Exploring Geochemical and Mineralogical Characteristics of Clay Deposits in The Karoo Basin: A Focus on The Makhanda Region and Its Surrounding Areas in The Eastern Cape, South Africa

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ABSTRACT

This research paper is based on the clay deposits of Makhanda and its surrounding environs in Eastern Cape, South Africa. They are of great importance because of their kaolinite content and its influence in providing insights into the geological history and processess that formed the Karoo Basin. The aim of this study is to provide new insights and data on the geochemical and mineralogical properties and distribution of the clays present in this part of the Karoo Basin. The sampling employed during this study encompasses all cardinal sections of Makhanda (Beaconsfield, Collingham, Cradock and Strowan deposits). The chemical and mineralogical compositions of the clays were investigated using different laboratory methods such as X-Ray Diffraction analysis (XRD), X-Ray Fluorescence (XRF), Inductively Coupled Plasma-Mass Spectrometry (ICPMS) and Rare Earth Elemental analysis (REE) to determine their provenance, weathering history and most appropriate use in the industry. Previous studies carried out on the clays were solely localized to a minute section of the Beaconsfield deposits using lithological logs on a micro scale to show some chracteristics of the northern part of the peneplain. This study, however, is focused on the internal variability and diversity among different clay deposits in Makhanda and its environs. XRD analysis shows kaolinite as the main clay mineral (11.4 wt% to 60.4 wt. %), indicating an extreme weathering of aluminium-rich source rocks. The non-clay minerals in the assemblages are quartz, rutile, pyrophyllite, muscovite, and calcite. Results of the geochemical analysis show a predominance of SiO_2 (58.76 wt% to 85.42 wt%) and Al_2O_3 (9.29 wt% to 20.05 wt%), which affects the morphology and nature of the clay deposits. The high average values of the Chemical Index of Alteration (CIA) at a weight percentage of 90.45 wt% and the Chemical Index of Weathering (CIW) of 99.19 wt% indicate an extremely intense chemical weathering in the study area. Geochemical indices plot of TiO2 versus Al_2O_3 ratios gives an insight into a felsic source and provenance. The clays are characterized by fineness, low-moderate Loss on Ignition (LOI), mineral assemblage and chemical composition, making them useable in the ceramics and refractory bricks industry. Also, the paleoenvironment reconstruction analysis indicates that the investigated clays were deposited in a continental setting.

Keywords: Clay, Kaolin, Provenance, Weathering, Paleoenvironment

1INTRODUCTION

This study sheds insights on the clay deposits from the Makhanda locality which belongs to the Karoo Basin and its environs in the Eastern Cape, South Africa. The location of the study area falls within the Grahamstown 3226 sheet (1:250000), lying between longitudes N 33° 14' 5" S and latitudes 26° 25' 29" E (Figure 1). A considerable amount of these deposits has been mined locally by the locals. A previous study by Jacob et al. (2004) shows a localized study on exclusively the clays from the Beaconsfield mine. Their study gave a brief insight on the mineralogy of the clays in the Northern part of Grahamstown (now Makhanda). There has been little comprehensive investigation on the geochemistry and mineralogy of the Makhanda clay deposits to determine its suitability in various fields of applications. In addition, questions that still need to be addressed include, What kind of provenances characterize the Collingham, Cradock and Strowan clay deposits? What paleoenvironment were they formed during the formation of Karoo Basin? What is the degree of weathering and possible industrial applications of these clay deposits?

Clay minerals are naturally occurring materials typically composed of fine-grained minerals, which tend to have a

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plastic behaviour depending on appropriate water content such that they harden when dried (Guggenheim, 1990). Previous studies indicate that clay is abundant on earth and plays a crucial role in human life and it is one of the most extensively utilized minerals with a great range of applications: economics, civil engineering, oil absorbents, iron casting, animal feeds, pottery, China clay, drilling fluids, pharmaceuticals, wastewater treatment, food preparation, and paint (Ihekweme et al., 2020; Sallau et al., 2017; Semiz & Çelik, 2020). Kaolinite is one of the major clay minerals characterized by many industrial applications. Kaolin exploitation remains a financially sustained profit-making interest in the mining industry, such that it contributes immensely to the economics of the world (Ekosse, 2010).

Kaolinitisation can be due to surface weathering, groundwater activity, or the action of hydrothermal fluids. The four polymorphs of the Kaolin group are kaolinite, nacrite, dickite and halloysite . These clay minerals are also typified by their polymorphic properties. The kaolinite mineral comprises of a triclinic crystal structure, dickite and nacrite are entirely composed of a monoclinic crystal structure while halloysite has a tubular or rolled sheet-like crystal structure. Dickite and nacrite are usually restricted to hydrothermal occurrences (Murray & Keller, 1993) but halloysite is found in hydrothermal and residual deposits and rare in kaolins of sedimentary origin (Murray, 1991, 1999).

Secondary kaolins, also known as sedimentary kaolin, are genetically sedimentary, resulting from erosion and transportation of clay-size particles, which are mineralogically altered and deposited as beds and lenses associated with other sedimentary rocks, such as in lacustrine, paludal, deltaic and lagoonal environments (Murray & Keller, 1993). One significant difference between primary and secondary kaolin deposits is that the primary kaolin's are less platy and coarser than secondary kaolin deposits. Also secondary kaolins are also much purer (mono-mineralic) than primary kaolins (Hill, 2000). The genesis of a kaolin deposit must be known because it is vital in determining its corresponding potential applications (Murray, 1991; Peter and Ajibad 2007; Ekosse and Forcheh 2007). Ekosse (2010) discovered that more than 27 non-clay mineral assemblages affect the quality of a typical kaolin in Africa. Examples of calcium-bearing minerals are aragonite, dolomite, calcite which generally affects firing behaviour properties in kaolin, iron rich minerals such as hematite, pyrite, siderite, goethite, and limonite, affects primarily the colour and finally, feldspars, mica and quartz, in turn, influences the size distribution. In addition, trace and major elements, which are characterized as immobile elements such as Ti, Th, Sc, Zr, Cr, Al, Ni, Fe and Co in conjunction with the rare earth elements, do offer reliable insights regarding the provenance of the deposits and their corresponding weathering history signatures (Adepoju, 2014).

