Mineralogy and geochemistry of clay fractions in soils developed from different parent rocks in Limpopo Province, South Africa

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ARTICLE INFO

Keywords: Soil kaolin Mineralogy Geochemistry Crystallinity Risk assessment

ABSTRACT

This study investigates the mineralogical and geochemical characteristics of clay fractions in soils developed from different parent rocks in Limpopo Province, South Africa using the X-ray diffraction (XRD), X-ray Fluorescence (XRF) Spectrometry, Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS), Fourier Transform Infrared (FTIR) Spectrophotometry, Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA-DSC) analytical techniques. Health risk associated with the presence of some trace elements was also investigated. The results revealed that the clay fractions had kaolinite as the dominant clay component occurring with other weatherable minerals. The crystallinity based on FTIR for the soil kaolinites correspond to partially - poorly ordered structures. The geochemical data showed appreciable accumulation of trace elements in the clay fractions. The absence of negative Ce anomaly in the chondrite-normalised rare earth elements (REE) pattern in the clay fractions suggest the alteration of the primary minerals took place under suboxic conditions. The average non-carcinogenic hazard index (HI) were 1.52, 1.08, and 2.01 for children and 0.18, 0.13, and 0.24 for adults in the clay fractions from basalt, granite, and arkosic sandstone, respectively. The HI > 1 for children suggest non-carcinogenic health risk to children with ingestion pathway contributing the highest. The average carcinogenic risk index values were >10^-3 for children and adults with respect to Cr, Ni, and Pb in the clay fractions. This suggests very high carcinogenic risk to children and adult population in decreasing order from clay fractions in arkosic sandstone > basalt > granite, respectively.

1. Introduction

Kaolin minerals usually dominate the clay fractions of most weathered soil profiles in tropical and subtropical regions. The most common kaolin minerals occurring in soils are kaolinite followed by halloysite (Trakoonyingcharoen et al., 2006). Kaolin minerals in soils could be of primary origin through the weathering of rocks rich in aluminium or secondary in origin through the weathering of arkosic rocks (Ekosse, 2005).

The most popular of all South African soils is the Hutton form, which accounts for the marvelous redness of the landscape across the Country. According to Mzeeza et al. (2010), the Hutton form soil type in the study areas is similar to Rhodic Eutrustox (Soil Survey Staff, 2006) or Rhodic Ferralsol (WRB, 2006). The apedal (structureless) soils in the group are characterised by a relatively low CEC (<11 cmol, kg^-1) reflecting oxidic mineralogy with predominantly kaolinitic assemblage (Fey, 2010). The geochemical and mineralogical composition of the clay fraction has significant implications on soil fertility, geochemical exploration and engineering properties (Schafer et al., 2008). Trace elements in soil clay fractions are important in health risk assessment because of their ability to accumulate higher amounts relative to the bulk soil (Luo et al., 2011). The elements can leach into groundwater or end up in the food chain through plant uptake (Acosta et al., 2009). Hence, the fraction in which trace elements are more accumulated would pose the most serious health threat (Kicinska, 2018).

Despite the dominance of kaolin in these soils, little is known of their properties in the medium (Yoothong et al., 1997). Previous researches conducted in South Africa on kaolins are limited to standard kaolins with little or no publication on soil kaolin leading to a great omission in the overall clay minerals body of knowledge. The study of pure or standard clay deposit may serve as a basis in understanding kaolin in soils. Hart et al. (2002) and Hughes et al. (2009) reported that soil kaolin characteristics differ greatly when compared to standard mineral kaolin in that the former typically have high defect structures, complex crystal
morphologies, smaller crystal size, and significant structural iron. Based on studies on soil kaolins from Indonesia, Western Australia, and Thailand, Hart et al. (2002, 2003) observed significant differences in their properties within a single geographic region and particularly within a single profile. Therefore, this study is directed towards unraveling the variations in the clay mineralogical and geochemical characteristics in soils developed from different parent rocks (basalt, granite, and arkosic sandstone) in Limpopo Province, South Africa. Several studies have reported health implications associated with trace elements in clay fractions to plants (e.g Kabata-Pendias, 2011; Luo et al., 2011; Gomes et al., 2016). The risk assessment based on some trace elements present in the clay fractions (0–20 cm) was also investigated.

