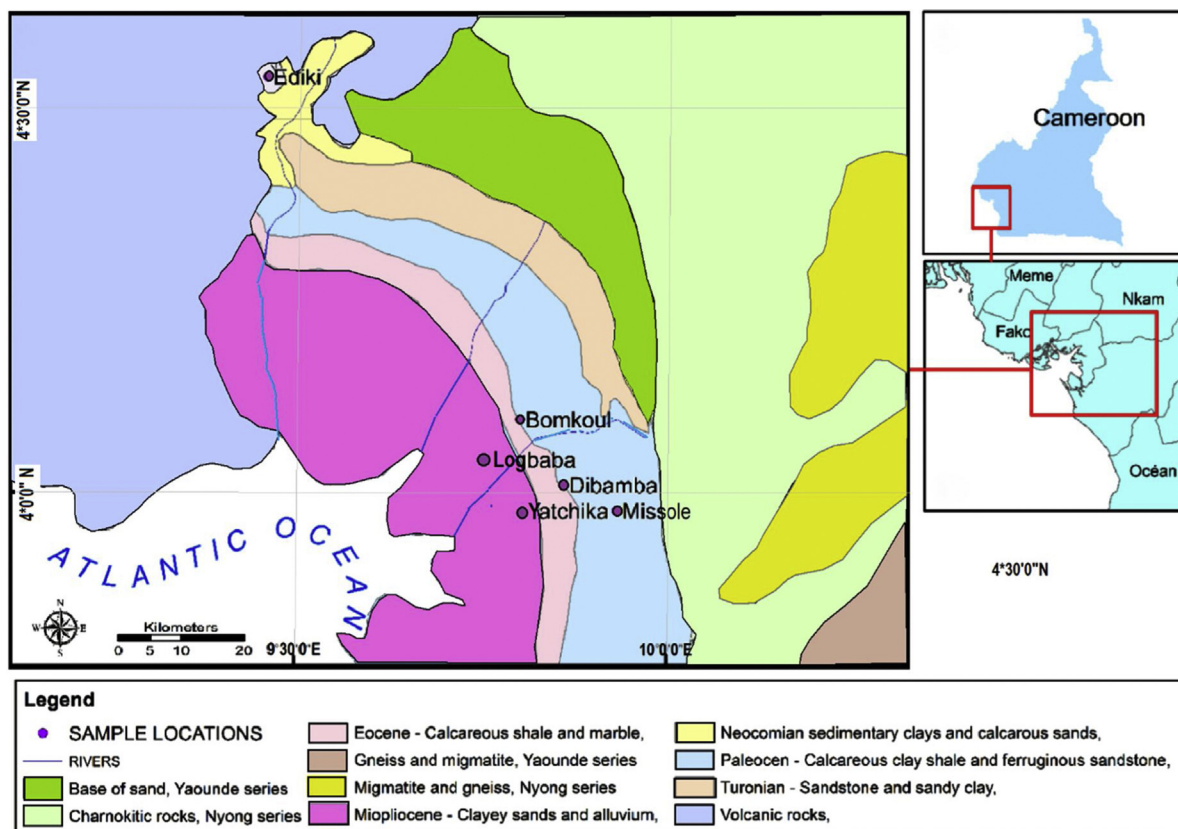
Fig. 1. Geologic map of the Douala Sub-Basin (modified from SNH/UD, 2005).

mineral fraction on the field, sample preparation and physical purification were carried out.

Organic matter was removed using hydrogen peroxide (H_2O_2) and the samples were dispersed using calgon (a mixture of 40 g of sodium hexametaphosphate ($NaPO_3)_6$ and 10 g of soda (Na_2CO_3)), according to the method described by van Reeuwijk (2002). After the dispersion of the samples, the sedimentation technique was used to remove sand and silt fraction, and clay fractions ($< 2\,\mu m$ fraction) were obtained with the use of a centrifuge, after removal of sand and silt fractions (Jackson, 1979; van Reeuwijk, 2002). Removal of carbonates, iron oxides and hydroxides was not carried out, because the presence of these minerals does not affect the stable isotopic compositions of clay minerals (Bird and Chivas, 1988, 1989).

The bulk and $< 2\,\mu m$ fractions of the kaolins were analysed for their mineralogy by X-ray diffractometry (XRD) using a Rigaku Ultima IV diffractometer working with 40 kV and 30 mA, and using a cobalt source ($\lambda = 1.789\,Å$) and an alpha filter (Co Kα). Samples were scanned from $3^{\circ}\,2\theta$ to $40^{\circ}\,2\theta$ at a rate of 2° per minute. The results of this analysis are reported in Bukalo et al. (2018). Eight samples, representing the samples in each locality with the highest amounts of kaolinite, were selected based on their mineralogical compositions (Table S3). The samples selected for isotopic analyses were the $< 2\,\mu m$ fraction, enriched in kaolinite (> 80 wt%) and with lesser amounts of other minerals based, in order to avoid oxygen contamination from other minerals.

In the selected samples, the other minerals present were illite, smectite, quartz, anatase, rutile, goethite, and hematite. Based on a study by Hassanipak and Elsinger (1985), there is little or no correlation between iron oxide minerals and the stable isotopic composition of kaolinite. Since the stable isotopic fractionation factors of smectite and kaolinite are very similar under low-temperature weathering conditions, smectite will not be regarded as a potential contaminant on the stable isotopic composition of kaolins (Clauer et al., 2015). Clauer et al. (2015) also proved that the isotopic compositions of kaolinite-rich samples also containing quartz and illite fall in the analytical uncertainty of the stable isotopic compositions of pure kaolinite. Therefore, mineral phase separation was not carried out.

The method used for stable isotopes analyses was similar to the method described by Harris et al. (1999). Approximately 20 mg of each sample was placed in a glass container and attached to the vacuum line. The content was then frozen in liquid nitrogen. The air in the sample was then outgassed and the absorbed water was cryogenically distilled to a second vessel by heating the sample at 150 °C with an air gum. The mass of the original sample and the produced water were measured and used to determine the wt % of absorbed water.

