



## Geochemistry and possible industrial applications of Cretaceous-Tertiary kaolins of the Douala Sub-Basin, Cameroon

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### ABSTRACT

The geochemistry and diagnostic evaluation of Cretaceous-Tertiary kaolins in the Douala Sub-Basin in Cameroon were carried out in order to determine their potential industrial applications. The mineralogical, physical, physico-chemical and geochemical characteristics of the kaolins were determined. Quartz and kaolinite are the most dominant mineral phases in bulk kaolins (means of 45.25 and 33.90 wt%, respectively); whereas in the <2 μm fraction, kaolinite is the most dominant mineral phase (mean of 72.17 wt%). The texture of half of the samples is sandy loamy clay or sandy loam texture, and the colour from white to light reddish brown. The moisture content is generally <2 wt% in all the size fractions. The kaolins have an acidic pH, and the electrical conductivity is below 55 μS/cm. The major oxides geochemistry shows that the most abundant major oxides are silica and alumina, followed by iron oxide and titania. As physical, physico-chemical and geochemical characteristics of kaolins determine their potential industrial applications, these were inferred. Based on the interpretation of the results, the investigated kaolins could be used in the pharmaceutical, construction, pottery and cosmetics industries.

Keywords: Cretaceous-Tertiary; diagnostic evaluation; Douala Sub-Basin; geochemistry; industrial applications; kaolins.

### INTRODUCTION

Four minerals constitute the kaolin group, namely; kaolinite  $[Al_2Si_2O_5(OH)_4]$ , halloysite  $[Al_4Si_4O_{10}(OH)_8 \cdot 8H_2O]$ , nacrite  $[Al_2Si_2O_5(OH)_4]$  and dickite  $[Al_2Si_2O_3(OH)_4]$  (Kearey, 2001; Obaje et al., 2013). The most common of these minerals is kaolinite, which can form over a wide range of temperatures, due to weathering, diagenesis, or hydrothermal deposition and alteration (Schroeder and Hayes, 1968). Kaolinite is a two-layer clay (phyllosilicate mineral) which has a sheet of silica tetrahedral combined through octagonal hydroxyls which are shared with an alumina octahedral

sheet (Murray, 1999). The alumina octahedral sheet and the silica tetrahedral sheet share a common plane of oxygen atoms and repeating layers of the mineral are hydrogen bonded together (Miranda-Trevino and Coles, 2003). The functional groups consist of the outer and the inner hydroxyl groups (Frost, 1998). The theoretical formula of kaolin is 46.54% SiO<sub>2</sub>, 39.50% Al<sub>2</sub>O<sub>3</sub> and 13.96% H<sub>2</sub>O (Deer et al., 1992).

Kaolin genesis has a direct bearing on its industrial applications (Ekosse, 2000). Physical and physico-chemical properties of kaolins are closely related to their mineralogical and geochemical compositions (Cravero

et al., 1997). Moreover, kaolin impurities affect its industrial applications. The physical, physico-chemical, mineralogical and geochemical parameters of kaolins aid in its diagnostic assessment for economic benefits. These parameters do not only assist in the determination of potential industrial applications of a kaolin deposit; but they also determine which beneficiation process is required to improve its value. A correlation exists between specific physical and physico-chemical parameters of a kaolin deposit and its mineralogy and geochemistry. Clay fraction and iron content could aid in determining kaolin application (Negroni, 2015; Dehaine et al., 2019). Iron contained in iron-bearing minerals such as goethite and hematite present in kaolin reduces its whiteness (Bertolino et al., 2010). Scott et al. (1996) showed that the amount of clay size fraction in a kaolin deposit is not the best factor for determining the kaolin's unfired strength (important in the ceramic industry). The excellent firing properties and relatively high melting point of kaolin (Aja and Randy, 2013) advantage it as a suitable mineral for varied industrial applications (Choudhary et al., 2012).

Kaolins are used in several industries, including the construction, pharmaceutical, cosmetic industries amongst others (Heckroodt, 1991; Siddiqui et al., 2005; Matike et al., 2011; Obaje et al., 2013; Tassongwa et al., 2014). In the pharmaceutical industry, kaolin is used as excipient or active ingredient due to its excellent physical, chemical and surface physicochemical properties (Awad et al., 2017). Four types of bricks can be made from kaolin in the construction industry; these include common bricks, vertically perforated bricks, roofing tiles, masonry bricks, and hollow products (Dondi et al., 1992). In cosmetic industry, kaolin is used as a filler since it provides the necessary specific structure and also acts as a riser (Aja and Randy, 2013). Kaolin is also used as a filler and coating pigment in the paper industry (Jepson, 1984). Ceramics applications of kaolins include the production of sanitary ware, tableware, fine china, electrical porcelain, wall tiles and floor tiles. Whereas, in the paint and polymer industry, the fine particle size, aspect ratio and white colour of kaolins make them useful as extenders (Jepson, 1984).

In 2015, the world mine production of kaolins was estimated at approximately 36 billion metric tons (Flanagan, 2018). Though kaolin occurrences are common and known on all continents of the world except Antarctica, only ten countries produced up to 25 billion metric tons of kaolins. These countries were the United States of America, Brazil, China, Czech Republic, Germany, India, Kyrgyzstan, Turkey, Ukraine and the United Kingdom (Flanagan, 2018). Two of the best known and highly utilised kaolin deposits are those from the Amazon region in Brazil (Capim River kaolin) (Murray, 1999; Costa and Souza, 2009), and the high grade sedimentary kaolin

deposits in Georgia, USA (Georgia kaolin) (Pruett, 2016; Lang et al., 1965).

In Africa, more than 292 kaolin deposits and occurrences have been reported, with Cameroon having 27 deposits (Ekosse, 2010). Being a lower middle-income country with a population of 23.3 million people, Cameroon could invest in its kaolin occurrences to promote its economy. In the Douala Sub-Basin, kaolins have been identified (Diko and Ekosse, 2012; Ngon Ngon et al., 2012; Logmo et al., 2013). The mineralogy, stable isotopes geochemistry and U-Pb ages of zircons in Bomkoul, Dibamba, Ediki, Logbaba, Missole and Yatchika kaolins in the Douala Sub-Basin have been documented (Bukalo et al., 2017, 2018 a,b, 2019). In this paper, the authors present the geochemistry and paleoenvironments of formation of the clays; and where applicable, utilize referred published data to infer on possible industrial applications.

## MATERIALS AND METHODS

### Study Area

The studied kaolin occurrences are located in the Douala Sub-Basin, which extends on the South coast of Cameroon, covering a total surface area of 19,000 km<sup>2</sup> (Mbesse et al., 2012). It is subdivided into seven Formations (Logmo et al., 2013). The studied kaolin deposits are the Bomkoul, Dibamba, Ediki, Logbaba, Missole and Yatchika deposits (Figure 1), which belong to four Cretaceous-Tertiary Formations; namely, the Mundeck, Logbaba, Nkapa and Souellaba Formations. 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; and the Upper Eocene to Oligocene Souellaba Formation, composed of sandstones and marls, shales, clayey sands, sands and gravels (Effoudou-Priso et al., 2014). A general description of the studied kaolins is presented in Bukalo et al. (2019).

### Materials

As described in Bukalo et al. (2018a), the sampling method used was judgemental, i.e. the choice of samples was based on (i) the availability of Cretaceous-Tertiary kaolins in the Douala Sub-Basin, (ii) availability of an outcrop and its size, and (iii) presence of profiles and lithological variations in the outcrop. Table 1 shows the location, sample codes, geographical coordinates, age and Formation of studied kaolins.

### Methods

The bulk and <2 µm fractions of the kaolins were analysed for their mineralogy by X-ray diffractometry