2. Location and geological setting

The studied soil profiles developed from basalt, arkosic sandstone, and granite are in Sibasa (Thulamela Municipality), Sagole (Musina Municipality), Matoks (Molemole Municipality) areas, respectively, Limpopo Province, South Africa (Figure 1).

The soil profiles developed from basalt and arkosic sandstone occur within the Sibasa Basalt Formation and Wyllie’s Poort Formation respectively of the Soutpansberg Group (Figure 2a). The stratigraphy of the Group comprises of both volcanic and sedimentary succession which has been subdivided into six formations namely: Nzhelele, Musekwa, Wyllie’s Poort, Fundudzi, Sibasa, and Tshifhefhe, respectively (SACS, 1980; Brandl, 1999 and Barker et al., 2006).

The Sibasa Basalt Formation is a sequence composed of cyclically erupted basalts. They are generally aphanitic – fine grained with colour variation from blackish to light green depending on the degree of epidotisation. Amygdaloidal varieties have vesicles filled with quartz and chalcedony. The matrix is made up of clinopyroxene (mainly augite) and plagioclase. Interbedded clastic sediments which include quartzite, shale, and minor conglomerate locally reach a maximum of 400 m. The formation thickness is estimated to reach about 3000 m (Barker et al., 2006).

The Wyllie’s Poort Formation according to Brandl (1981) underlies the major part of the more mountainous ground of the Soutpansberg Group. Its basal contact has been interpreted as a regional unconformity (Cheney et al., 1990). It is medium-to coarse grained with prominent agate conglomerate at the base in some areas. Towards the eastern part of Tshipise, the uppermost portion of the formation is well-bedded, light coloured feldspathic (arkosic) sandstone. In addition, minor lenticular intercalations of basaltic lava and pyroclastic rocks are developed in the eastern regions. Its maximum recorded thickness is 1,500 m.

The soil profiles developed from granite occur within the Matok Granite Suite of the Southern Marginal Zone, Limpopo Belt (Figure 2b). The Matok Granite is emplaced north of the Hout River Shear zone. It intruded an earlier charno-enderbitic unit which occurs preferentially in the northern part of the granite body. The granite is whitish to pink in colour, medium grained to porphyritic with a range of composition from granitic to granodioritic while the charnockitic suite comprises of both enderbitic and charno-enderbitic. The charno-enderbitic units are fine-to medium grained, greyish green to olive green rocks that are composed of quartz, plagioclase, orthoclase, hyperstene, and augite. Radiometric ages between 2663 and 2666 Ma from zircon U–Pb dating have been recorded for the granitic suite (Barton et al., 1992).

3. Materials and methods

Soil profiles developed from basalt, granite, and arkosic sandstone, respectively were sampled at depths ranging from 0 - 20, 20–50, and 50–100 cm depending on where the hard rock begins using a soil auger. Information on the geology, coordinates, soil types, profile description, climate, and number of samples are presented in Table 1a. Disaggregated (by gentle crushing) and air-dried samples were dispersed with Calgon (Sodium hexametaphosphate and Soda) (Van Reeuwijk, 2002) and

![Figure 1](Modified after Hall et al., 2013).

![Figure 2a](Geologic Map of the Soutpansberg Group showing the study areas (Modified after Barker et al., 2006).)
ultrasonic disintegrator as described by Suslick and Price (1999), Jakubowska (2007), and Raty and Peltovuori (2008) to obtain the clay fractions \(<2 \mu m\). The ultrasonication was done with an energy input of 300 J m/L (1 min) using probe type ultrasonic disintegrator UP400S equipped with 7 mm diameter sonotrode S7 at the Department of Ecology and Resource Management, University of Venda (UNIVEN), South Africa.