This paper is initiated to provide more information and fill the scientific gaps about these clay deposits with emphasis on the area's geology, weathering history, provenance and mineralogical, and paleoenvironmental settings in the Karoo Basin. The new data acquired for this study includes sampling clays from the Beaconsfield deposits, Collingham, Strowan and Cradock clay deposits.

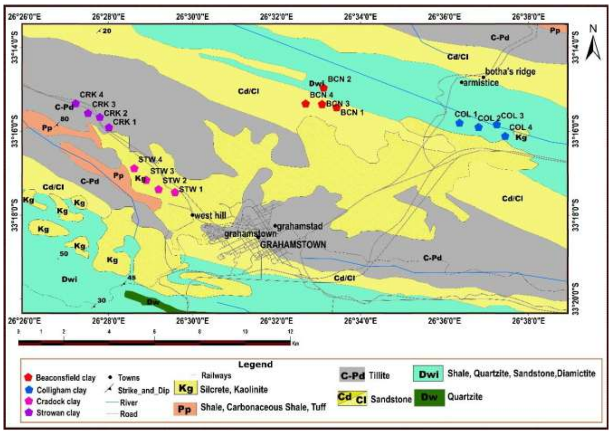

Figure 1: Simplified geological map of the area around Grahamstown showing the location of the Beaconsfield clay deposit. (Adapted from 1:250 000 scale sheet 3326 Grahamstown (now Makhanda), (Jacob *et al.,* 2004).

GEOLOGIC SETTING

The Makhanda structural geology shows that the clay deposits are solely dependent on the formation of the Grahamstown peneplain (Schmidt, 1976). Makhanda is located geographically in the Eastern cape of South Africa. The region of study (Makhanda) is characterized with rock sequences spanning from the Devonian period to the Permain-Triassic period. Two supergroups dominate geology setting in the study area: the Cape Supergroup and the Karoo Supergroup (Johnson et al., 1996) (Figure 2). This spans from rocks from the Table Mountain group overlain by the Bokkeveld group, followed by the Witteberg group, Ecca and Dwyka rocks of the Karoo supergroup. The Table Mountain group ranges from the Ordovician age to the Silurian age. According to physical evidence and previous study by Johnson et al., (1996), the lithographic rock types (Tillite and Granite) which makes up the Table Mountain Group are not seen in the study area. Hence the visible oldest rock types were evidenced to be from the Bokkeveld group. Rocks from the Bokkeveld spans from Early Devonian to Middle Devonian age.

This group is subdivided into two subgroups and they include Ceres Subgroup and the Traka subgroup. Stratigraphically in this group the Ceres Subgroup underlies the Traka Subgroup. The Ceres subgroup can be sub divided into sandstone and mud rock formations. Overlying the Bokkeveld Group are the Witteberg group sequences. This group predominantly occurs as the upper most group of the Cape super group (Smuts, 1983). It solely envelopes the entire highland in Makhanda. This can also be subdivided into four different sections geologically and they include the Weltevrede formation, Witpoort formation, Lake Mentz subgroup and the kommadagga sub group respectively (Johnson *et al.,* 1996).

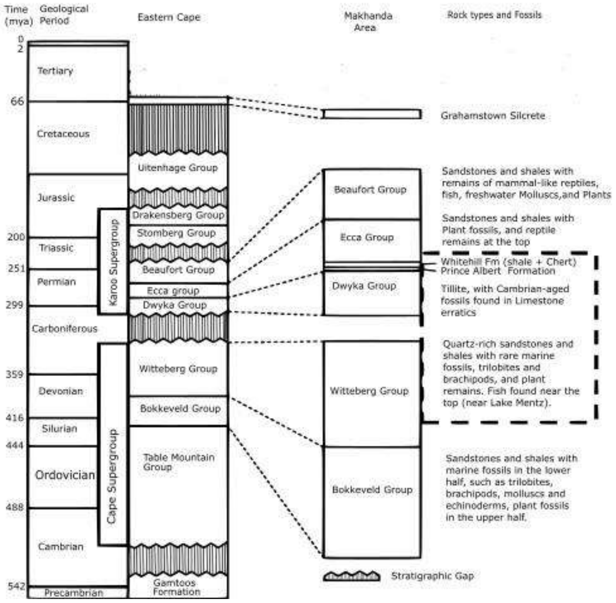

Figure 2: Simplified geological stratigraphic map of Makhanda (formally known as Grahamstown) Modified after (Büttner *et al.,* 2015)

MATERIALS AND METHODS

The study includes a well thought sampling strategy (field work) and laboratory work. The field work includes a geological mapping of the area and collection of samples for laboratory studies. Fresh, uncontaminated samples were collected from surface outcrops across the Makhanda region and at different sites. These sites were Beaconsfield (samples BCN 1 – BCN 4), Collingham mine (samples COL 1- COL 4), Cradock (CRK 1 - CRK 4) and Strowan mine (STW 1 - STW 4). The well-labelled samples packaged in cellophane bags were subjected to laboratory analysis.

X-ray diffraction analyses were carried out on 16 samples to decipher the quantitative mineralogical composition at XRD Analytical and Consulting in Pretoria, South Africa. About 150g of each sample was firstly dried, crushed gently and carefully sieved before processing. The samples were analysed using a PAnalytical X'Pert Pro powder diffractometer in θ–θ configuration with an X'Celerator detector and variable divergence and fixed receiving slits with Fe filtered Co-Kα radiation (λ=1.789Å). The corresponding relative peak intensities determined the mineralogical percentage compositions in the XRD diffractograms. However, the geochemical composition and bulk elemental analysis were performed using the Inductively Coupled Plasma-Mass Spectrophotometer (ICP-MS) and X-ray Fluorescence (XRF) laboratory methods at UIS Analytical Services in Centurion, Pretoria, South Africa. In addition, rare earth elemental (REE) analysis was performed on the investigated samples to provide insights on the provenance and paleo conditions in which the clays were deposited. A total of 8 samples were collected from the study for rare earth elemental analysis (this implies that two samples were collected to depicted each area of interest). This analysis was performed at the UIS Analytical Services in Pretoria South Africa.