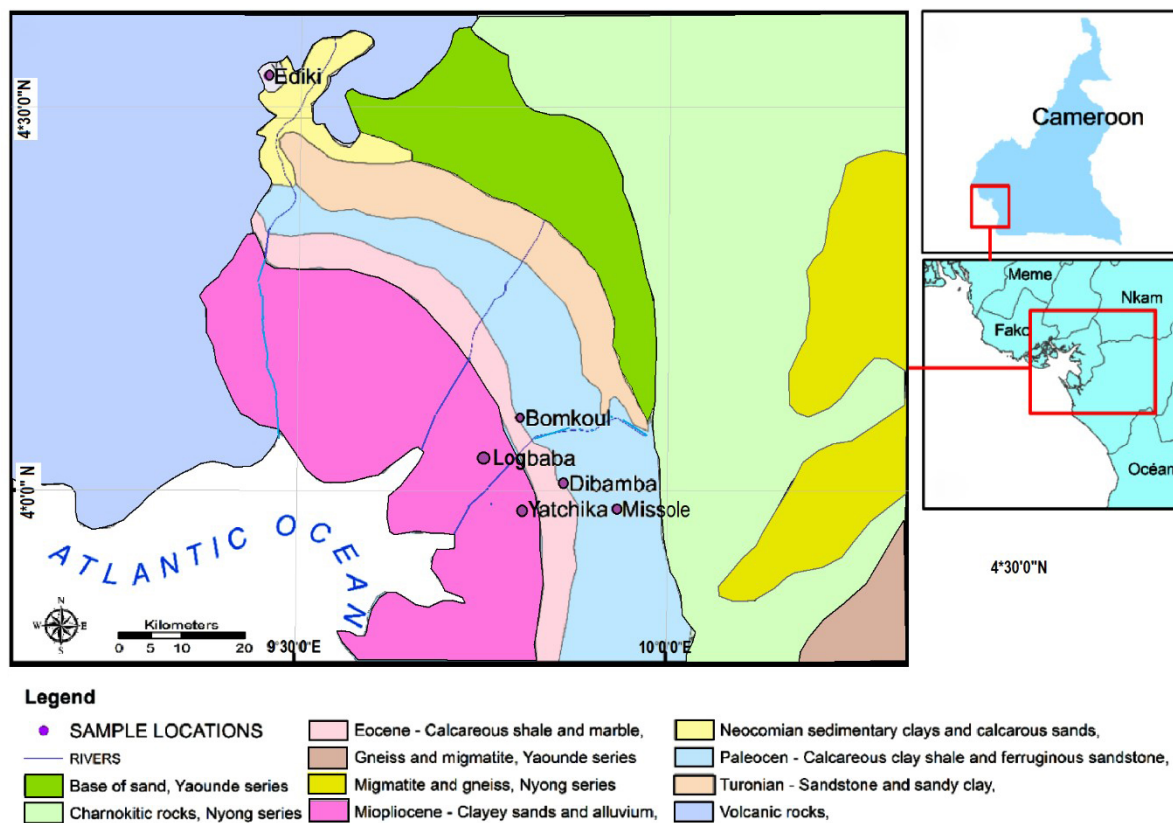


Figure 1. Geologic map of the Douala Sub-Basin (modified from SNH, 2005).

(XRD) using a Rigaku Ultima IV diffractometer working with 40 kV and 30 mA, with a cobalt source ( $\lambda=1.789 \text{ \AA}$ ) and an alpha filter (Co  $K\alpha$ ). Samples were scanned from  $3^\circ 2\theta$  to  $40^\circ 2\theta$  at a rate of  $2^\circ$  per minute. Mineral phase identification was carried using X'Pert Highscore Plus Software; and quantification of relative phase amounts (weight %) were estimated using the Rietveld method (Bukalo et al., 2018a). Diffractograms of this analysis are presented in Bukalo et al. (2018a).

The texture of the kaolins was determined according to the hydrometer method, as described by van Reeuwijk (2002). The colour of bulk kaolin samples was determined by using the Munsell® Soil Colour Charts (2000). Each sample was placed on a white paper and was visually compared with soil colours in the Munsell Soil Colour Charts to obtain its hue, value and chroma characteristics (Matike et al., 2011). The colour of the sample was then deduced from its characteristics.

The method that was used for the determination of the moisture content, was the one described by van Reeuwijk (2002). Five grams of each bulk kaolin sample was weighed in a 2.11 g tin. The samples were heated in an oven for 24 hours at  $105^\circ \text{C}$ . After removing the samples from the oven, they were placed in a desiccator in order

to prevent accumulation of moisture. Each sample was weighed again to note the weight difference. The moisture content (MC) was calculated using Equation (1) (van Reeuwijk, 2002).

$$MC = \frac{m_2 - m_3}{m_3 - m_1} \times 100 \quad (1)$$

Where, MC is the moisture content,  $m_1$  is the mass of tin (g),  $m_2$  is the mass of wet kaolin + tin (g), and  $m_3$  is the mass of dry kaolin + tin (g)

After determining their moisture content, the bulk and  $<2 \mu\text{m}$  samples were placed in a muffle furnace and heated at  $1000^\circ \text{C}$  for two hours. After two hours, the samples were removed from the furnace and were placed in desiccators. When cooled, samples were weighed, and LOI was calculated using Equation (2) (van Reeuwijk, 2002).

$$LOI = \frac{m_A - m_B}{m_B - m_C} \times 100 \quad (2)$$

Where, LOI is the loss on ignition,  $m_C$  is the mass of tin (g),  $m_A$  is the mass of the kaolin sample after heating for

24 hours at 105 °C+tin (g), and  $m_B$  is the mass of kaolin sample heating for two hours at 1000 °C+tin (g).

The pH of bulk kaolin samples was determined by using the method described in The Non-Affiliated Soil Analysis Work Committee (1990). Prior to measurements, a Crison Basic 20 pH meter was calibrated with buffers of pH=7 and pH=4. Ten grams of dry sample (<2 mm) was weighed and placed in a beaker. Fifty milliliters of 1 M potassium chloride (KCl) solution (74.5 g KCl dissolved in 1 L of distilled water) was added in the beaker. The mixture was stirred rapidly for 5 seconds, using a glass rod then allowed to stand. After 50 minutes, the mixture

was stirred again, then allowed to stand for 10 minutes. Then the pH was measured with the calibrated pH meter, with the electrodes placed in the supernatant.

Prior to the electrical conductivity (EC) measurement, a Crison Basic 30 conductivity meter was calibrated using a standard of EC=1413  $\mu\text{S}/\text{cm}$  at a temperature of 25 °C. The EC was determined by weighing 10 g of each bulk sample and placing it in a beaker. Distilled water was then added to the sample and the mixture was vigorously stirred using a glass rod. The EC was then measured by using the calibrated conductivity meter, with the electrode placed in the supernatant.

Major oxides concentrations of bulk and <2  $\mu\text{m}$  kaolin samples were determined using X-ray fluorescence spectrometry. The analysis was carried out on pressed pellets using a Rigaku ZSX Primus II XRF spectrometer. Prior to analysis, bulk kaolin samples were air dried and organic matter was removed from the samples (van Reeuwijk, 2002). Then the samples were dispersed using a mixture of 40 g of sodium hexametaphosphate ( $\text{NaPO}_3$ )<sub>6</sub> and 10 g of soda ( $\text{Na}_2\text{CO}_3$ ) according to (van Reeuwijk, 2002). Clay size fractions (<2  $\mu\text{m}$ ) were obtained by sedimentation and using a centrifuge, following the method described by (Jackson, 1979; van Reeuwijk, 2002). Pellets were then produced by using a hydraulic press and a die set (die body, base, plunger, and two polished metal disks), made up of tungsten alloy. Then the pressed pellets were placed in an oven at 105 °C for one hour. After removal from the oven, the pellets were allowed to cool; then XRF analysis was carried out.

Table 1. Location, sample codes, geographical coordinates, age and Formation of studied kaolins

Location	Sample code	Geographical Coordinates	Age	Formation
Bomkoul	BKL 01	N04°05'49.1" E09°48'16.7"	Tertiary	Matanda
	BKL 02			
	BKL 03			
Dibamba	DBB	N04°00'30.4" E09°51'48.3"	Tertiary	Nkapa
	DBB CN 01			
	DBB CN 02			
Ediki	EDK 01	N04°33'25.4" E09°27'59.9"	Cretaceous	Mundeck
	EDK 02			
	EDK 03			
Logbaba	LBB 01	N04°01'42.9" E09°45'25.7"	Cretaceous	Logbaba
	LBB 02			
	LBB 03			
Missole	MSL I 01	N03°58'27.9" E09°56'03.7"	Tertiary	Nkapa
	MSL I 02			
	MSL II 01			
	MSL II 02			
Yatchika	YTK 01	N03°58'28.8" E09°48'16.8"	Cretaceous	Logbaba
	YTK 02A			
	YTK 02B			
	YTK 03			

## RESULTS

### Mineralogical Characteristics

Table 2 summarises the minerals quantification in bulk and <2  $\mu\text{m}$  fraction of the kaolins. In bulk samples, quartz and kaolinite are the most dominant mineral phases, with means of 45.25 and 33.90 wt%, respectively; whereas anatase, rutile, goethite and hematite occur in trace amounts, with means of 1.25, 0.58, 1.64 and 0.75 wt%, respectively. In the <2  $\mu\text{m}$  fraction of the kaolins, kaolinite is the most dominant mineral phases, with a mean of 72.15 wt% (Bukalo et al., 2018a).

### Physical Characteristics

The Cretaceous-Tertiary kaolin samples of the Douala Sub-Basin have textures that vary from clay to sandy loam, with most samples containing sand (Table 3 and Figure 2).

Pure kaolin usually has a whitish colour; but most often impurities (iron and titanium) contained in kaolins will cause the clay to have a different tint. Different minerals present in kaolins could also influence their colour. The presence of orthoclase and/or iron-bearing minerals in

Table 2. Quantification in wt% of mineral phases\* identified in bulk and &lt;2 µm fraction samples.