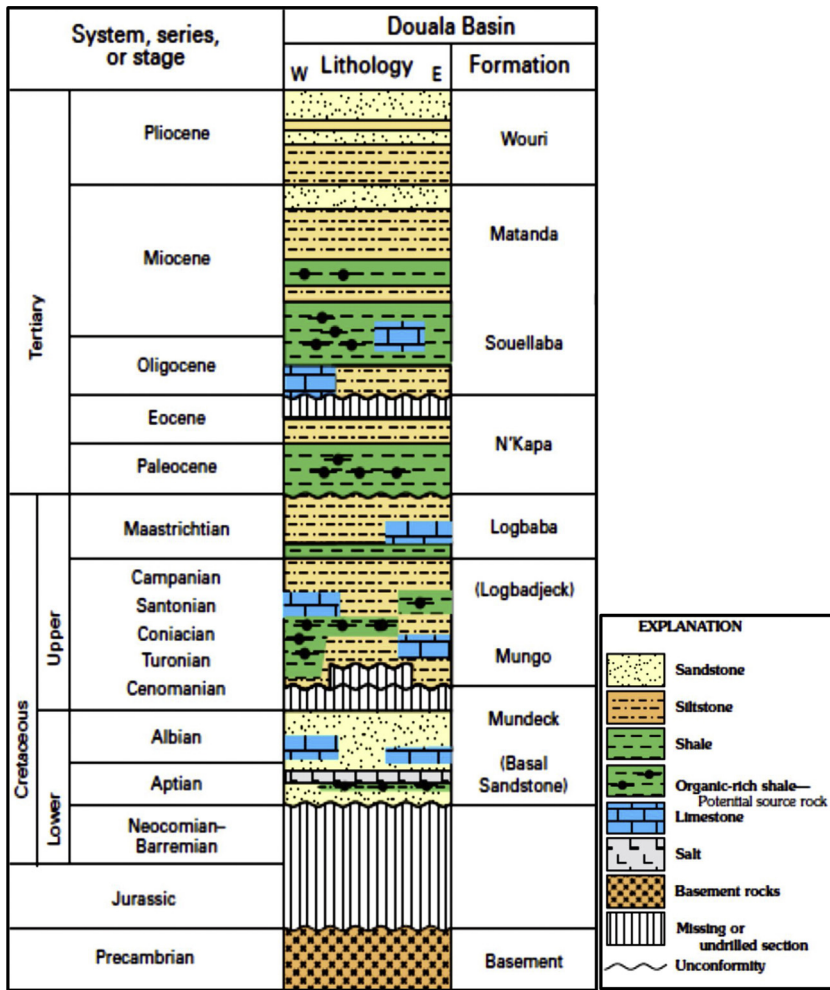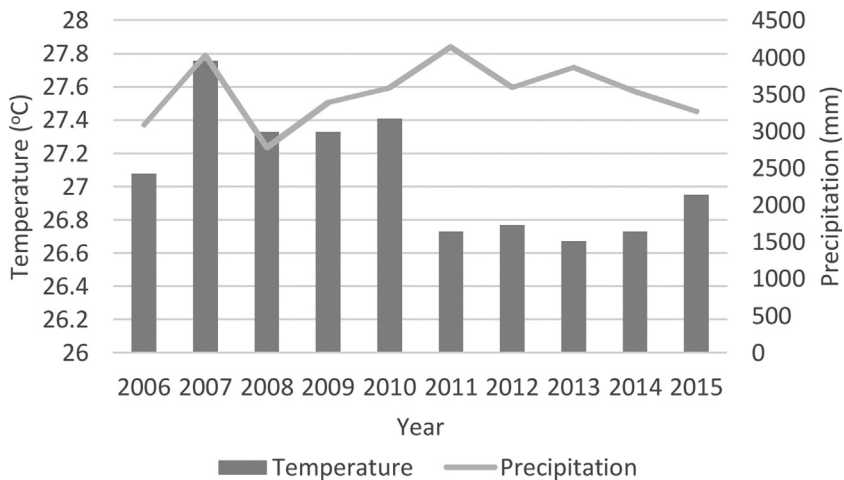**Fig. 2.** Lithostratigraphy of the Douala Sub-Basin (modified from Brownfield and Charpentier, 2006).

Fig. 3. Mean annual temperatures and precipitation in Douala between 2006 and 2015 (IAEA/WMO, 2017).
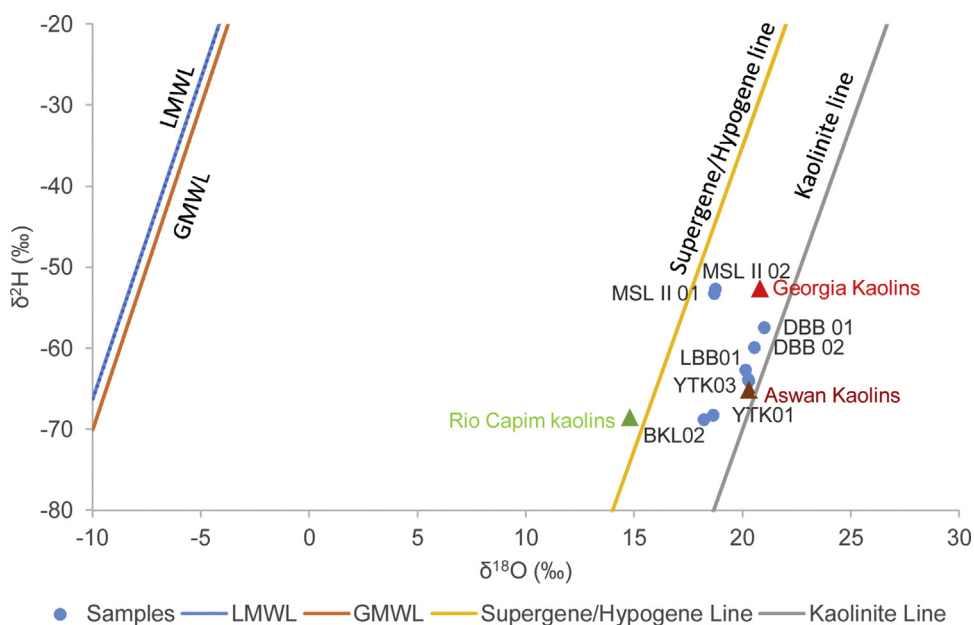
Fig. 4. $\delta^{18}O$ versus δ^2H plot of clay fractions of selected samples. The LMWL, GMWL, S/H line and the kaolinite line are plotted for reference. Values of the Cretaceous–Tertiary Georgia kaolins in USA (Hassanipak and Elsinger, 1985), Cretaceous Rio Capim kaolins in Brazil (Santos et al., 2007), and Cretaceous Aswan kaolins in Egypt (Baouimy, 2013) are also included for comparison.