RESULTS

Mineralogical Composition

The results of mineralogical composition determined by the X-ray diffraction analysis are presented in Table 1, while the diffractogram charts are shown in Figure 3. The major clay mineral in all the clay samples is kaolinite while the non-clay minerals comprise quartz, rutile, haematite, pyrophyllite, and muscovite. In Cradock clays, the average content of kaolinite mineral is about 44wt%. Muscovite has an average of 1.98wt% (Table 1) ranging from zero to 3.70wt% whereas, calcite concentrations in the Cradock clays are characterized by a minimum limit of zero (0) to an upper concentration limit of 0.10wt%. The average concentrations of the calcite and smectite minerals are about 0.03wt% and 0.78wt%, respectively. It is generally noted that the high silica content, shown by the samples analysed with significantly low alumina, highly indicates kaolinitic features. Also, there were no significant traces of rutile and haematite in the Cradock samples, as seen in the Collingham samples.

Quartz is generally high in the Collingham clays (COL 1, COL 2, COL 3 and COL 4), with an average composition of 30.55wt% ranging from 23.90wt% to 36.70wt% (Table 1), whilst the kaolinite mineral abundance across the COL clays averages at 16.70 with a lower limit of 11.40wt% and an upper limit of 26.80wt%. The average muscovite mineral abundance is 18.88wt% across the clays, with a minimum value of 12.0wt% and a maximum of 35.80wt%. Following this trend, the average concentrations of calcite, pyrophyllite and hematite were 7.25wt%, 23.20wt% and 2.90wt% respectively (Table 1).

Furthermore, kaolinite also has an average concentration of 18.43wt% in the Strowan clays, with lower and upper concentrations limit values of zero (0) and 27.60wt%, respectively. The average mineral composition of quartz in the Strowan clays is 73.23wt%, with concentrations ranging from 63.30wt% to 99.40wt%. Muscovite concentrations in the Strowan clays ranged from 0.50wt% to 18.20wt%, with an average composition of 8.38wt% (Table 1).

Table 1: Average mineralogical compositions of the clays in the Makhanda area.

Mineral	Beaconsfield Clays			Collingham Clays			Cradock Clays			Strowan Clays		
	Mean	Lower Limit	Upper limit	Mean	Lower Limit	Upper limit	Mean	Lower limit	Upper limit	Mean	Lower Limit	Upper Limit
Quartz	48.4	43.8	51.7	30.6	23.9	36.7	53.0	35.9	99.5	73.2	63.3	99.4
Kaolinite	31.6	17.1	39.7	16.7	11.4	26.8	44.3	nd	60.4	18.4	nd	27.6
Muscovite	19.0	11.9	27.3	18.9	12.0	35.8	2.0	nd	3.7	8.4	0.5	18.2
Calcite	nd	nd	nd	7.3	nd	29.0	nd	nd	0.1	nd	nd	nd
Smectite	1.0	nd	3.9	nd	nd	nd	0.8	nd	3.1	nd	nd	nd
Rutile	nd	nd	nd	nd	nd	0.8	nd	nd	nd	nd	nd	nd
Pyrophyllite	nd	nd	nd	23.2	nd	32.0	nd	nd	nd	nd	nd	nd
Hematite	nd	nd	nd	2.9	nd	6.4	nd	nd	nd	nd	nd	nd

*nd= non-detected

In the Beaconsfield, BCN 4 shows a high concentration of quartz with an average value of 51.7wt% coupled with very low kaolinite (17.1wt%) composition compared with BCN 1, BCN 2 and BCN 3. The BCN 2 sample displayed a higher muscovite concentration, totalling 27.3wt%, with a compositional presence of smectite of 3.9wt%. Compositionally, Beaconsfield clays have an average quartz composition of 48.4wt% ranging from 43.80wt% to 51.50wt%; whilst the average kaolinite presence across the Beaconsfield clays is about 31.6wt% with a lower compositional limit of 17.10wt% and a maximum value of 39.70wt%. In addition, the average concentrated value of muscovite across the Beaconsfield clays is 19.0wt%, with a range of 11.90wt% to 27.30wt%. However, in Table 1, the smectite average value is 0.96wt%, with its compositional range from zero (0) to 3.90wt%.

Chemical Composition

The chemical composition gives insights into the provenance origin hence the need to determine the composition of the samples under investigation. The chemical analysis results also provide information on the suitability of the clay deposits studied for industrial applications and uses. The trace and major elemental concentrations are presented in Tables 2 and 3.

Major Elements

Results from the major elemental composition analysis showed that Makhanda's deposits are dominated by SiO_2 (58.76 wt% to 85.42 wt% with an average of 69.55 wt%) presented in Table 2. The Al_2O_3 concentration ranged from 9.29 wt% to 20.05 wt% with an average value of 15.75 wt%, and an average concentration of Fe_2O_3 4.29 wt% and ranged from 0.01 wt% to 13.5 wt%. The major oxides from this study compare relatively with the standard Post Archean Australian Shales (PAAS), North American Shale Composite (NASC) and Upper Continental Crust (UCC) (Taylor & McLennan, 1995). Samples from the Collingham site showed oxide average compositions of SiO_2 and Al_2O_3 with weight concentrations of 58.76wt% and 17.96wt% respectively while clay deposits from the Cradock site shows an average wight concentration of 61.16wt% and 20.05wt% respectively (Table 2), which are like the standard compositional oxides of pure kaolinite. Additionally, the results are also supported by the SiO2/Al2O3 ratio >3.0, which is higher than the normal value generally found in pure kaolinite as 1.18. The result indicates the presence of other silicate phases besides kaolinite. This however implies that the pure kaolinite was replaced by quartz-bearing kaolinite.