The clay fractions were analysed using a PANalytical X'Pert Pro powder X-ray diffractometer with an X'Celerator detector and variable divergence- and fixed receiving slits with Fe filtered Co-Kα radiation (\(\lambda = 1.789 \text{ Å}\)). Samples were scanned from 2° to 85° at a counting time of 0.5 s. The X'Pert Highscore plus software was used for phase identifications and the Rietveld method was used to compute their relative percentages with an accuracy within approximately \(\pm 3\) wt % as described by Hillier (2000). The peaks at 14 Å and 7 Å could also be attributed to clay minerals such as chlorite, vermiculite and/or smectite, which would require further analysis to confirm the mineral species.

Table 1a. Information on the study areas and number of samples (Adapted from Oyebanjo, 2020).

| S/N | Lithology/Location | Coordinates           | Soil Type          | Profile Description                                      | Climate                                      | Number of samples |
|-----|--------------------|-----------------------|--------------------|----------------------------------------------------------|----------------------------------------------|-------------------|
|     |                    |                       |                    |                                                          |                                              |                   |
| 1.  | Basalt/Sibasa      | S1 - 22° 57' 09" S    | Hutton             | Orthic A with deep red apedal B horizon                 | Semi-Arid, dry hot (BSh)                     | 6 (0–20, 20–50, 50–100 cm) |
|     |                    | 30° 27' 10" E         |                    |                                                          |                                              |                   |
|     |                    | 30° 27' 51" E         |                    |                                                          |                                              |                   |
| 2.  | Granite/Matoks     | MAT1 - 23° 27' 46" S  | Hutton             | Orthic A with shallow yellow-brown apedal B horizon     | Warm temperate, winter dry, hot summer (CWa) | 4 (0–20, 20–50 cm) |
|     |                    | 29° 44' 03" E         |                    |                                                          |                                              |                   |
|     |                    | MAT2 - 23° 27' 16" S  |                    |                                                          |                                              |                   |
|     |                    | 29° 44' 48" E         |                    |                                                          |                                              |                   |
| 4.  | Arkosic Sandstone/Sagole | SA1 - 22° 31' 01" S | Hutton             | Orthic A with shallow yellow-brown apedal B horizon     | Semi-Arid, dry hot (BSh)                     | 3 (0–20, 20–50 cm) |
|     |                    | 30° 36' 54" E         |                    |                                                          |                                              |                   |
|     |                    | SA2 - 22° 30' 20" S   |                    |                                                          |                                              |                   |
|     |                    | 30° 36' 44" E         |                    |                                                          |                                              |                   |
Reference standards were run for calibration procedures. The geochemical analyses were carried out at the Central of Analytical Facilities, University of Stellenbosch, South Africa.

For the major element compositions of the clay fractions, glass disks were prepared for X-ray fluorescence (XRF) and measured on a PANalytical Axios Wavelength Dispersive Spectrometer fitted with a Rh tube. Reference standards were run for calibration procedures. The Loss on Ignition (LOI) was determined following the procedures described by Van Reeuwijk (2002).

A Resolution 193 nm Excimer laser from ASI connected to an Agilent 7700 Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) was used in the analysis of trace elements in the clay fractions. The samples were ablated using a frequency of 10 Hz and 2 mJ energy in helium gas at 0.35 L/min mixed with argon (0.9 L/min) and nitrogen (0.004 L/min) before measurement (Gunther and Hattendorf, 2005). Reference standards were run for calibration procedures. The geochemical analyses were carried out at the Central of Analytical Facilities, University of Stellenbosch, South Africa.