	Bulk samples										<2 µm fraction samples							
	Ka	Il	Sm	Qz	Mx	An	Ru	Go	He	Ka	Il	Sm	Qz	Mx	An	Ru	Go	He
BKL 01	56	4	3	36	-	1	1	0	-	88	4	4	-	-	3	1	-	-
BKL 02	58	3	6	31	-	2	0	-	-	89	4	4	-	-	3	1	-	-
BKL 03	2	1	13	54	-	1	1	2	-	82	4	10	1	-	2	1	-	-
DBB	54	3	6	37	-	1	-	0	-	91	3	3	-	-	3	1	-	-
DBB CN 01	14	6	5	73	-	1	-	-	-	92	2	2	-	-	3	1	-	-
DBB CN 02	8	3	4	85	-	0	-	-	-	89	2	5	-	-	3	1	-	-
EDK 01	16	12	36	32	-	2	2	-	-	41	14	40	2	-	1	1	-	-
EDK 02	25	4	10	32	28	0	0	1	-	63	10	23	1	-	0	2	-	-
EDK 03	13	10	38	21	15	2	2	-	-	8	22	42	6	16	3	4	-	-
LBB 01	50	3	2	43	-	2	0	-	-	90	3	3	-	-	3	1	-	-
LBB 02	54	1	8	33	-	2	-	2	-	90	4	2	-	-	3	1	-	-
LBB 03	41	2	4	52	-	1	-	1	-	91	2	3	-	-	3	1	-	-
MSL I 01	12	1	7	79	-	0	-	1	-	59	3	17	20	-	1	1	-	-
MSL I 02	5	3	3	88	-	1	-	-	-	31	1	10	57	-	0	1	0	-
MSL II 01	52	3	4	38	-	2	1	-	-	87	5	3	0	-	4	1	-	-
MSL II 02	56	5	6	32	-	2	-	-	-	86	6	3	0	-	4	1	-	-
YTK 01	42	5	9	41	-	1	0	3	0	83	-	4	1	-	2	1	8	1
YTK 02A	16	5	31	41	-	1	0	5	0	12	-	20	16	-	1	-	49	2
YTK 02B	46	6	16	31	-	1	0	0	0	84	2	10	-	-	1	1	-	2
YTK 03	58	5	3	26	-	2	0	3	3	87	4	4	0	-	2	1	-	1
Mean	33.9	4.25	10.7	45.25	21.5	1.25	0.58	1.64	0.75	72.15	5.28	10.60	9.45	16.00	2.25	1.21	19.00	1.50
n	20	20	20	20	2	20	12	11	4	20	18	20	11	1	20	19	3	4

\*Ka: Kaolinite, Il: Illite, Sm: Smectite, Qz: Quartz, Mx: Microcline, An: Anatase, Ru: Rutile, Go: Goethite, Hm: Hematite.

-: Not detected; n: count of samples with detected minerals from which the mean was calculated.

kaolins will result in a pink, brown, orange or reddish colour. The colour of Cretaceous-Tertiary kaolins of the Douala Sub-Basin, using the hue, value and chroma of samples, is shown in Table 3. The colour of these kaolins varies greatly in hue, value and chroma; hence, different colours are determined. The most dominant colour is light reddish brown, i.e. three of the samples; and the least colours are brownish yellow, dark grey, grey, pink and reddish yellow, each represented by one sample each.

The moisture content of the bulk samples varies between 0.00 wt% (DBB CN 02) to 7.00 wt% (YTK 01). YTK samples have a moisture content  $\geq 2.00$  wt%. Except EDK 01, EDK 03 and LBB 01, which have a moisture content

of 1.40 wt%, the remaining samples have a moisture content  $\leq 0.80$  wt% (Table 3).

#### Physico-chemical Characteristics

The  $\text{pH}_{(\text{KCl})}$  and electrical conductivity (EC) are plotted in Figure 4. Cretaceous-Tertiary kaolins are all acidic, varying between 1.87 (MSL I 02) and 3.81 (LBB 01), with an average of 3.29. Missole I samples have the lowest pH values; whereas Logbaba samples have the highest pH values (Table 3).

The EC of Cretaceous-Tertiary kaolins varies from 98  $\mu\text{m}/\text{cm}$  (LBB 03) to 8710  $\mu\text{S}/\text{cm}$  (MSL I 02). Missole I samples have very high EC compared to other samples,

Table 3. Physical and physico-chemical properties of the kaolin samples.

	Clay (%)	Silt (%)	Sand (%)	Texture	Moisture content (%)	pH <sub>(KCl)</sub>	EC ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	Hue/Value/Chroma	Colour
BKL 01	46	8	46	Sandy Clay	0.40	3.59	51.3	5YR/6/4	Light Reddish Brown
BKL 02	55	6	39	Clay	0.80	3.52	40.7	5YR/6/4	Light Reddish Brown
BKL 03	25	7	68	Sandy clay loam	0.80	3.46	32.2	10YR/6/6	Brownish yellow
DBB	28	2	70	Sandy clay loam	0.60	3.26	76.7	5YR/8/2	Pinkish white
DBB CN 01	14	2	84	Sandy loam	0.20	3.33	80.6	5YR/8/2	Pinkish white
DBB CN 02	10	16	74	Sandy loam	0.00	3.75	26.5	10YR/8/6	Yellow
EDK 01	27	15	58	Sandy clay loam	1.40	3.12	21.5	GLEYS 1/2/5G	Pale green
EDK 02	24	19	57	Sandy clay loam	0.20	3.2	29	GLEYS 1/8/5GY	Light greenish grey
EDK 03	33	23	44	Clay loam	1.40	3.06	23.9	GLEYS 1/7/5G	Pale green
LBB 01	36	8	56	Sandy clay	1.40	3.81	11	2.5Y/7/1	Light grey
LBB 02	36	6	58	Sandy clay	0.40	3.74	16	2.5Y/8/1	White
LBB 03	36	6	58	Sandy clay	0.20	3.75	9.8	2.5Y/7/1	Light grey
MSL I 01	9	13	78	Sandy loam	0.40	1.81	7860	5Y/5/1	Grey
MSL I 02	7	15	78	Loamy sand	0.20	1.87	8710	5Y/4/1	Dark grey
MSL II 01	53	13	34	Clay	0.20	3.45	70.7	GLEYS 1/8/N	White
MSL II 02	37	5	58	Sandy clay	0.20	3.5	24.2	GLEYS 1/8/10Y	Light greenish grey
YTK 01	22	8	70	Sandy clay loam	7.00	3.35	45.5	10YR/7/8	Yellow
YTK 02A	19	23	58	Sandy Loam	3.80	3.35	26.7	7.5YR/6/6	Reddish Yellow
YTK 02B	10	14	76	Sandy loam	2.40	3.33	22	5YR/7/3	Pink
YTK 03	53	7	40	Clay	2.00	3.47	34.8	5YR/6/4	Light reddish brown

7860 and 8710  $\mu\text{m}/\text{cm}$  for MSL I 01 and MSL I 02, respectively. Excluding these two samples, the mean of EC for all other samples is 35.73  $\mu\text{S}/\text{cm}$  (Table 3).

### Geochemistry

The concentrations of oxides in bulk and  $<2\ \mu\text{m}$  fraction samples are presented in Table 4. The most dominant oxides are  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , as reflected by the dominance of quartz ( $\text{SiO}_2$ ) and kaolinite [ $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ] in their mineralogy. The mineralogy of the kaolins strongly correlates with their geochemistry. The CaO and  $\text{Na}_2\text{O}$  had very low concentrations in bulk and  $<2\ \mu\text{m}$  fraction samples. These oxides are relatively higher in samples rich in smectite, such as some Bomkoul and Ediki samples. Ediki samples present the highest  $\text{K}_2\text{O}$  concentrations (mean of 7.95 wt%) due to the presence of illite in these samples. Other samples reveal  $\text{K}_2\text{O}$  concentrations  $<2\ \text{wt}\%$ .

Titania and  $\text{Fe}_2\text{O}_3$  are usually considered as impurities in kaolins. The low titania contents are observed in all

samples reflect the low rutile and anatase concentrations in the mineralogy. The mineralogy also showed higher Fe-rich minerals (goethite and hematite) than Ti-rich minerals (anatase and rutile), as confirmed by the geochemistry. As a general trend,  $\text{Fe}_2\text{O}_3$  is higher in clay fractions than in bulk samples. Bulk samples present lower  $\text{P}_2\text{O}_5$  and  $\text{SO}_3$  concentrations than  $<2\ \mu\text{m}$  fractions. This trend could be due to the use of sodium hexametaphosphate as dispersing agent to obtain clay fractions. However, MSL I samples contained abnormally high  $\text{SO}_3$  concentration ( $>3.00\ \text{wt}\%$ ), though no sulphate mineral was detected by x-ray diffractometry.

### DISCUSSION

#### Physical and Physico-chemical Properties as Indicators of Environments of Formation of Kaolins

Cretaceous-Tertiary kaolins of the Douala Sub-Basin are mainly dominated by sand (60.20%), followed by clay (29.00%) and silt (10.80%), averagely. The dominance of

**USDA-NRCS  
Soil Texture Classes**

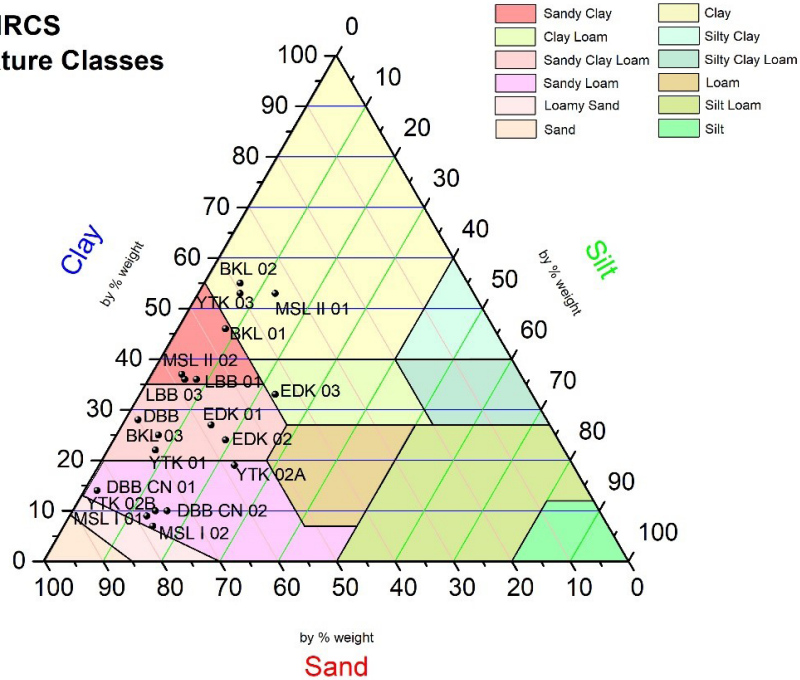


Figure 2. Ternary diagram showing kaolins' textures (Modified from Schroeneberg et al., 2012).