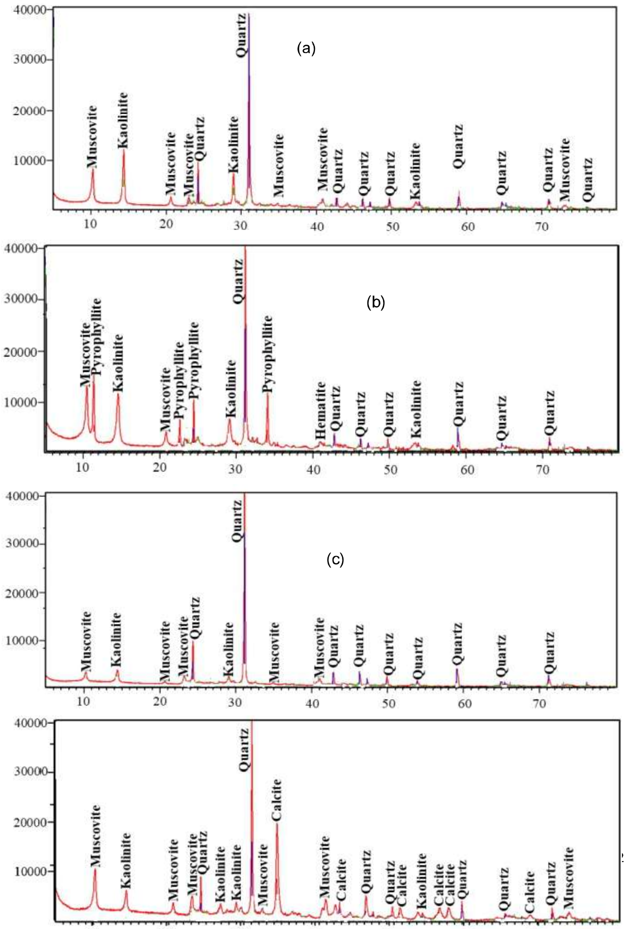

Figure 3a – 3d: Diffractogram charts showing the mineralogical composition of the clay deposits in the Makhanda area. (a) = BCN 1, (b) = COL 1, (c) = STW 3, (d) = CRK 1.

The Cradock samples (CRK 1 – CRK 4) are distinctively characterized with the highest kaolinite content, and they show the highest Al_2O_3 concentration and Loss on Ignition (LOI) of about 20.05wt% and 10.85wt%, respectively. According to Ekosse, (2010), the Loss on the ignition and Al_2O_3 parameters increase proportionally as the kaolinization process progresses, and the formation of hydrated clay minerals like kaolinite occurs. Also, the silica -aluminium oxide ratio ranged from 3.05 to 4.64 wt%/wt% ; this indicates the presence of siliceous sands in Beaconsfield, Strowan, Collingham and Cradock clay deposits. The quartz mineral could occur as crystalline disseminated fine particles in kaolinite or even deposited with tiny clay minerals which in turn makes the composition of quartz greater than 50% (Bain & Smith, 1994; Wilson, 1990). Quartz is the main constituent of the clay samples. The STW, BCN and CRK are characterized by low Fe_2O_3 concentration. This could result from the lack of iron oxide minerals like haematite in the clay samples. However, the case is different from the Collingham (COL) samples. The COL samples are characterized by about 13.5 wt% concentration of Fe_2O_3, which explains the distinct red coloration that set this deposits apart from other corresponding sites.

Low MgO, K_2O, CaO and Na_2O concentrations also characterize the Makhanda clay deposits. This major elemental composition suggests that the clay deposits in the study area have swelling and non-expandable properties and low feldspar content (Millot, 2013). Titanium oxide values ranged from 0.38 wt% to 0.78 wt% with an total average concentration of 0.58 wt%. The highest concentration of TiO_2 of 0.7 wt% was observed in the Collingham clay and 0.67wt for the Beaconsfield clay and this could be as a result of TiO2 being concentrated in the fine kaolinite samples that is supported by Bedassa *et al.,* 2019; Bundy et al., 1966. The occurrence of TiO2 concentrations in the clay samples, as observed in the analysed samples, suggests the incorporation of titanium with detrital minerals such as rutile with kaolinite. A similar trend of Rutile occurrence was also observed in the Collingham samples.

The Loss on Ignition (LOI) reflects the structurally bound water molecules which are present within the crystal lattice structure observed within the clay deposists. The Makhanda clay deposits (BCN, COL, STW, CRK) show an average LOI weight percentage of 6.30 wt%.

Trace Elements

The abundance of the trace elements such as Cu, Pb, Zn, Zr, Ni, Co, Ba, V, Sc, Rb, Y, Cr, and Mn (Table 3) when in comparison with standard values of the UCC (Upper Continental Crust), NASC (North American Shale Composite), and PAAS (Post Archean Australian Shale), show a significantly wide variation as observed in Table 3. According to Nesbitt and Young (1989), the abundance and distribution of trace elements in clay deposits are highly dependent on the source rock's corresponding nature and the weathering process. In the investigated clay deposits, elements such as V, Co, Zn, and Ni are highly depleted when compared with the industrial standard values of UCC, PAAS and NASC, whilst elements like Ba are enriched with about an average of 336.76ppm and similar enrichment trends are also observed in Rb and Zr. This can be attributed to the large occurrence of potassium feldspar at the source and the stability of feldspar (Adepoju, 2014).

Rare Earth Elements (REEs)

Rare earth elemental (REE) analysis is a major tool

Table 2: Average percentage composition of major elements in Makhanda Clays and comparison with some industrial values.