To assess the enrichment of some trace elements in the clay fractions reported in this study such as Cr, Ni, Zn, Pb, Co, and Cu considered to be

Table 1b. Description of parameters and values used in Equations 2-6 (Adapted from Qing et al., 2015; Weissmannova et al., 2019 and references therein).

| Parameters | Description | Values |
|------------|-------------|--------|
| C (mg kg⁻¹) | Element content in soil | 10⁶ |
| CF (kg mg⁻¹) | Conversion factor | |
| EF (day yr⁻¹) | Exposure frequency | 350 |
| ED (yr) | Exposure duration | 6 and 30 for children and adults, respectively |
| BW (kg) | Body weight | 16 and 70 for children and adults, respectively |
| ATex (day) | Average time for non-carcinogenic effects | 2190 and 10950 for children and adults, respectively |
| ATcin (day) | Average time for carcinogenic effects | 25550 |

Ingestion

| Ingest (mg day⁻¹) | Ingestion rate | 200 and 100 for children and adults, respectively |

Inhalation

| Inhal (m³ day⁻¹) | Respiratory rate | 20 |
| PEF (m³ kg⁻¹) | Particulate emission factor | 1.39 × 10⁶ |

Dermal contact

| SA (cm²) | Skin Surface Area | 2800 and 5700 for children and adults, respectively |
| AF (mg cm⁻² day⁻¹) | Adherence factor | 0.2 and 0.07 for children and adults, respectively |
| ABS (Unitless) | Absorption factor | 0.001 for all metals |

RfD – reference dose; SF – slope factor, - not available.

Table 2. Results of quantitative analyses of minerals present (wt %) in the clay fractions developed from different parent rocks.

| Parent rock | Sample ID | Kao | Qtz | Anatase | Goe | Hem | Plag | Mic | Mus/Ill | Gibbsite | Chlorite | Artinolite |
|-------------|-----------|-----|-----|---------|-----|-----|------|-----|---------|-----------|----------|------------|
| Basalt      | S1 0–20 cm | 62  | 22  | 8      | 8   | -   | -    | -   | -       | -         | -        | -          |
|             | S1 20–50 cm| 64  | 18  | 7      | 4   | 7   | -    | -   | -       | -         | -        | -          |
|             | S1 50–100 cm| 82  | 8   | 2      | 5   | -   | -    | -   | -       | -         | -        | -          |
|             | S2 0–20 cm | 77  | 10  | 3      | 5   | 4   | -    | -   | -       | 1         | -        | -          |
|             | S2 20–50 cm| 85  | 7   | 2      | 5   | -   | -    | -   | -       | 1         | -        | -          |
|             | S2 50–100 cm| 77  | 9   | 3      | 6   | 4   | -    | -   | -       | 1         | -        | -          |
|             | Average   | 74.50 | 12.33 | 4.17 | 5 | 5.75 | - | - | 1.50 | - | - |
| Granite     | MAT1 0–20 cm| 31  | 21  | -     | -   | -   | -    | 20  | 10      | 17        | -        | -          |
|             | MAT1 20–50 cm| 24  | 20  | -     | -   | -   | -    | 24  | 14      | 14        | 2         | 2          |
|             | MAT2 0–20 cm| 26  | 19  | -     | -   | -   | -    | 32  | 9       | 13        | -         | 1          |
|             | MAT2 20–50 cm| 29  | 20  | -     | -   | -   | -    | 22  | 9       | 14        | -         | 4          |
|             | Average   | 27.50 | 20  | -     | -   | -   | -    | 24.50 | 10.50   | 14.50     | -         | 3.50       |
| Ark. Sst    | SA1 0–20 cm| 23  | 35  | -     | -   | -   | -    | -   | 17      | 25        | -         | -          |
|             | SA2 0–20 cm| 26  | 27  | -     | -   | -   | -    | -   | 19      | 24        | -         | 5          |
|             | SA2 20–50 cm| 24  | 38  | -     | -   | -   | -    | -   | 13      | 19        | -         | 6          |
|             | Average   | 24.33 | 33.33 | -   | -   | -   | -    | 16.30 | 22.66   | 5.50      | -         | -          |