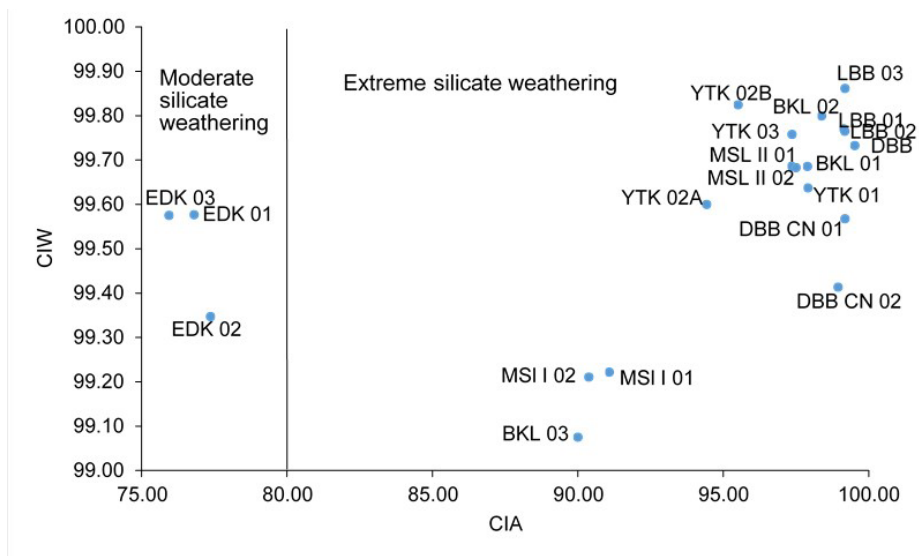


Figure 3. Chemical index of weathering (CIW) versus chemical index of alteration (CIA) of bulk samples.

sands in these kaolins is due to the nature of sediments found in the Sub-Basin. These sediments are mainly arkosic sandstones, suggesting an acidic source, from which feldspars are believed to have weathered to form kaolins. The lower percentage of silt over clay shows that there is on-going reworking of sediments taking place in

the Sub-Basin (Bukalo et al., 2018a).

The whitish colour of some of the studied kaolins is indicative of secondary alteration, formed after the recycling of first cycle sediments. As reported in Bukalo et al. (2018a), the morphology of these white kaolins is made up of books of kaolinite grains. This type of

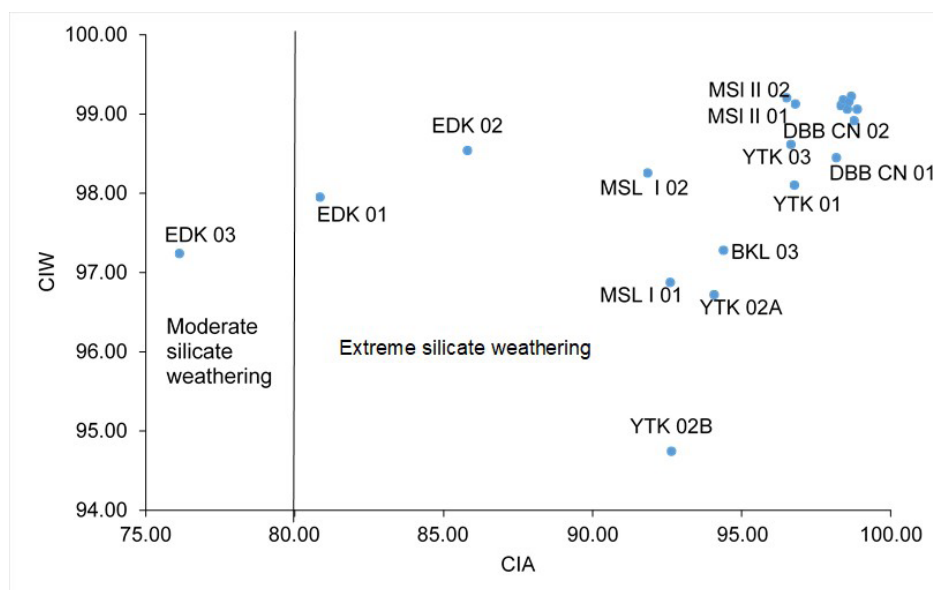


Figure 4. Chemical index of weathering (CIW) versus chemical index of alteration (CIA) of  $< 2 \mu\text{m}$  samples.

morphology is characteristic of kaolinite flakes which have been transported and deposited in piles (Keller, 1978). The association of this morphology and the white colour has also been observed in the Georgia kaolins, which are second cycle kaolins (Schroeder et al., 2004). However, Missole I kaolin is grey. The grey Missole I kaolin has an  $\text{SO}_3$  content of approximately 3.00 wt%, unlike all other kaolins which have an  $\text{SO}_3$  content less than 0.2 wt%. Therefore, the colour of the Missole I kaolin is probably linked to its  $\text{SO}_3$  content. This is comparable to the study by Schroeder et al. (2004), which indicates that grey Georgia kaolins had the highest  $\text{SO}_3$  content (1.31 wt%) relative to cream and white Georgia kaolins, with  $\text{SO}_3$  content of 0.00 wt% and 0.01 wt%, respectively. The grey Missole I kaolins have the lowest pH among all the samples. Manju et al. (2001) argued that oxidised weathering conditions can enhance the dissolution of the  $\text{FeS}_2$  present in grey kaolins, creating an environment with very low pH, and consequently high EC. This is supported by the negative correlation between pH and EC (-0.92), and high positive correlation between  $\text{SO}_3$  and EC (1.00). Such very acidic environment favours reworking of microcrystalline quartz and authigenic kaolinite (Manju et al., 2001). Therefore, the grey Missole I kaolin were deposited or formed in a reducing environment; then the environment became oxidising, resulting in the very low pH observed in Missole I kaolin. The oxidation of the Missole I kaolin probably led to the formation of the light grey and subsequently white Missole II kaolin by oxidative alteration (Schroeder et al., 2004; Pruett, 2016). This confirms that Missole II kaolins is a product of secondary alteration, i.e. formed from post-depositional alteration

of Missole I kaolins. The light grey and white Logbaba kaolin might have formed in the same conditions, though their colour might be as result of anatase contamination due to its high  $\text{TiO}_2$  concentrations.

The low pH of the kaolins, indicating high acidity ( $\text{pH} < 4$ ), is also an indicator of continuous weathering and intense hydrolysis processes kaolinite (Manju et al., 2001). The yellowish, reddish and brownish colours portrayed in Bomkoul, Dibamba and Yatchika kaolins are indicative of an oxygen-rich environment (oxic), favouring the alteration of feldspar and the presence of iron-rich minerals such as goethite. The greenish colour of Ediki samples is as a result of the presence of microcline and illite in these kaolins (Bukalo et al., 2018a).

### Geochemical Properties as Indicators of Environments of Formation of Kaolins

#### *Paleoweathering and sedimentary provenance*

Information on paleoweathering of sedimentary rocks can be obtained from geochemical indices such as the chemical index of alteration (CIA), chemical index of weathering (CIW) and index of compositional variability (ICV) (Nesbitt and Young, 1982; Cox et al., 1995; Fiantis et al., 2010). Ninety percent of bulk kaolins exhibit extreme silicate weathering ( $\text{CIA} > 80\%$ ) against 10% (Ediki kaolins) that exhibit moderate silicate weathering (Figure 3). Clay fractions have lower CIA and CIW values than bulk samples. In the clay fractions, 95% of samples exhibit extreme silicate weathering against 5% (EDK 03) that exhibits moderate silicate weathering (Figure 4).

The ICV values of bulk samples range from 0.05 (DBB CN 01) to 0.61 (EDK 03); whereas in  $< 2 \mu\text{m}$  samples



Table 4. Oxides concentrations (wt%) in bulk and <2 μm samples.