3.1. Oxygen isotopes

The samples were outgassed under high vacuum at 200 °C for 2 h, after having been dried in an oven at 110 °C. Then, the samples were reacted with an excess of ClF_3 at ~560 °C for 12–16 h. The evolved O_2 was quantitatively converted into CO_2 using a hot platinised carbon rod. The $\delta^{18}O$ of CO_2 was then measured using the Finnegan DeltaXP mass spectrometer. Duplicate splits of the MQ quartz standard were analysed with each batch of eight samples. These values were used to normalise the raw $\delta^{18}O$ to the SMOW scale, using $\delta^{18}O = 10.1‰$ for MQ. The precision of $\delta^{18}O$ measurements was ±0.2 ‰.

3.2. Hydrogen isotopes

Prior to the determination of δ^2H, three replicate analyses of the kaolinite standard, Bulk Serina Kao (SB8) from Serina Mine near Cape Town, gave structural water contents of 12, 12 and 13 wt%, and a mean δ^2H value of −57‰. The extracted absorbed water was converted to hydrogen gas using a variation of the closed tube Zn reduction (Harris et al., 1999). Hydrogen isotopic composition was then measured on the Finnegan DeltaXP mass spectrometer calibrated using SMOW. Internal standards (CTMP2010 and RMW, exactly 2 mg) were used to calibrate the raw data to the SMOW scale. This was done by correcting the raw data versus the reference gas value, then adjusted so that CTMP2010 = −7‰, then "stretched" so that RMW = −131‰. The silicates were then adjusted so that kaolinite = −57‰ (i.e. the δ^2H value of SB8, used as kaolinite standard).

4. Results

The $\delta^{18}O$ and δ^2H of the samples are shown in Table S4 and plotted in Fig. 4. $\delta^{18}O$ values varied between +18.2‰ (BKL 02) and +21.0‰ (DBB), whereas δ^2H values varied between −69‰ (BKL 02) and −53‰ (MSL II 01 and MSL II 02). The means of $\delta^{18}O$ and δ^2H are +19.5 ± 1.1‰ and −61 ± 6‰, respectively, indicating that $\delta^{18}O$ and δ^2H have homogenous values. All the samples fall between the kaolinite line and supergene-hypogene line.

Dibamba and Logbaba samples (DBB 01, DBB 02 and LBB 01) plot very close to the kaolinite line. These samples all have a kaolinite content > 90.0 wt%. Missole II samples (MSL II 01 and MSL II 02) plot on the right side of the supergene–hypogene line, but closer to this line than other samples. They have an anatase content of 4 wt% and lower kaolinite contents, 87 and 86 wt%, for MSL II 01 and MSL II 02, respectively.

5. Discussion

5.1. Temperature of kaolinisation

For reference, the local meteoric water line (LMWL) for Douala (Wirmvem et al., 2016), the global meteoric water line (GMWL) (Craig, 1961), the supergene–hypogene line for kaolinite in equilibrium with meteoric waters at ≈35 °C (Sheppard et al., 1969) and the kaolinite line, for kaolinite in equilibrium with meteoric waters at ≈20 °C (Savin and Epstein, 1970) are used for comparison in Fig. 4, according

to the equations below:

local meteoric water line for Douala : $\delta^2 H$

$$= 7.92\ \delta^{18}O + 12.99 \tag{1}$$

global meteoric water line : $\delta^2 H = 8\ \delta^{18}O + 10 \tag{2}$

supergene-hypogene line : $\delta^2 H = 7.5\ \delta^{18}O - 185 \tag{3}$

kaolinite line : $\delta^2 H = 7.5\ \delta^{18}O - 220 \tag{4}$

The stable isotopes composition of kaolins, as well as of other clay minerals, is a function of the isotopic composition of the water from which they formed. The equilibrium isotopic fractionation factors between kaolinite and water were developed by Gilg and Sheppard (1996) and Sheppard and Gilg (1996) (Eqs. (5) and (6)).

Hydrogen : $1000\ln\alpha_{\text{kaolinite-water}} = -2.2 \cdot 10^6 T^{-2} - 7.7 \tag{5}$

Oxygen : $1000\ln\alpha_{\text{kaolinite-water}} = 2.76 \cdot 10^6 T^{-2} - 6.75 \tag{6}$

These fractionation factors are a function of the temperature of kaolinisation; therefore, the isotopic composition of kaolinite can provide information about its genesis (Fernández-Caliani et al., 2010). By combining Eqs. (2), (5), and (6), the kaolinisation temperature can be derived as follows (Clauer et al., 2015):

$$3.04 \cdot 10^6 T^{-2} = \delta O_k - 0.125\delta D_k + 7.04 \tag{7}$$

The temperatures of kaolinisation (T_G) of the studied kaolins were computed and presented in Table S5. The kaolins found in Cretaceous Formations had a mean T_G of $22 \pm 2\,°C$, whereas those found in Tertiary Formations had a mean T_G of $27 \pm 6\,°C$. These temperatures suggest that kaolins hosted in Cretaceous Formations formed at temperatures about $5\,°C$ cooler than those found in Tertiary Formations, and both Cretaceous and Tertiary temperatures are humid temperatures, favouring the formation of kaolins.