Samples					Average			
Oxides	BCN	STW	COL	CRK	UCC	NASC	PAAS	Makhanda
SiO_2	72.9	85.4	58.8	61.2	66.0	64.8	62.8	69.6
Al_2O_3	15.7	9.3	18.0	20.1	15.2	16.9	18.9	15.8
Fe_2O_3	2.57	nd	13.5	1.1	5.0	5.7	7.2	4.3
CaO	0.1	nd	nd	nd	4.2	3.6	1.3	nd
MgO	0.5	0.1	0.2	0.3	2.2	2.7	2.2	0.3
Na_2O	nd	0.1	0.1	0.1	3.9	1.1	3.7	0.1
K_2O	2.2	0.9	1.5	1.1	3.4	4.0	3.4	1.4
MnO	nd	nd	nd	nd	0.1	0.1	0.1	nd
TiO_2	0.7	0.4	0.7	0.6	0.5	0.7	1.0	0.6
LOI	4.9	3.0	6.4	10.9	nd	nd	nd	6.3
SiO_2/ Fe_2O_3	28.4	85420	4.4	57.2	13.2	11.5	8.7	2158.0
$CaO + Na_2O$	0.1	0.1	0.2	0.1	8.1	4.8	2.5	0.1
$CaO + Na_2O + K_2O$	2.3	1.1	1.6	1.3	11.5	8.7	6.2	1.6
$Fe_2O_3 + MgO$	3.1	0.1	13.7	1.3	7.2	8.3	9.4	4.6
CIA	89.5	86.6	91.8	93.9	56.9	65.9	75.3	90.5
CIW	99.6	98.6	99.2	99.4	65.2	78.0	88.3	99.2
SiO_2/Al_2O_3	4.6	9.2	3.3	3.1	4.34	3.8	3.3	4.4

*nd= non-detected

BCN - Beaconsfield Clay, COL - Collingham Clay, STW - Strowan Clays, CRK - Cradock Clay, UCC - Upper Continent Crust, NASC- North American Shale Composite and PAAS -Post Archean Australian Shales (Taylor & McLennan, 1995) (Taylor & McLennan, 1985b).

Table 3: Trace elements concentration (ppm) in Makhanda clays and comparison with some Industrial standard values.

Trace Elements	BCN	STW	COL	CRK	Average		
					UCC	NASC	PAAS
Cu	33.3	23.1	22.7	70.4	6.0	52.0	50.0
Pb	12.1	20.4	83.5	20.4	nd	nd	20.0
Zn	114.2	9.6	21.5	6.6	71.0	471.0	85.0
Zr	379.3	263.8	157.8	446.5	193.0	200.0	210.0
Ni	26.5	7.4	36.0	8.4	20.0	58.0	55.0
Co	0.6	4.8	0.6	10.5	nd	nd	23.0
V	85.6	93.3	130.2	166.0	nd	407.0	150.0
Ba	399.3	226.4	466.5	255.0	628.0	636.0	650.0
Sc	14.6	14.2	16.1	10.4	nd	nd	nd
Y	34.3	10.2	36.0	42.6	21.0	nd	nd
Rb	161.4	92.7	125.3	164.1	82.0	nd	160.0
Cr	876.9	1461.5	876.9	876.9	nd	nd	nd
Mn	129.1	129.1	129.1	129.1	nd	nd	nd
Th	19.0	14.7	22.6	38.7	nd	nd	14.6
Th/Co	31.2	3.0	40.4	3.7	nd	nd	nd
Th/Cr	nd	nd	nd	nd	nd	nd	nd
Cr/Th	46.2	99.6	38.8	22.7	nd	nd	nd

*nd= non-detected

BCN - Beaconsfield Clay, COL - Collingham Clay, STW - Strowan Clays, CRK - Cradock Clay , UCC - Upper Continent Crust, NASC- North American Shale Composite and PAAS -Post Archean Australian Shales (Taylor & McLennan, 1995) (Taylor & McLennan, 1985b) employed in paleoclimate and paleoenvironmental reconstruction. In addition, its significance helps gain insights into the origin and history of geologic materials as they act as geochemical tracers. Understanding the rare earth elemental abundance in the study area is crucial for adequate resource exploration, environmental monitoring and insights to the composition of the rocks and sediments present in the study area.

In this section the conventional spider diagrams were replaced with histograms and presented to show the abundance of the REEs as it relates to its enrichment and depletion in the studied Makhanda clay deposits to adequately quantify and interpret the presence and absence of the REEs, they were normalized relative to chondrite values (Taylor & McLennan, 1985a). After the rare earth elemental analysis was conducted, results showed the presence of elements such as La, Ce, Nd, Ho, Gd, Tb, Dy, Tm, Lu, Sm, Er, Yb.

Beaconsfield Deposits

The REE concentrations present in the Beaconsfield clay deposits which were normalized to chondrite values are shown in Figure 4. The Beaconsfield deposits showed enrichment of Eu, Tb, Ho, Tm and Lu and depletion in elements such as La, Ce, Nd, Sm, Gd, Dy, Er and Yb. A positive Eu anomaly was observed in the BCN 1 (1.20) and BCN 2 (1.15) respectively (Figure 4). A high concentration of Tm is also seen in the Beaconsfield clays and this trend of high Tm concentration of about 2.78 is consistent in the Cradock, Strowan and Collingham deposits in Makhanda.

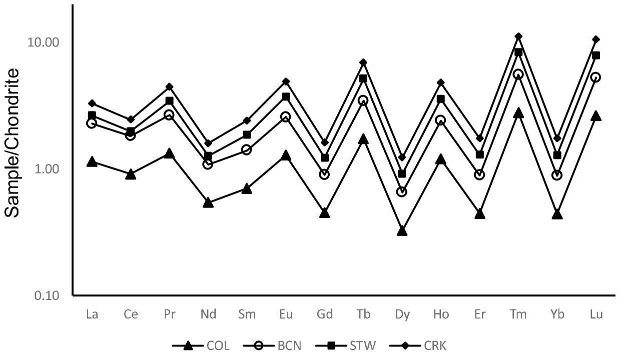

Figure 4: Normalized concentrations of rare earth elements to Chondrite values in Beaconsfield (BCN), Collingham (COL), Strowan (STW) and Cradock (CRK) samples.