Samples	Bulk samples											<2 μm fraction samples												
	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	LOI	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	LOI
BKL 01	0.03	0.20	30.18	49.01	0.12	0.11	0.56	0.07	2.08	0.01	8.47	8.72	0.27	0.14	34.84	40.34	0.54	0.06	0.27	0.04	1.88	0.0	7.27	14.14
BKL 02	0.01	0.21	32.02	47.41	0.10	0.13	0.45	0.05	2.12	0.00	7.23	9.68	0.27	0.12	35.83	41.76	0.49	0.05	0.28	0.02	2.03	0.0	5.64	13.03
BKL 03	0.13	0.54	22.51	60.21	0.16	0.11	2.30	0.08	1.90	0.00	6.84	4.72	0.78	0.72	30.19	43.05	0.92	0.06	0.95	0.06	1.7	0.0	9.02	12.22
DBB	0.03	0.16	29.04	64.80	0.15	0.11	0.07	0.05	0.84	0.00	0.85	3.83	0.35	0.14	38.02	44.67	0.55	0.06	0.07	0.01	0.67	0.0	1.62	13.74
DBB CN 01	0.00	0.13	21.78	71.73	0.93	0.15	0.08	0.09	0.27	0.00	0.58	3.42	0.48	0.14	37.27	42.18	2.04	0.14	0.1	0.11	0.2	0.0	1.41	13.82
DBB CN 02	0.00	0.10	9.14	87.88	0.10	0.08	0.04	0.05	0.18	0.00	1.15	1.21	0.38	0.12	36.68	42.34	0.68	0.07	0.06	0.03	0.38	0.0	5.71	13.46
EDK 01	0.07	1.08	25.93	54.83	0.09	0.03	7.71	0.04	1.58	0.00	2.68	5.51	0.59	1.33	29.06	48.24	0.37	0.04	6.28	0.02	1.74	0.0	4.17	7.76
EDK 02	0.11	0.48	28.09	56.36	0.10	0.04	8.04	0.07	1.14	0.00	0.82	4.29	0.48	0.79	33.78	47.46	0.3	0.05	5.09	0.02	1.11	0.0	2.6	8.14
EDK 03	0.06	1.57	25.87	53.46	0.15	0.05	8.09	0.05	1.58	0.01	4.32	4.29	0.71	1.83	26.42	48.61	0.52	0.03	7.55	0.04	1.53	0.0	5.63	6.8
LBB 01	0.03	0.09	30.32	60.31	0.18	0.10	0.19	0.04	2.48	0.00	1.10	4.95	0.28	0.07	37.91	42.39	0.58	0.1	0.2	0.02	2.12	0.0	1.51	14.57
LBB 02	0.03	0.09	32.28	58.45	0.18	0.15	0.18	0.04	2.46	0.00	1.07	4.87	0.31	0.07	38.21	42.6	0.62	0.08	0.21	0.02	2.22	0.0	1.48	14.01
LBB 03	0.00	0.07	26.36	65.38	0.19	0.10	0.18	0.04	2.12	0.00	0.94	4.46	0.35	0.07	37.82	42.66	0.62	0.07	0.21	0.01	2.22	0.0	1.5	14.29
MSL I 01	0.07	0.32	13.15	74.12	0.32	3.07	1.18	0.04	1.83	0.00	2.87	2.63	0.68	0.52	21.95	38.47	7.56	4.48	1.04	0.03	1.39	0.0	10.1	13.25
MSL I 02	0.08	0.44	13.78	72.27	0.29	3.33	1.36	0.03	1.99	0.00	2.91	3.04	0.29	0.52	18.24	54.7	4.69	3.22	1.3	0.03	2.09	0.0	5.95	8.3
MSL II 01	0.07	0.14	32.90	52.00	0.09	0.08	0.78	0.03	3.70	0.00	2.38	7.47	0.31	0.14	36.12	42.74	0.27	0.05	0.89	0.01	3.21	0.0	2.91	12.7
MSL II 02	0.05	0.13	32.35	55.67	0.07	0.08	0.74	0.05	3.09	0.00	1.76	5.79	0.28	0.13	36.23	43.04	0.21	0.05	1.01	0.01	3.2	0.0	2.68	12.96
YTK 01	0.08	0.60	29.83	50.53	0.24	0.18	0.52	0.03	1.57	0.00	7.73	8.06	0.57	0.41	31.01	36.99	1.31	0.1	0.44	0.03	1.28	0.0	14.34	13.26
YTK 02A	0.07	0.87	25.50	54.55	0.08	0.11	1.40	0.03	1.71	0.01	7.44	7.72	0.99	0.87	29.8	42.15	1.7	0.09	0.86	0.02	1.35	0.0	10.8	11.23
YTK 02 B	0.04	0.99	28.53	54.68	0.06	0.08	1.30	0.01	1.57	0.00	4.56	7.82	1.61	0.98	29.49	43.97	4.47	0.11	0.7	0.02	0.85	0.0	7.89	9.75
YTK 03	0.04	0.41	28.98	46.87	0.08	0.16	0.72	0.03	1.93	0.00	11.26	9.02	0.45	0.36	32.89	41.21	0.51	0.09	0.69	0.02	1.97	0.0	9.18	12.5
Mean	0.05	0.43	25.93	59.53	0.18	0.41	1.79	0.05	1.81	0.00	3.85	5.58	0.52	0.47	32.59	43.48	1.45	0.45	1.41	0.03	1.66	0.00	5.57	12.00



ranged from 0.07 (DBB and DBB CN 01) to 0.65 (EDK 03). There is no evident disparity of ICV between bulk and clay size fraction (Figure 5). Hence, major oxides geochemistry of clay minerals could be a best indicator for their compositional variability, thereby giving insights on their provenance, as well as environmental conditions prevailing during diagenesis (Cox et al., 1995). The lowest ICV values (<0.22) are observed in Dibamba, Logbaba and Missole II samples. Low ICV values correspond to high degree of maturity of the samples. Therefore, they might have been deposited in tectonically quiescent or cratonic environments, which is a characteristic of second cycle deposits; unlike immature sediments which tend to be found in tectonically active settings and are characteristic of first-cycle deposits (Cox et al., 1995). Though other samples do not have very low ICV values, their values however, fall in the range for clay minerals (0.03-0.78), which confirms the mineralogy varying from dominant clay minerals to minor feldspars (Nagarajan et al., 2015); and this case, the clay minerals being dominant.

The relationship between climate and the degree of weathering shows that higher rainfall corresponds to increased weathering and higher CIA values in the resulting sediments (Ahmad et al., 2014). A similar positive relationship exists between the intensity of weathering and CIW due to the immobility of Al and higher mobility of Na, K, and Ca (Akinyemi et al., 2014). However, as weathering progresses, ICV decreases due to conversion of feldspars from their source rocks to Al-bearing clays, such as kaolins. The  $\text{TiO}_2\text{-Al}_2\text{O}_3$  binary plots of both bulk and <2  $\mu\text{m}$  samples (Figure 6) suggest that the source rocks of these kaolins vary between rhyolite/granite and

rhyolite/granite + basalt, with Missole I samples being the closest to the rhyolite/granite + basalt line.

#### *Environments of formation or deposition*

The plot of  $\log(\text{K}_2\text{O}/\text{Al}_2\text{O}_3)/\log(\text{MgO}/\text{Al}_2\text{O}_3)$  has been used by Mousa et al. (2014) to discriminate between marine and non-marine environments or formation or deposition. For the studied kaolins, the plot of  $\log(\text{K}_2\text{O}/\text{Al}_2\text{O}_3)/\log(\text{MgO}/\text{Al}_2\text{O}_3)$  showed that the kaolins are dominantly of marine origin, except the Logbaba samples, which show a non-marine/deltaic environment (Figure 7). The Logababa samples are found in the Upper Cretaceous Logbaba Formation, which is believed to have sediments of lacustrine origin (Chavom et al., 2014).

#### **Potential Applications of Cretaceous-Tertiary Kaolins of the Douala Sub-Basin**

World known and exploited kaolins are the Cornwall (England), Capim River (Brazil), Georgia (USA) and Cape York Peninsula (Australia) kaolins. One of the common characteristics among these kaolin deposits is their location in Cretaceous-Tertiary sedimentary basins, next to granitic rocks (Harvey and Murray, 1997). These kaolins are exploited for various industrial applications including paper coating, paper filler, ceramics, soap, pharmaceuticals and cosmetics. Therefore, the geochemical and physico-chemical characteristics of the Cretaceous-Tertiary kaolins were compared to standards (Prasad et al., 1991) set for paper coating, paper filler, ceramics, pharmaceuticals and cosmetics (Figures 8-11).

The presence of impurities in kaolin usually hinders its potential uses in industries. Such impurities include the

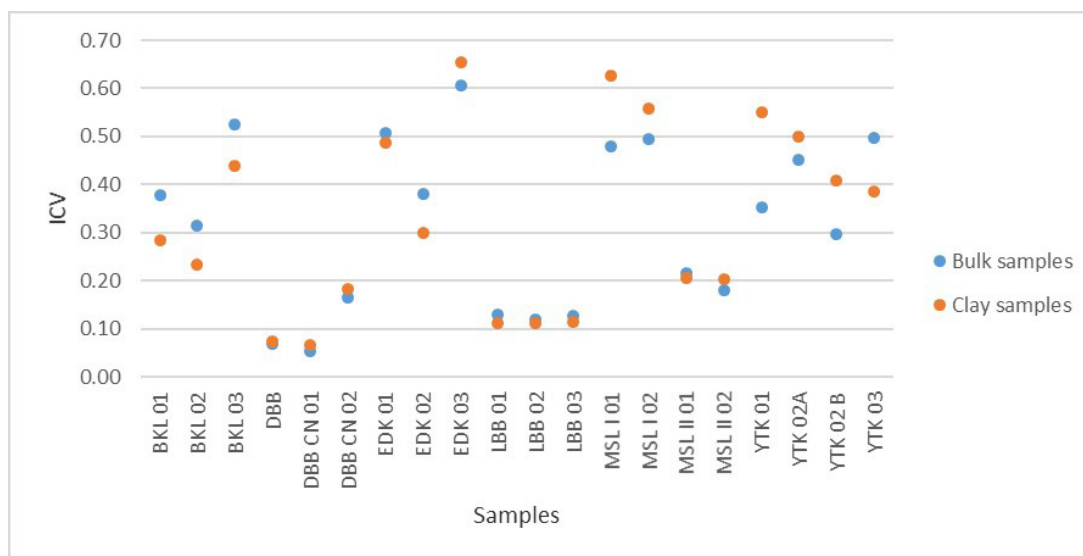


Figure 5. ICV of bulk and <2  $\mu\text{m}$  samples.