The local meteoric water line of Douala was developed for the years 2013 and 2014 by Wirmvem et al. (2016) (Eq. (1)). Using the same method and based on the same assumptions as in Delgado and Reyes (1996) and Clauer et al. (2015), the temperature of kaolinisation in equilibrium with the local meteoric water line of Douala is derived as follows:

$$3.04 \cdot 10^6 T^{-2} = \delta O_k - 0.126\delta D_k + 7.42 \tag{8}$$

Hence, the temperatures of kaolinisation (T_L) of the studied kaolins in equilibrium with the local meteoric water line were computed and presented in Table S5. The T_L values were slightly lower than the T_G values, with Cretaceous kaolins having a mean of $20 \pm 2\,°C$, and Tertiary kaolins having a mean of $25 \pm 6\,°C$. These values also show that kaolins hosted in Cretaceous Formations formed at temperatures about $5\,°C$ cooler than those found in Tertiary formations. Moreover, in both cases (kaolinites in equilibrium with the global meteoric water line or with the local meteoric water line), kaolinisation temperatures in Tertiary kaolins (the warmest) are slightly higher than present-day mean annual temperatures in Douala ($27\,°C$) (IAEA/WMO, 2017).

The studied kaolins are exposed occurrences that might have been formed through interactions with modern local meteoric water. Knowing the present-day mean isotopic composition of meteoric water in Douala, -3.1 and $-10‰$ for $\delta^{18}O_W$ and δ^2H_W, respectively (Wirmvem et al., 2016) and present-day mean annual temperature ($27\,°C$ in 2015) (IAEA/WMO, 2017), it is possible to evaluate the influence of modern local meteoric water on the kaolinisation of Cretaceous–Tertiary sediments in the Douala Sub-Basin. This could be done by computing the isotopic composition of Cretaceous–Tertiary kaolins in the Douala Sub-Basin using the modern mean annual temperature ($27\,°C$ in 2015) (IAEA/WMO, 2017), as in Eqs. (5) and (6) (Santos et al., 2007). From these calculations, kaolinites that formed under modern mean annual temperature should have an isotopic composition of $+20.8$ and $-40‰$ for $\delta^{18}O_K$
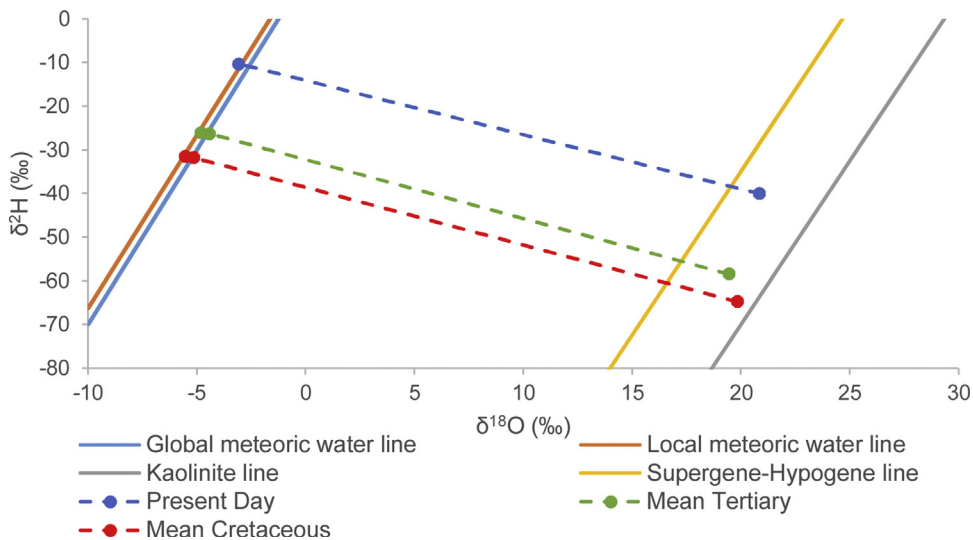

Fig. 5. Plot showing the mean isotopic composition of meteoric water in equilibrium with Cretaceous and Tertiary kaolins.

and δ^2H_K, respectively. Though DBB has a slightly heavier $\delta^{18}O_K$, Cretaceous–Tertiary kaolins have lighter $\delta^{18}O_K$ and δ^2H_K than computed modern kaolins. Thus, it can be concluded that Cretaceous–Tertiary kaolins of the Douala Sub-Basin are not in equilibrium with modern meteoric water.

5.2. Stable isotope composition of the meteoric water in equilibrium with Cretaceous–Tertiary kaolinites in the Douala Sub-Basin and equilibrium fractionation factors

Mean temperatures of kaolinisation determined using the GMWL and LMWL were used to determine the mean stable isotope composition of the meteoric water in equilibrium with Tertiary kaolins (300 and 298 K) and Cretaceous kaolins (295 and 293 K) using Eqs. (5)–(8). The results are shown in Table S6. Using the GMWL equation, the mean isotopic composition of the meteoric water in equilibrium with Cretaceous kaolins is −5.3 and −32‰, for $\delta^{18}O_W$ and δ^2H_W, respectively, whereas its mean isotopic composition when in equilibrium with Tertiary kaolins is −4.5 and −26‰, for $\delta^{18}O_W$ and δ^2H_W, respectively (Table S6 and Fig. 5).

Using the LMWL equation, the mean isotopic compositions of Tertiary meteoric waters (in equilibrium with Tertiary kaolins) are −4.8 and −26‰, for $\delta^{18}O_W$ and δ^2H_W, respectively, whereas the mean isotopic compositions of Cretaceous meteoric waters (in equilibrium with Cretaceous kaolins) is −5.7 and −31‰, for $\delta^{18}O_W$ and δ^2H_W, respectively (Table S6 and Fig. 5). These results, as well as the temperature of kaolinisation, are slightly lower than those obtained when using the GMWL equation. However, the equilibrium fractionation factor of ^2H between kaolinite and water (α_{K-W} ^2H) using the GMWL or the LMWL has remained constant from the Cretaceous to the Present (α_{K-W} $^2H = 0.97$), whereas the equilibrium fractionation factor of ^{18}O between kaolinite and water (α_{K-W} ^{18}O) has decreased from 1.025 or 1.026, during the Cretaceous, to 1.024 since the Tertiary.