Collingham Deposits

Unlike the corresponding study sites, the Collingham clays shows a different rare earth element compositional trend. The deposits in Collingham are characterized with an enrichment of La with COL 1 having an estimated value of 1.19 and COL 2 averaging at 1.09. The La showed a moderate to large depletion in other deposits except the Collingham clays (Figure 4). A positive Eu anomaly is also observed, and very low Ce depletion is shown within the Collingham clay deposits. In comparison with other clay deposits, the resulting Pr composition shows an interesting low to moderate enrichment, which is quite different in other clay deposit under investigation. In the study area, the Collingham clays are characterized with the lowest Ce depletion in comparison with corresponding study sites of interest hence peaking at 0.88 in COL 1 and 0.98 in COL 2 respectively. In addition, the Ce concentrations in the Collingham deposits are very similar to the Chondrite standard values (Taylor & McLennan, 1985a).

Strowan Clay deposits

In the Strowan clays, the depletion of the La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Yb elements ranges from low to high reduction rate. On the other hand, the Europium (Eu), Tb, Ho, Tm and Lu seems to be well enriched in these deposits. A positive Europium (Eu) anomaly is observed in STW 1 (with 1.15) and STW 2 (with 1.16) respectively (Figure 4). These REE values were normalized to Chondrite standard values. Also observed is the depletion of Pr in the Strowan clay deposits in STW 1 (0.77) and STW 2 (0.80) unlike its enrichment in the Beaconsfield, Cradock and Collingham clays. In the study area, the Strowan clays are characterized with the highest Ce depletion in comparison with corresponding study sites of interest, hence peaking at 0.15 in STW 1 and 0.17 in STW 2 respectively. However, the La concentrations in the Strowan clay deposits which includes STW 1 (0.34) and STW 2 (0.38) are very similar to Chondrite Standard La values (Taylor 1985).

Cradock deposits

The Light Rare earth elements present in the Cradock clay deposits are characterized with a high depletion. This includes La, Ce, Nd and Sm with values ranging from 0.25 to 0.90. Europium was enriched in CRK 1 (1.15) and CRK 2 (1.23) hence an occurrence of a positive anomaly in the study area. However, in the Cradock clays, the most abundant REE is Tm with normalized chondrite values peaking at 2.78 in sampled clays within the Cradock sites (Figure 4). Also observed is the depletion of other REE elements such as Dy, Gd, Er, and Yb with values ranging from the lowest depletion in Dy concentration of 0.29 in CRK 1 and the highest depletion rate in Er and Yb with chondrite values of 0.49 respectively in the Cradock clays.

The REE normalized data analysis results for the different geological sites (Beaconsfield (BCN 1-4), Strowan (STW 1-4), Cradock (CRK 1-4) and Collingham (COL 1-4)) are displayed in Table 4 below. The highest elemental concentration of the rare earth elements Ce and La in the studied clay deposits from the Cradock samples (CRK) was observed to have occurred amongst the LREE (Light Rare Earth Elements).

Table 4: REE Elemental Normalized Concentrations (ppm) of Makhanda Clay Deposits.

	CRK 1	CRK 2	BCN 1	BCN 2	STW 1	STW 2	COL 1	COL 2
La	0.8	0.5	0.6	0.5	0.3	0.4	1.2	1.1
Ce	0.6	0.4	0.5	0.4	0.2	0.2	0.9	0.9
Pr	1.1	0.9	1.0	0.9	0.8	0.8	1.4	1.3
Nd	0.4	0.3	0.3	0.3	0.2	0.2	0.6	0.5
Sm	0.6	0.5	0.5	0.5	0.5	0.5	0.7	0.7
Eu	1.2	1.2	1.2	1.2	1.2	1.2	1.3	1.3
Gd	0.4	0.4	0.4	0.4	0.3	0.3	0.5	0.5
Tb	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
Dy	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Ho	1.3	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Er	0.5	0.4	0.4	0.4	0.4	0.4	0.5	0.4
Tm	2.8	2.8	2.8	2.8	2.8	2.8	2.8	2.8
Yb	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Lu	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6

Discussion

Paleoenvironment and Provenance

The chemical and mineralogical characteristics of clay deposits highly depend on the environment in which they are deposited (Keller, 1970; A. Singer & Stoffers, 1980). The mineralogical composition of the Makhanda clays (BCN, STW, COL, CRK) shows a positive correlation with the composition of continental deposits (Figure 3a-3d). This is also observed with the Akerebiata clays in Ilorin Nigeria, where the whitish but slightly coloured clay deposits, to a large extent, were deposited in a continental environment according to Adepoju, (2014) and similar occurrence in the Southern Bida Basin clay deposits in Nigeria (Omali *et al.,* 2019). These deposits comprise of 80% to 100% kaolinite, with quartz as the main impurity mineral. However, the presence and abundance of the kaolinite mineral in the Beaconsfield samples (BCN 1-4), Collingham Samples (COL 1-4), Strowan Samples (STW 1-4) and Cradock samples (CRK 1-4) solely suggest an intense and extreme weathering of aluminium rich parent rocks in the study area. A high amount of kaolinite mineral is a typical marker for clay deposits in the continental environment.