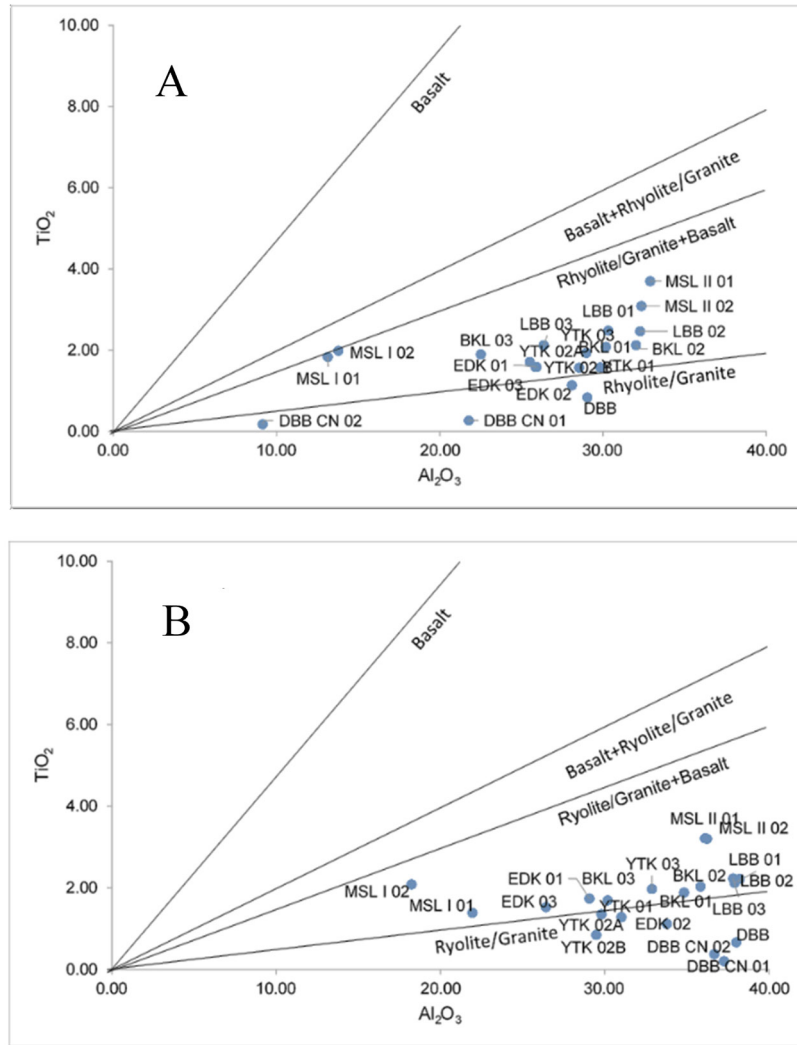


Figure 6.  $\text{TiO}_2$ - $\text{Al}_2\text{O}_3$  binary plot of A) bulk samples and B)  $<2 \mu\text{m}$  samples (Fields are from Ekosse, 2001).

presence of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ . The relatively high  $\text{Fe}_2\text{O}_3$  averages in Cretaceous-Tertiary kaolins of the Douala Sub-Basin are caused by intense oxidation of iron-bearing silicate minerals (Ariffin et al., 2008). High titania in kaolins also reduces their quality for specific industrial applications. In Cretaceous-Tertiary kaolins of the Douala Sub-Basin, iron oxides are highly correlated with goethite and hematite; whereas titanium dioxide positively correlates with anatase. Though these impurities are present in the studied kaolins, it is to be noted that some of their characteristics could be useful for specific industries (pottery and bricks making).

The ranges of major oxides and LOI do not correspond to the standards in Prasad et al. (1991), except the recommended values for CaO in kaolins to be used in pharmaceuticals and cosmetics. However, Dibamba, Logbaba and Missole

II kaolins' clay fractions fall in the ranges set for major oxides to be used for paper coating, paper filler, ceramics, pharmaceuticals and cosmetics. Therefore, in order for these kaolins to be used for any of these applications, particle size separation must be carried out to obtain the  $<2 \mu\text{m}$  fraction. When compared to major oxides concentrations of clays used for traditional and industrial pottery in Eastern Cape (Jumban et al., 2013), it is observed that Dibamba and Missole I kaolins have similar geochemical compositions as the clays used for traditional and industrial pottery in Eastern Cape (Figure 12).

Pruett (2016) derived a classification of kaolin ores mined for kaolin used in industrial applications based on selected oxides. Cretaceous-Tertiary kaolins of the Douala Sub-Basin mainly fall in the sandy kaolin and kaolinitic sandstone fields (Figure 13). Such kaolins, which plot in

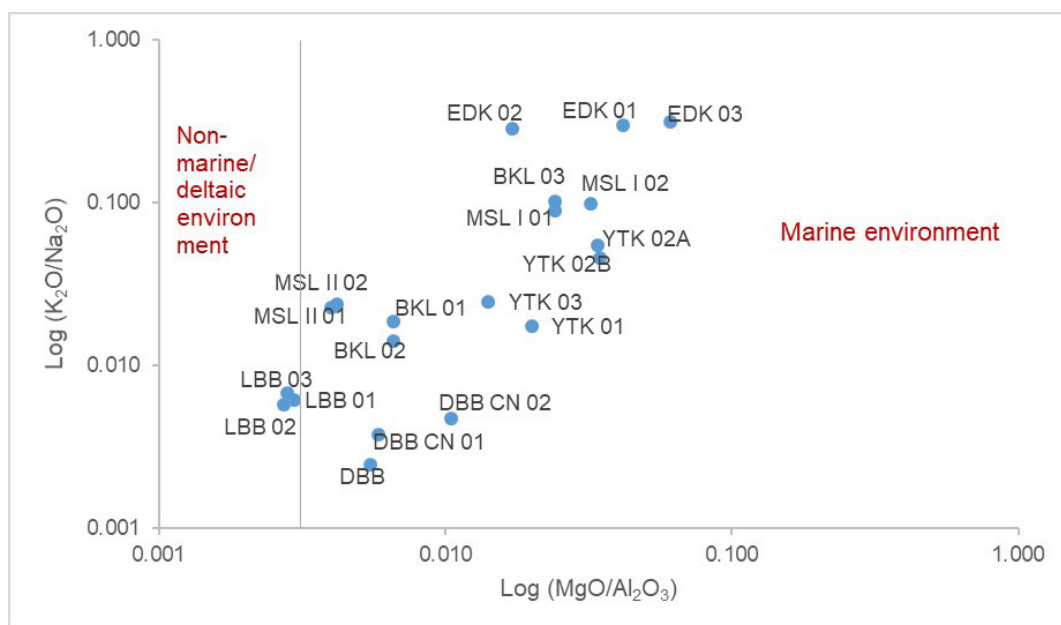


Figure 7. Plot of  $\log (K_2O/Al_2O_3)/\log (MgO/Al_2O_3)$  of bulk kaolins showing a marine environment of formation.

the fields of nearly pure kaolin to kaolinitic sandstone, or primary kaolin having up to about 90% quartz particles are used for pigments and additives (Pruett, 2016). Figure 14 shows the plot of the clay fractions of studied kaolins. This plot shows that after particle size reduction, all the kaolins can be used as pigments and additives except Missole I and Ediki kaolins.

The low moisture content indicates that the samples are very dry. This characteristic makes the kaolins suitable for use as paint fillers and for soap production, which should not exceed 2% (Ariffin et al., 2008; Aja and Randy, 2013). Kaolins are used to cure natural and synthetic rubber, and as a skin cleanser in the cosmetics industry. The pH of kaolins plays an important role in the rubber and cosmetics industries. Both industries require a pH between 4.5 and 5.5 (Ekosse, 2000; Matike et al., 2011). Therefore, the low pH values of Cretaceous-Tertiary kaolins of the Douala Sub-Basin, make the kaolins unsuitable for the rubber and cosmetics industries. Moreover, pH and EC of kaolins are used to detect impurities and salts. High EC values of Missole I kaolin correspond to the presence of  $SO_3$  in these kaolins. Sulphur causes cracks and pores during firing at elevated temperatures and it is usually required that  $SO_3$  content of kaolins used for ceramics be reduced to <0.5% (Ekmekci et al., 2001). Unlike other deposits that have low EC values and  $SO_3$  content, Missole I kaolin cannot be used for ceramics.