5.3. Paleoenvironmental reconstruction

The low temperatures of kaolinisation ($20\,°C \leq T_G \leq 33\,°C$) and the positioning of the samples between the kaolinite and supergene/hypogene lines imply that kaolinisation took place in a supergene environment; therefore, Cretaceous–Tertiary kaolins of the Doula Sub-Basin are of weathering origin. As indicated by Bird and Chivas (1988), kaolins in a supergene environment generally have $\delta^{18}O$ values between +17 and +23‰, and δ^2H values between −80 and −40‰. This is sustained by the isotopic compositions of other kaolins formed by weathering, amongst which are the Cretaceous–Tertiary Georgia kaolins in the USA (Hassanipak and Elsinger, 1985), the Tertiary Lastarria kaolins (Gilg et al., 1999), the Cretaceous–Tertiary Rio Capim semi-flint kaolins in Brazil (Santos et al., 2007), the Permian Variscan kaolins in Spain (Fernández-Caliani et al., 2010; Clauer et al., 2015), the Cambrian Burela kaolin deposit in Spain (Gálan et al., 2016), and the Cretaceous–Tertiary Patagonia kaolins in Argentina (Domínguez et al., 2016).

Since kaolinite mostly preserves its original $\delta^{18}O$ compositions, isotopic exchange after deposition is unlikely (Boulvais et al., 2000). However, the little oxygen isotopic exchange between kaolinite and water reported by several authors was exhibited in the studied kaolins from the Cretaceous (+19 ‰) to the Present (+21‰). An increase in $\delta^{18}O$ values with time was also observed in Australian kaolinites (Bird and Chivas, 1989). Conversely, hydrogen isotopic exchange between kaolinite and water occurs at a more rapid rate and is responsible for the shift of samples from the kaolinite line (Bird and Chivas, 1989). Since their formation, these kaolins have been undergoing continual low-temperature isotopic exchange with meteoric waters of successively heavier isotopic compositions.

Subsequently, the kaolinisation temperatures of Cretaceous–Tertiary kaolins in the Douala Sub-Basin ($< 35\,°C$) reflect supergene environments, with Tertiary temperatures being higher than Cretaceous temperatures. This suggests a cooler climate during the Cretaceous than during the Tertiary. An increase in precipitation usually corresponds to an increase in δ^2H, either in kaolinite or its corresponding meteoric water (Sheppard and Gilg, 1996). Therefore, the increasing mean δ^2H values of kaolins in the Douala Sub-Basin means that there has been an increase in precipitation in the study area since the Cretaceous, favouring the formation of kaolins.

The Douala Sub-Basin is found in the Equatorial domain, which has precipitations ranging above 2000 mm per year, and mean temperatures around 25 °C (Pamo, 2008). In west and Central Africa, this Equatorial domain has a humid tropical climate, due to their low altitudes (Tardy et al., 1991). Regarding temperatures, Tardy et al. (1991) argued that western and central Africa have higher temperatures at the equator (> 5–$6\,°C$) and at the tropics ($> 20\,°C$) than at the same latitudes in South America (Brazil) and East Africa. Hence, when moving northwards from the equator to the Tropic of Cancer, temperatures increase, whereas when moving southwards from the equator to the Tropic of Capricorn, temperatures decrease (Tardy et al., 1991).

Using the paleolatitude calculator for paleoclimatic studies developed by van Hinsbergen et al. (2015) and the reference frame for paleoclimate studies proposed by Torsvik and Van der Voo (2002), the paleolatitude of the Douala Sub-Basin has been moving northwards, towards the Tropic of Cancer from the Cretaceous to the Present (Fig. 6).

According to the argument of Tardy et al. (1991), the climate in the Douala Sub-Basin has become warmer from the Cretaceous to the Present. The results obtained in the frame of this research converge towards this conclusion, showing that the Cretaceous had cooler temperatures than the Tertiary in the Douala Sub-Basin ($20 \pm 2\,°C$ and $25 \pm 6\,°C$, respectively), with mean annual temperatures between 2006 and 2015 of $27 \pm 0.35\,°C$.

Even though warm temperatures are required for kaolin formation, precipitation and leaching are the main factors influencing the formation of kaolins (Bird and Chivas, 1988). According to the rainfall patterns during the Mesozoic to Cenozoic derived by Parrish et al. (1982), Douala and its environs fall in the high rainfall domain
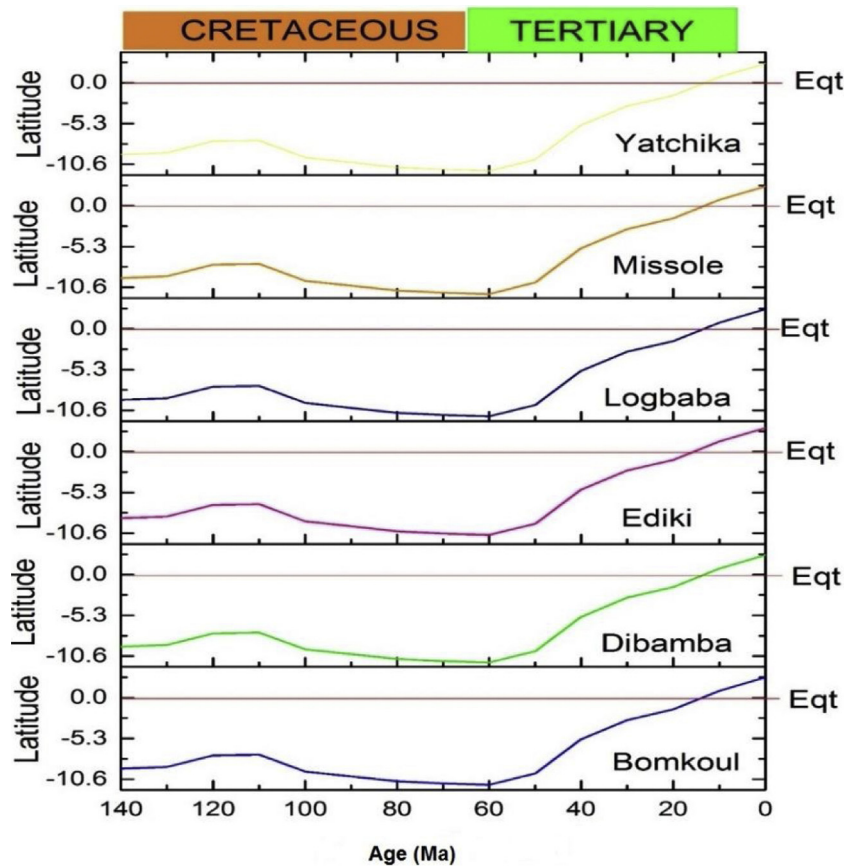
Fig. 6. Paleolatitudinal evolution of the Douala Sub-Basin from the Cretaceous to the Present (van Hinsbergen et al., 2015). Eqt: equator.