Provenance Indicators

Rare earth elements (REE) and Trace elements, when used in confluence elemental ratios (Table 5), they act as vital indicators of the geologic setting, environment and tectonic processes that played a role in the deposition of the sediments under investigation. The high concentration of the LREE in the Collingham clay deposits (COL 1 – COL 2) and Cradock clay deposits (CRK 1 – CRK 2) indicates a high influx of terrigenous sediments. However, the Low to moderate REE concentrations in the Beaconsfield and Strowan sediments are due to the quartz dilution in the study area (Cullers, 1994, 2000; Wronkiewicz & Condie, 1990). Elemental ratios (Table 5) such as the La/Co, Th/Cr, Cr/Th, Th/Co are often employed as markers indicative of the sediments provenance (Cullers, 2000; Wronkiewicz & Condie, 1990)

Table 5: Elemental ratios for the different sampled sites of the study area compared to felsic rocks and mafic rocks

Elemental Ratio	Present Study				** Range of Elements		UCC*	PAAS*
	BCN	STW	COL	CRK	Felsic rocks	Mafic rocks		
Th/Co	31.2	3.0	40.4	3.7	0.7 - 19.4	0 - 1.4	0.6	0.6
Th/Cr	nd	nd	nd	nd	0.1 - 2.7	0 - 0.9	0.1	0.1
La/Co	40.8	6.5	32.6	5.3	1.8 – 13.8	0.1 – 0.4	nd	nd
Cr/Th	46.2	99.6	38.8	22.7	4.0 – 15.0	25.0 -500.0	7.8	7.5

**(Cullers, 1994, 2000), **(Cullers & Podkovyrov, 2000), *(Taylor & McLennan, 1985a)
*nd not detected
BCN - Beaconsfield Clays, COL - Collingham Clays, STW - Strowan Clays, CRK - Cradock Clays
UCC - Upper Continent Crust,
NASC- North American Shale Composite,
PAAS -Post Archean Australian Shales

The studied samples were characterized with Th/Co ratios varying from 3.0 to 40.4 across the study area. This ratio points to the fact that the Strowan (STW) and Cradock (CRK) originated from a felsic source with a Th/Co ratio of 3.3 and 3.7 respectively. Also observed were the La/Co ratios of both the Strowan mine and Cradock deposits. They were characterized with ratios significantly from felsic origin (6.5 and 5.3 respectively). Also, the BCN and COL samples shows a Th/Co and La/Co and Th/Cr ratio which was beyond the minimum and maximum reported for felsic and mafic rocks (Table 5).

Weathering Effect

The chemical composition observed during the different laboratory analyses can be employed to gain insights into other parameters and properties regarding the investigated deposits. This implies that they can be used as weathering indicators. In addition, to determining the extent of weathering, the chemical composition can also be used to define and determine other properties such as high kaolinite content, depletion of other mobile elements, insights on the high value of the Chemical index of alteration (CIA), and enrichment of chemically immobile elements such as Zr, TiO_2, Al_2O_3 and Scandium (Sc). These different parameters suggest that the primary source rock(s) must have been subjected to a relatively intense form of chemical weathering. Chemical index alteration (CIA) values of the investigated Makhanda clays ranged from 86.61 wt% to 93.92 wt%. According to (Depetris & Probst, 1998), that CIA values ranging from about 45 wt% to 55 wt% indicate a lack of weathering. Also, (Nesbitt & Young, 1989) proposed a CIA value of nearly a 100 wt% for a typical kaolinite deposit, whilst (Nyakairu & Koeberl, 2001) studied clays with CIA values of 87 wt% to 96 wt%. However, since the chemical index values of the analysed clay samples from the Beaconsfield (BCN), Strowan (STW), Cradock (CRK), and Collingham sites are greater than 80 wt%, It is imperative to state that the Makhanda clay deposits reflect the dominance of clay minerals and a high degree of chemical weathering. The Cradock (CRK) clay deposits display a high kaolinite content of an average concentration of 44.25 wt% with low feldspar compared with other site samples; hence, the CRK samples are characterized with the highest chemical index of alteration (CIA).

Also, the high mean value of the chemical index of weathering (CIW) for the studied samples is 99.19 wt% which is exceptionally high. This value surpasses the standard CIA values for UCC, PAAS and NASC; hence, it suggests an intense weathering of the source rock (Table 2).

In this study, ternary diagrams (A C N K diagram (Figure 5) was employed to determine weathering trends (Nesbitt et al., 1996; Nesbitt & Young, 1989). This ternary diagram shows the different variations of the concentration of Aluminium oxide (Al_2O_3), Calcium oxide (CaO), Na_2O and potassium oxide K_2O. The Makhanda clays plotted generously in the highest Al_2O_3 region, the kaolinite boundary section. This observation from the ternary triangular plot, however, indicates the presence of an active intense weathering in the study area (Figure 5).

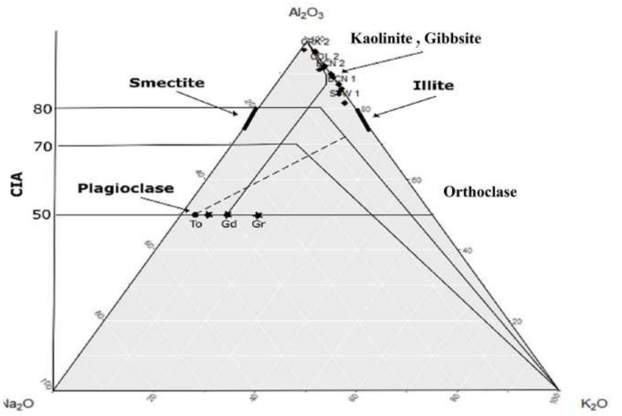

Figure 5: A C N K plot and CIA showing the weathering trend in the study area (BCN, STW, CRK, COL). (Where BCN is Beaconsfield, STW is Strowan, CRK is Cradock and COL is Collingham) (Nesbitt *et al.,* 1996).

Provenance

According to Ekosse (2001), the origin or provenance of a deposit can be determined by evaluating the ratio concentration of Aluminium oxide and Titanium oxide (TiO_2). This geochemical binary plot was used in a neighbouring basin to decipher the provenance of certain (Bukalo *et al.,* 2018) clay deposits in the Doula basin; Cameroon, West Africa. The classification for these plots determines if the sediments provenance spans from a basaltic origin or a basalt rhyolite/granite, rhyolite/granite basalt and finally a rhyolite/granite origin. The geochemical indices used in this plot are predominantly stable chemical immobile elements. Using a binary plot of TiO_2 versus Al_2O_3, the plot shows that the investigated deposits were sourced predominantly from a Rhyolite granitic origin (Figure 6).