The fine particle size of kaolins enables them to be used for polymer reinforcement in the plastic industry; the finer the particle size, the greater the reinforcement

(Ekosse, 2000). Hence, the studied Cretaceous-Tertiary kaolins of the Douala Sub-Basin can only be used in the plastic industry if particle size reduction is carried out. The white colour of kaolins is one of the most important characteristics of kaolins to be considered in the paper industry, especially for paper coating. Calcined kaolin can replace up to 60% titanium dioxide (which is usually used in the paper industry because of its exceptionally high brightness and opacity) with little or no loss in brightness and opacity (Al-Ani and Sarapää, 2008). The white colour of kaolins also makes them excellent ingredients in ceramics, and sanitary wares. Reddish and brownish kaolins are associated to the presence of iron minerals and oxides. These colours are preferable in the manufacturing of bricks.

## CONCLUSION

The physical, physico-chemical and geochemical characteristics of Cretaceous-Tertiary kaolins of the Douala Sub-Basin were presented. The physical and physico-chemical characteristics of studied kaolins show that the kaolins have an acidic parent rock from which feldspars and/or micas altered to form the kaolins. There is reworking and continuous weathering of the kaolins leading to low pH and whitening of some of the kaolins. The geochemical composition of the kaolins suggest that source rocks of these kaolins vary between rhyolite/granite and rhyolite/granite + basalt, which are mostly enriched in kaolinite. The geochemistry also suggests that the kaolins mainly formed in a marine environment. The moisture

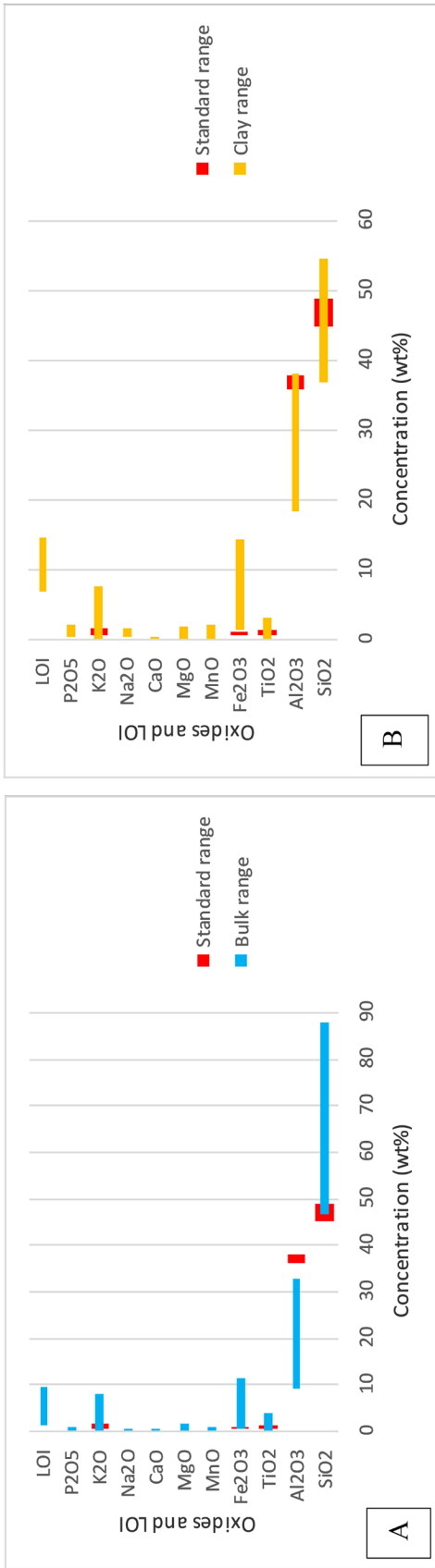


Figure 8. Oxides and LOI concentrations ranges for paper coating a) Bulk and b) Clay fraction.

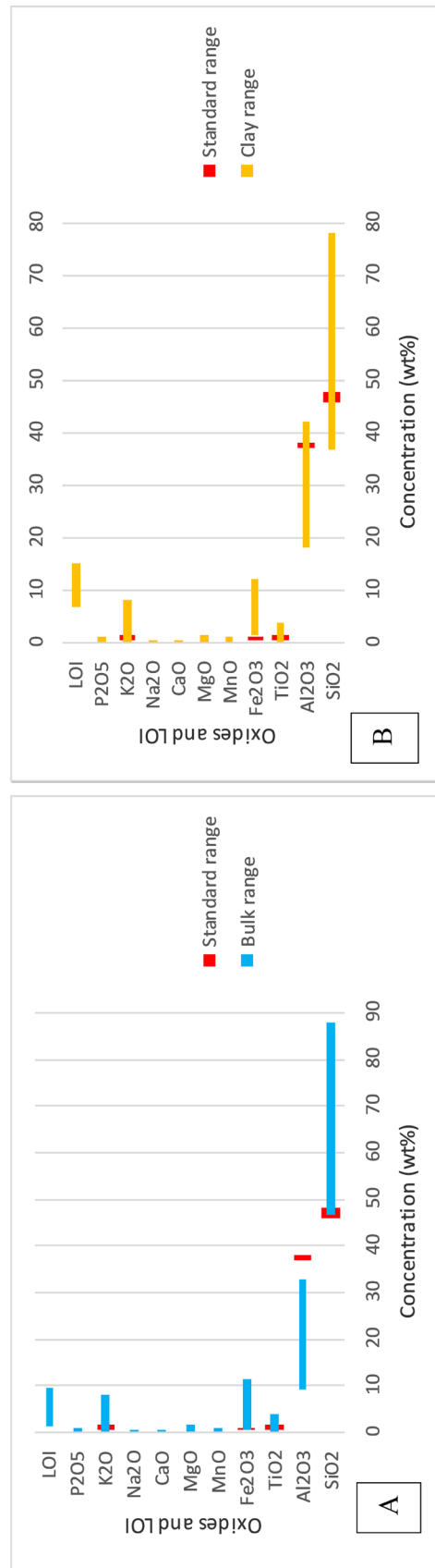


Figure 9. Oxides and LOI concentrations ranges for paper filling a) Bulk and b) Clay fraction.

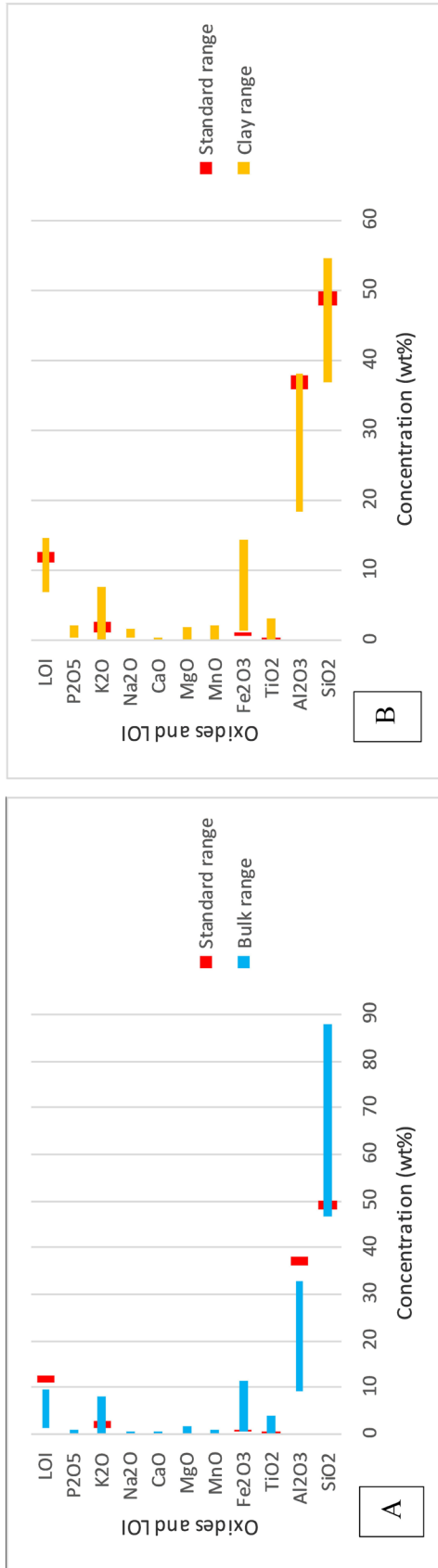


Figure 10. Oxides and LOI concentrations ranges for ceramics a) Bulk and b) Clay fraction.