since the Cretaceous. However, the wettest months (June–October) also correspond to the coolest ones. Therefore, the formation of Cretaceous–Tertiary kaolins in the Douala Sub-Basin was more influenced by high precipitation than by high temperatures, and seasonal characteristics show that these kaolins were formed in a humid tropical climate. It implies that Douala had a humid climate during the Cretaceous, and the climate is gradually becoming hotter as concluded by Tardy et al. (1991), regarding the climate in West and Central Africa; but more humid.

6. Conclusion

Cretaceous–Tertiary kaolins in Douala Sub-Basin were formed in a weathering (supergene) environment. The temperatures of kaolinisation (assuming equilibrium with the global meteoric water line) were $22 \pm 2\,°C$ for Cretaceous kaolins and $27 \pm 6\,°C$ for Tertiary kaolins. Assuming equilibrium with the local (Douala) meteoric water line, the temperatures of kaolinisation were $20 \pm 2\,°C$ for Cretaceous kaolins and $25 \pm 6\,°C$ for Tertiary ones. The mean isotopic composition of the meteoric water in equilibrium with Tertiary kaolins (300 K and 299 K) and Cretaceous kaolins (295 and 293 K), using the GWML, is -5.3 and $-32‰$, for $\delta^{18}O_W$ and δ^2H_W, respectively during the Cretaceous and -4.5

and $-26‰$, for $\delta^{18}O_W$ and δ^2H_W, respectively during the Tertiary, whereas present-day mean isotopic composition of meteoric water in Douala is -3.1 and $-10‰$ for $\delta^{18}O_W$ and δ^2H_W, respectively. Douala had a cooler and rainy climate during the Cretaceous, and the climate is gradually becoming hotter and more humid, favouring refinement of the existing kaolins and the kaolinisation of kaolin-forming minerals in the Sub-Basin.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.crte.2018.11.007.

References

Baouimy, H., 2013. Hydrogen and oxygen isotopic compositions of sedimentary kaolin deposits, Egypt: Paleoclimatic implications. Appl. Geochem. 29, 182–188.

Becker, A., Ammann, B., Anselmetti, F.S., Hirt, A.M., Magny, M., Millet, L., Rachoud, A.-M., Sampiero, G., Wüthrich, C., 2006. Paleoenvironmental studies on Lake Bergsee, Black Forest, Germany. N. Jb. Geol. Paläont. Abh. 240 (3), 405–445.

Bird, M.I., Chivas, A.R., 1988. Stable-isotope evidence for low-temperature kaolinitic weathering and post-formational hydrogen-isotope exchange in Permian kaolinites. Chem. Geol. 72, 249–265.

Bird, M.I., Chivas, A.R., 1989. Stable-isotope geochronology of the Australian regolith. Geochim. Cosmochim. Acta 53, 3239–3256.

Blackwatch, 2016. Logbaba Field Reserves Report. Victoria PLC Oil and Gas Report. Blackwatch Petroleum Services Limited, Aberdeenshire, Scotland, UK (28 p.).

Boulvais, P., Vallet, J.-M., Estéole-Choux, J., Fourcade, S., Martineau, F., 2000. Origin of kaolinitisation in Brittany (NW France) with emphasis on deposits over granite: stable isotopes (O, H) constraints. Geochem. Geol. 168, 211–223.

Brownfield, M.E., Charpentier, R.R., 2006. Geology and total petroleum systems of the West-Central Coastal Province (7203), West Africa. U.S. Geol. Surv. Bull. 2207-B, (52 p.).

Bukalo, N.N., Ekosse, G.E., Odiyo, J.O., Ogola, J.S., 2018. Mineralogical characteristics of Cretaceous–Tertiary kaolins of the Douala Sub-basin, Cameroon. J. Afr. Earth Sci. 141, 130–147, http://dx.doi.org/10.1016/j.jafrearsci.2018.02.010.

Clauer, N., Fallick, A.E., Gálan, E., Aparicio, P., Miras, A., Fernández-Caliani, J.C., Aubert, A., 2015. Stable isotope constraints on the origin of kaolin deposits from Variscan granitoids of Galicia (NW Spain). Chem. Geol. 417, 90–101, http://dx.doi.org/10.1016/j.chemgeo.2015.09.022.

Craig, H., 1961. Isotopic variations in meteoric waters. Science 133, 1702–1708.

Das, S.S., Rai, A.K., Akaram, V., Verma, D., Pandey, A.C., Dutta, K., Prasad, G.V.R., 2013. Paleoenvironmental significance of clay mineral assemblages in the southeastern Arabian Sao during last 30 kyr. J. Earth Syst. Sci. 122 (1), 173–185.

Delgado, A., Reyes, A., 1996. Oxygen and hydrogen isotope compositions in clay minerals: A potential single-mineral geothermometers. Geochim. Cosmochim. Acta 60 (21), 4285–4289.