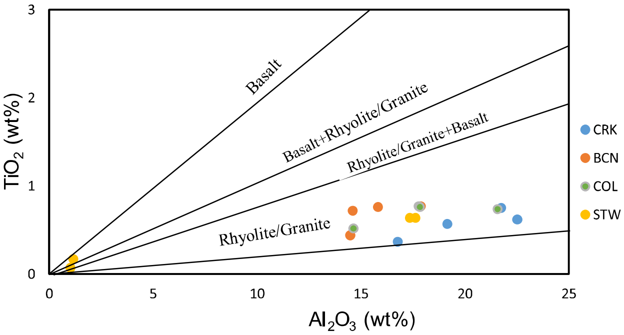

Figure 6: TiO_2 - Al_2O_3 plots of Beaconsfield (BCN), Cradock (CRK), Strowan (STW) and Collingham (COL) clay deposits (modified after Ekosse (2001).

Rare earth elements such as La, Nd, Ce, Sc, Th, Ti, Y are instrumental to deciphering tectonic discrimination and provenance. This is possible because of their stable property during sedimentary processes. They are characterized by low mobility hence information which they carry about the parent materials are not easily leached away(Cox *et al.,* 1995; Cullers, 1995).

Triangular plots such as plots proposed by (Bhatia & Crook, 1986) was used to show the tectonic settings accompanying the deposition of the clay deposits of Makhanda. The investigated deposits were plotted on the La, Th, Sc ternary diagram to depict and give insight to their deposition (Figure 7). The La, Th, Sc ternary diagram largely depicts that the clay deposits in the study area were deposited along the active continental margin and passive margin. While clay deposits from the Strowan site and Collingham predominantly plot in the CIA (continental island arc) fields. Few samples from the Strowan mine falls in the ocean island arc (OIA).

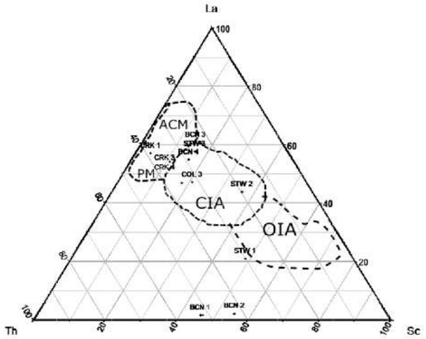

Figure 7: La. Th. Sc, Ternary diagram using rare earth elements to discriminate depositional environments associated with the Makhanda clays (ACM - Active continental margin, PM - passive margin, CIA - Continental Island arc, OIA - Oceanic island arc) (López *et al.,* 2005) (Descourvieres *et al.,* 2011) .

Table 6: Composition of major Elements of the Makhanda clays and composition of some industrial standard values.

Oxides	BCN	STW	COL	CRK	References							
					A	B	C	D	E	F	G	H
SiO_2	72.9	85.4	58.8	61.7	47.8	47.7	48.0	45.3-47.9	67.5	51.0-70.0	47.8	49.9
Al_2O_3	15.7	9.3	18.0	20.1	37.0	36.0	37.0	38.4-39.9	26.5	25.0-44.0	38.1	37.7
Fe_2O_3	2.6	nd	13.5	1.1	0.6	0.8	0.6	13.4-13.8	0.5-1.2	0.5-2.4	0.3	0.9
CaO	0.1	nd	nd	nd	0.4	0.1	0.1	0-0.3	0.2-0.3	0.1-0.2	0.4	0.3
MgO	0.5	0.1	0.2	0.3	0.2	0.3	0.3	0.2-0.3	0.1-0.2	0.2-0.7	nd	0.1
Na_2O	nd	0.1	0.1	0.1	0.1	0.1	0.1	0.2-0.4	0.2-1.5	0.8-3.5	0.27	0.2
K_2O	2.2	0.9	1.5	1.1	1.1	2.1	1.6	1.1-0.4	1.10-3.1	nd	0.4	1.6
TiO_2	0.7	0.4	0.7	0.6	nd	0.1	nd	0.1-1.0	0.1-1.2	1.0-2.8	0.5	0.1
LIO	4.9	3.0	6.4	10.9	13.1	13.1	12.4	12.1	nd	13.1	13.5	12.4

*nd- not detected

(A,B & C) (Odo *et al.,* 2009), (D) Paints, (Payne & Myers, 1961), (E) (F. Singer & Singer, 1971) Ceramics, (F) Refractory Bricks (Parker, 1967), (G) Fertilizer, (NAFCON, 1985), (H) Agriculture (J. M. Huber, 1985)

BCN – Beaconsfield Clay, COL - Collingham Clay, STW - Strowan Clays, CRK - Cradock Clay

Resource Industrial Potential

To adequately define the industrial potential of clays, the mineralogical and chemical composition need to be employed in conjunction with the grain size and physical property. One major parameter that makes kaolin clay viable and important economically is its fine particle size (Bristow, 1987)). It serves as a major raw material in manufacturing and producing ceramics, bricks, fillers, and electrical insulators. Comparing the chemical constituents and composition of the investigated clay deposits with the standard industrial specifications (Table 6), the Collingham and Cradock clay deposits show a consistent value for use in the ceramics and bricks industry with little beneficiation to reduce the iron content (Parker, 1976). With further beneficiation to reduce the silica content, these deposits can also be employed to produce fertilizer and other agricultural purposes.

CONCLUSION

The Makhanda clays from the Karoo Basin are dominated by kaolinite. However, there is a minute significant amount of haematite in the Collingham clay deposits, which explains their predominant red colouration. The elemental enrichments of the clay deposits with chemically immobile major elements and high chemical index of alteration (CIA) values suggest an intense chemical weathering in the study area.

The major element compositions indicate that the investigated clay deposits are from a felsic provenance. Also, the absence of swelling clays, expandable minerals, and moderate LOI shows their use in the ceramic and refractory brick industry. The geochemical and paleoenvironment indicators conclude that the investigated clays were deposited in a continental environment.

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