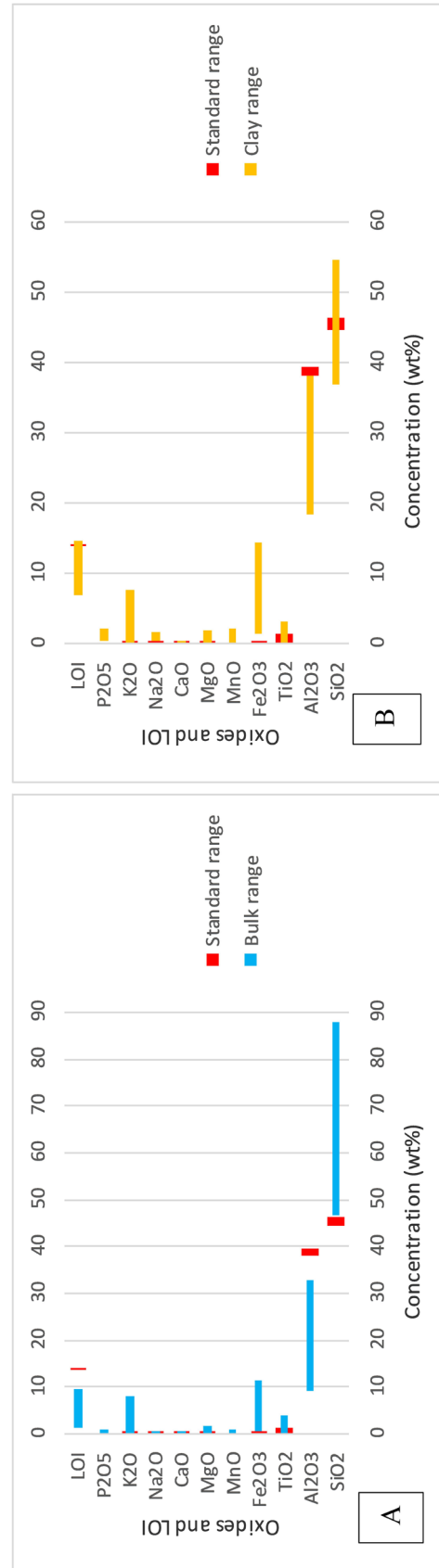


Figure 11. Oxides and LOI concentrations ranges for pharmaceuticals a) Bulk and b) Clay fraction.

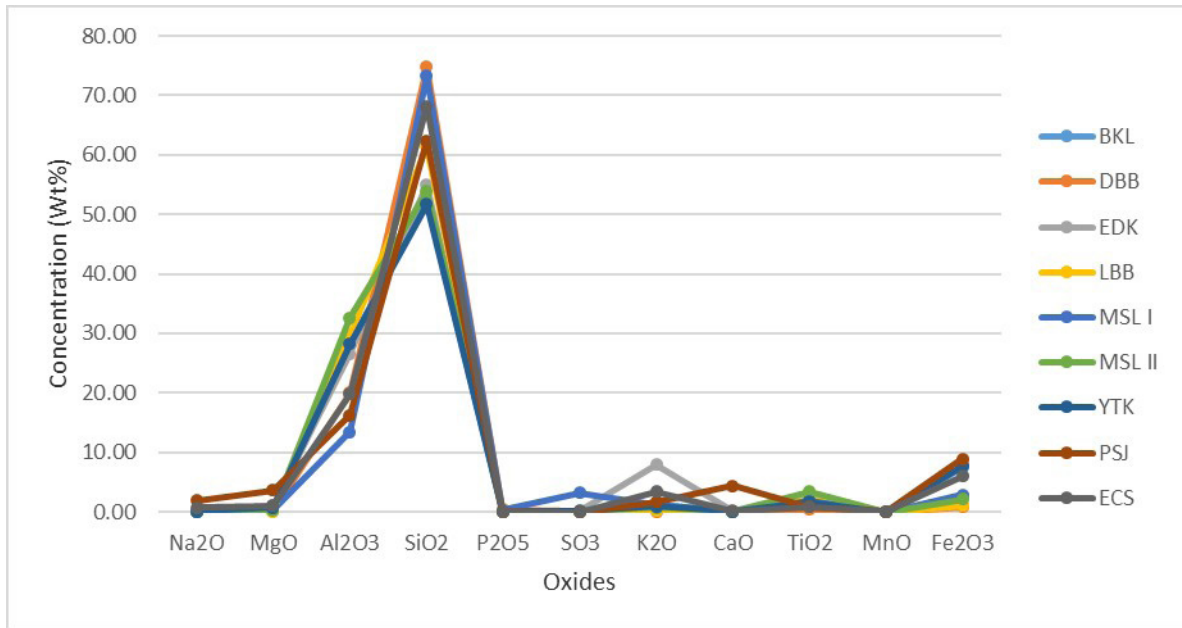


Figure 12. Means oxides concentrations of Cretaceous-Tertiary kaolins of the Douala Sub-Basin compared with values of clays used for pottery in Eastern Cape Province, South Africa (PSJ and ECS).

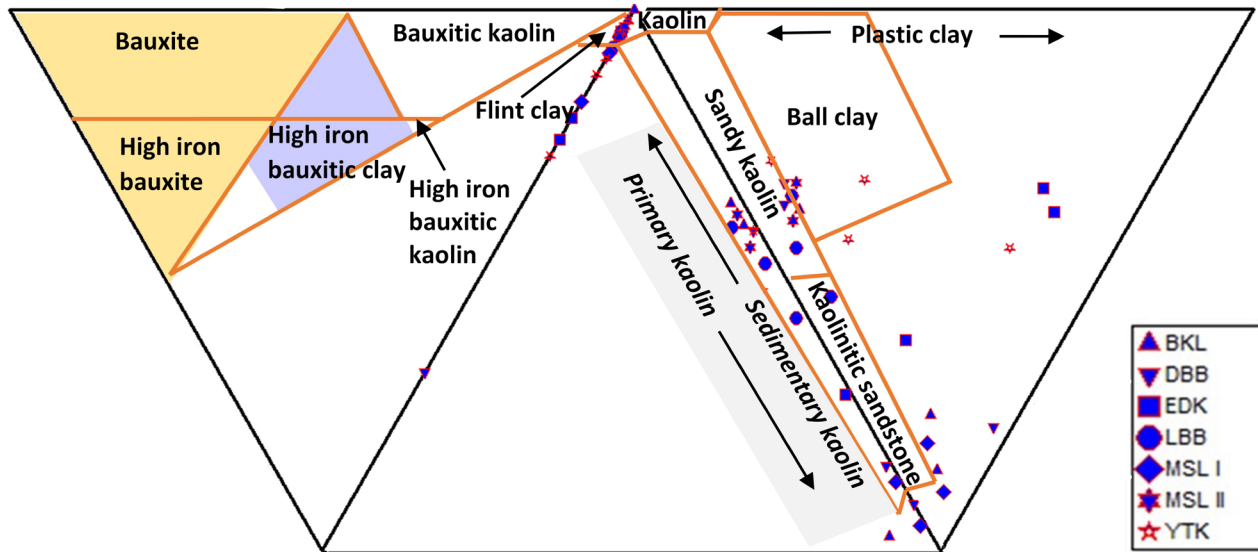


Figure 13. Ternary diagrams used for the classification of industrial kaolins showing the fields in which studied kaolins fall (developed from Pruett, 2016).

content of the kaolins makes the kaolins suitable as paint fillers and in soap production. The investigated kaolins could be used in the pharmaceutical, construction, pottery and cosmetics industries, provided suitable particle size reduction and beneficiation could be achieved to improve their overall quality.

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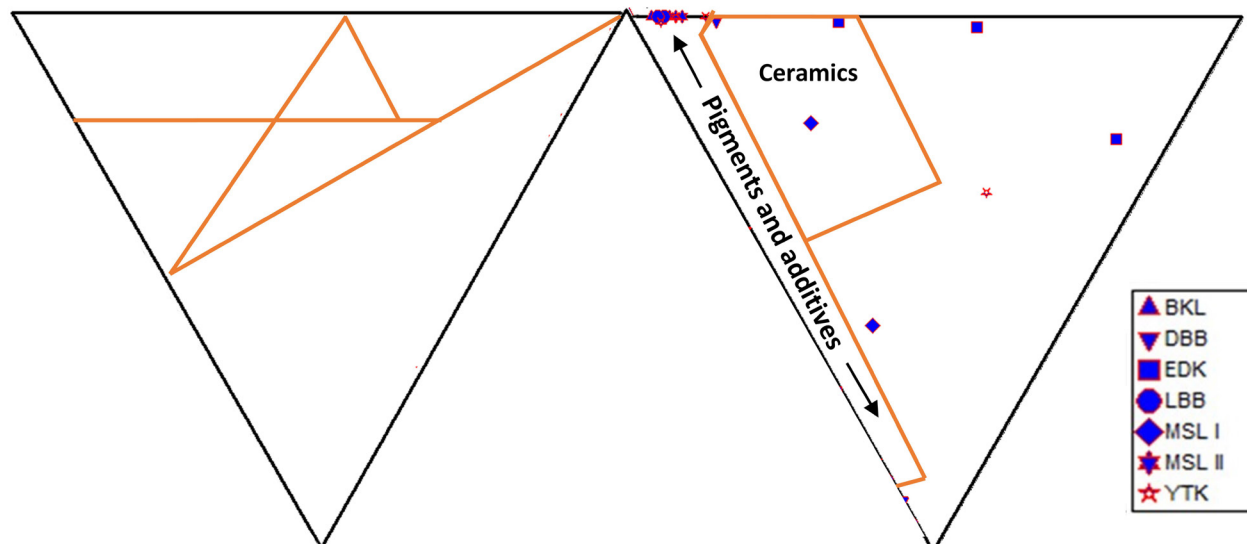


Figure 14. Ternary diagram showing potential industrial applications of clay fractions of studied kaolins (developed from Pruett, 2016).

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