Domínguez, E., Dondi, M., Etcheverry, R., Recio, C., Iglesias, C., 2016. Genesis and mining potential of kaolin deposits in Patagonia (Argentina). Appl. Clay Sci. 131, 44–47, http://dx.doi.org/10.1016/j.clay.2015.12.031.

Effoudou-Priso, E.N., Onana, V.L., Boubakar, L., Beyala, V.K.K., Ekodeck, G.E., 2014. Relationships between major and trace elements during weathering processes in a sedimentary context: Implications for the nature of source rocks in Douala, Littoral Cameroon. Chem. Erde, http://dx.doi.org/10.1016/j.chemer.2014.05.003.

Ekosse, G.-I.E., 2007. Thermoanalytical characterisation, stable isotope and paleoenvironmental considerations of kaolinite from two genetic sources. Fresen. Environ. Bull. 16 (12), 1–15.

Elliot, W.C., Savin, S.M., Dong, H., Peacor, D.R., 1997. A paleoclimatic interpretation derived from pedogenic clay minerals from the Piedmont Province, Virginia. Chem. Geol. 142, 201–211.

Fagel, N., Boës, X., 2007. Clay-mineral record in Lake Baikal sediments: The Holocene and Late Glaciation transition. Palaeogeogr. Palaeoclimatol. Palaeoecol. 259, 230–243.

Fernández-Caliani, J.C., Gálan, E., Aparicio, P., Miras, A., Márquez, M.G., 2010. Origin and geochemical evolution of the Nuevo Montecastelo kaolin deposit (Galicia, NW Spain). Appl. Clay Sci. 49, 91–97, http://dx.doi.org/10.1016/j.clay.2010.06.006.

Fürsich, F.T., Singh, I.B., Joachimski, M., Krumm, S., Schlirf, M., Schlirf, S., 2005. Palaeoclimate reconstructions of the Middle Jurassic of Kachchh (western India): An integrated approach based on palaeoecological, oxygen isotopic, and clay mineralogical data. Palaeogeogr. Palaeoclimatol. Palaeoecol. 217, 289–309.

Gálan, E., Aparicio, P., Fernández-Caliani, J.C., Miras, A., Márquez, M.G., Fallick, A.E., Clauer, N., 2016. New insights on mineralogy and genesis of kaolin deposits: The Burela kaolin deposit (Northwestern Spain). Appl. Clay Sci. 131, 14–26, http://dx.doi.org/10.1016/j.clay.2015.11.015.

Gilg, H.A., 2000. D-H evidence for the timing of kaolinisation in Northeast Bavaria, Germany. Geochem. Geol. 170, 5–18.

Gilg, H.A., Sheppard, S.M.F., 1996. Hydrogen isotope fractionation between kaolinite and water revised. Geochim. Cosmochim. Acta 60 (3), 529–533.

Gilg, H.A., Hall, A.M., Ebert, K., Fallick, A.E., 2013. Cool kaolins from Finland. Paleogeogr. Paleoclimatol. Paleoecol. 392, 454–462.

Gilg, H.A., Hülmeyer, S., Miller, H., Sheppard, S.M.F., 1999. Supergene origin of the lastarria kaolin deposit, South-Central Chile, and paleoclimatic implications. Clays Clay Miner. 47 (2), 201–211.

Harris, C., Compton, J.S., Bevington, S.A., 1999. Oxygen and hydrogen isotope composition of kaolinite deposits, Cape Peninsula, South Africa: Low-temperature, meteoric origin. Econ. Geol. 94, 1353–1366.

Hassanipak, A.A., Elsinger, E., 1985. Mineralogy, crystallinity, O^{18}/O^{16}, and D/H of Georgia kaolins. Clays Clay Miner. 33 (2), 99–106.

Heckroodt, R.O., 1991. Clay and clay minerals in South Africa. J. South Afr. Inst. Mining Metall. 91 (10), 343–363.

Horbe, A.M.C., 2011. Oxygen and hydrogen isotopes in pedogenic minerals–Implications for paleoclimate evolution in Amazonia during Cenozoic. Geoderma 163, 178–184.

IAEA/WMO, 2017. Global Network of Isotopes in Precipitation. The GNIP Database. , https://www.nucleus.iaea.org/wiser.

Jackson, M.L., 1979. Soil Chemical Analysis–Advanced Course, 2nd ed. University of Wisconsin, Madison, WI (497 p.).

Kenfack, P.L., Njike Ngaha, P.R., Ekodeck, G.E., Ngueutchoua, G., 2012a. Fossils Dinoflagellates from the Northern Border of the Douala Sedimentary Sub-Basin (South-West Cameroon): Age Assessment and Paleoecological Interpretations. Geosciences 2 (5), 117–124.

Kenfack, P.L., Njike Ngaha, P.R., Ekodeck, G.E., Ngueutchoua, G., 2012b. Mineralogic Characterization and Petroleum Potential of Clays (Shales) of the N'Kapa Formation (Paleocene-Eocene) in the Douala Sedimentary Sub-basin (South-West Cameroon). Int. J. Geosci. 3, 696–709.

Logmo, E.O., Ngon Ngon, G.F., Samba, W., Mbog, M.B., Etame, J., 2013. Geotechnical, mineralogical and chemical characterisation of the Missole II clayey materials of Douala Sub-Basin (Cameroon) for construction materials. Open J. Civil Eng. 3, 46–53.

Martinez-Ruiz, F., Comas, M., Vasconcelos, C., 2014. Clay mineral assemblages as proxies for reconstructing Messinian paleoenvironments in the Western Mediterranean. Geophys. Res. Abstr. 16, (EGU2012-16767).

Mbesse, C.-O., Roche, E., Ngos III, S., 2012. La limite Paléocène-Eocène dans le bassin de Douala (Cameroun), Biostratigraphie et essai de reconstruction des paléoenvironnements par l'étude des Dinoflagellé. Geo-Eco-Trop. 36, 83–119.

Moriarty, K.C., 1977. Clay minerals in southeast Indian Ocean sediments, transport mechanisms and depositional environments. Mar. Geol. 25, 149–174.

Ngon Ngon, G.F., Etame, J., Ntamack-Nida, M.J., Mbog, M.B., Mpondo, A.M.M., Gerard, M., Yongue-Fouateu, R., Bilong, P., 2012. Geological study of sedimentary clayey materials of the Bomkoul area in the Douala region (Douala sub-basin, Cameroon) for the ceramic industry. C. R. Geoscience 344, 366–376.

Ortega, M., Palomo, I., Martinez, F., Gonzalez, I., 1998. Geological factors controlling clay mineral patterns across the Cretaceous–Tertiary boundary in Mediterranean and Atlantic sections. Clay Miner. 33, 483–500.

Pamo, E.T., 2008. Country Pasture/Forage Resource Profiles: Cameroon. Food and Agricultural Organisation, http://www.fao.org/ag/agp/AGPC/doc/Counprof/cameroon/cameroon.htm.

Parrish, J.T., Ziegler, A.M., Scotese, C.R., 1982. Rainfall patterns and the distribution of coals and evaporates in the Mesozoic and Cenozoic. Palaeogeogr. Palaeoclimatol. Palaeoecol. 40, 67–101.

Roseneau, N.A., Tabor, N., 2013. Oxygen and hydrogen isotope composition of paleosol phyllosilicates: Differential burial histories and determination of Middle-Late Pennsylvanian low-latitude terrestrial palaeotemperatures. Palaeogeogr. Palaeoclimatol. Palaeoecol. 392, 382–397.

Santos Jr., A.E.A., Rosetti, D.F., Murray, H.H., 2007. Origins of the Rio Capim kaolinites (northern Brazil) revealed by $\delta^{18}O$ and δD analyses. Appl. Clay Sci. 37, 281–294.

Savin, S.M., Epstein, S., 1970. Oxygen and hydrogen isotope geochemistry of clay minerals. Geochim. Cosmochim. Acta 34, 25–42.

Savin, S.M., Hsieh, J.C.C., 1998. The hydrogen and oxygen isotope geochemistry of pedogenic clay minerals: principles and theoretical background. Geoderma 82, 227–253.

Sheldon, N.D., Tabor, N.J., 2009. Quantitative paleoenvironmental and paleoclimatic reconstruction using paleosols. Earth Sci. Rev. 95, 1–52.

Sheppard, S.M.F., Gilg, H.A., 1996. Stable isotope geochemistry of clay minerals. Clay Miner. 31, 1–24.

Sheppard, S.M.F., Nielsen, R.L., Taylor, H.P., 1969. Oxygen and hydrogen isotope ratios of clay minerals from porphyry copper deposits. Econ. Geol. 64, 755–777.

SNH/UD, 2005. Stratigraphie Séquentielle et tectonique des dépôts mésozoïques synrifts du bassin de Kribi/Cam-po. (Unpublished report).

Stern, L.A., Chamberlain, C.P., Reynolds, R.C., Johnson, G.D., 1997. Oxygen isotope evidence of climate change from pedogenic clay minerals in Himalayan molasses. Geochim. Cosmochim. Acta 61 (4), 731–744.

Tabor, N.J., Montanez, I.P., 2005. Oxygen and hydrogen isotope compositions of Permian pedogenic phyllosilicates: Development of modern surface domain arrays and implications for paleotemperature reconstruction. Palaeogeogr. Palaeoclimatol. Palaeoecol. 223, 127–146.

Tabor, N.J., Montanez, I.P., Southard, R.J., 2002. Paleoenvironmental reconstruction from chemical and isotopic composition of Permo-Pennsylvanian pedogenic minerals. Geochim. Cosmochim. Acta 66 (17), 3093–3107.

Tardy, Y., Kobilsek, B., Paquet, H., 1991. Mineralogical composition and geographical distribution of African and Brazilian periatlantic laterites. The influence of continental drift and tropical paleoclimates during the past 150 million years and implications for India and Australia. J. Afr. Earth Sci. 1 2 (1/2), 283–295.

Torsvik, T.H., Van der Voo, R., 2002. Refining Gondwana and Pangea palaeogeography: estimates of Phanerozoic non-dipole (octupole) fields. Geophys. J. Int. 151, 771–794.

Turc, L., Chevalier, M., Flavier, C., Cheddadi, R., Meadows, M.E., Scott, L., Carr, A.S., Smith, G.F., Chase, B.M., 2013. Quantification of climate change for the last 20,000 years from Wonderkrater, South Africa: Implications for the long-term dynamics of the Intertropical Convergence Zone. Palaeogeogr. Palaeoclimatol. Palaeoecol. 386, 575–587.

van Hinsbergen, D.J.J., de Groot, L.V., van Schaik, S.J., Spakman, W., Bijl, P.K., Sluijs, A., Langereis, C.G., Brinkhuis, H., 2015. A Paleolatitude Calculator for Paleoclimate Studies (model version 2.0). PLOS ONE 10 (6), e0126946, http://dx.doi.org/10.1371/journal.pone.0126946.

van Reeuwijk, L.P., 2002. Procedures for soil analysis. International Soil Reference and Information Centre, Wageningen, The Netherlands, Tech. Paper 9. 100 p.

Westermann, S., Duchamp-Alphonse, S., Fiet, N., Fleitmann, D., Matere, V., Adatte, T., Föllmi, K.B., 2013. Palaeoenvironmental changes during the Valanginian: New insights from variations in phosphorous contents and bulk-and clay mineralogies in the western Tethys. Paleogeogr. Paleoclimatol. Paleoecol. 392, 196–208.

Wirmvem, M.J., Ohba, T., Kamtchueng, B.T., Taylor, E.T., Fantong, W.Y., Ako, A.A., 2016. Variation in stable isotope ratios of monthly rainfall in the Douala and Yaounde cities, Cameroon: local meteoric lines and relationship to regional precipitation cycle. Appl. Water Sci., http://dx.doi.org/10.1007/s13201-016-0413-4.