Kao – kaolinite; Qtz – quartz; Goe – goethite; Hem – hematite; Plag – plagioclase; Mic – microcline; Mus – muscovite; Ill – illite.
of most interest in South African context (Herselman, 2007), the accumulation factor (AF) was calculated using the relationship as expressed in Eq. (1) (Ajmone-Marsan et al., 2008).

\[
\text{AF} = \frac{X_{\text{ef}}}{X_{\text{bulk}}}
\]  

(1)

where, \(X_{\text{ef}}\) and \(X_{\text{bulk}}\) are the concentrations (ppm) of the trace element in the clay fraction and the bulk soil, respectively. The trace element concentrations in the bulk soils have been earlier reported (Oyebanjo et al., 2019). Trace elements with AF > 1 suggests that it is accumulated in the clay fraction (Acosta et al., 2009).

The AF does not reflect the level of health risk to human. The non-carcinogenic hazard index (HI) and carcinogenic risk index (CRI) were used to assess the health risk associated with the trace elements present in the clay fractions (topsoils, 0–20 cm) since they are preferential enriched in them. The HI and CRI through the different routes were computed using Equations 2–6 (Luo et al., 2012; Gao et al., 2019; Kumar et al., 2019). The definition of parameters and values used in equations are listed in Table 1b.

\[
\text{HI} = \sum_{i=1}^{n} \frac{\text{EF}_{i}}{R_{\text{F}}D_{i}} = \sum_{i=1}^{n} \left( \frac{AD_{i}^{\text{ef}}}{R_{\text{F}}D_{i}} \right) + \sum_{i=1}^{n} \left( \frac{AD_{i}^{\text{ih}}}{R_{\text{F}}D_{i}} \right) + \sum_{i=1}^{n} \left( \frac{AD_{i}^{\text{dem}}}{R_{\text{F}}D_{i}} \right)
\]  

(2)

\[
\text{CRI} = \sum_{i=1}^{n} \left( \text{CRI}_{i}^{\text{ef}} + \text{CRI}_{i}^{\text{ih}} + \text{CRI}_{i}^{\text{dem}} \right)
\]

\[
= \sum_{i=1}^{n} \left( AD_{i}^{\text{ef}} \times SF_{i}^{\text{ef}} \right) + \sum_{i=1}^{n} \left( AD_{i}^{\text{ih}} \times SF_{i}^{\text{ih}} \right)
\]

\[
+ \sum_{i=1}^{n} \left( AD_{i}^{\text{dem}} \times SF_{i}^{\text{dem}} \right)
\]

(3)

\[
\text{ADI}_{\text{ef}} = \frac{C \times \text{IngR} \times EF \times ED \times CF}{\text{BW} \times \text{AT}}
\]  

(4)
The percentages of the various minerals present in the clay fractions are presented in Table 2. The clay fractions in soils developed from basalt were mainly composed of kaolinite, quartz, anatase, goethite, hematite, and gibbsite. Kaolinite and quartz were the dominant components ranging from 82 to 92 wt % with >60 wt % kaolinite. The non-clay minerals constituted <18 wt % in all the samples with Ti-bearing mineral, anatase, Fe-bearing minerals, goethite and hematite dominating. Gibbsite was present mainly in minor amounts. The formation of gibbsite could be either through neoformation from the weathering offeldspars which are primary minerals in basalt or by progressive dissolution of kaolinite through desilication under intense weathering (Schaefer et al., 2003). The dominance of kaolinite coupled with gibbsite is indicative of high degree of weathering in the latter by leaching and oxidation associated with greater moisture regime (Kheouruenromne and Sudhijprakarn, 1984; Kanket, 2006). This could be attributed to the more advanced soil developmental stage in the latter by leaching and oxidation associated with greater moisture regime (Kheouruenromne and Sudhijprakarn, 1984; Kanket, 2006).

4. Results and discussion

4.1. Mineralogical characteristics

The percentages of the various minerals present in the clay fractions are presented in Table 2. The clay fractions in soils developed from basalt were mainly composed of kaolinite, quartz, anatase, goethite, hematite, and gibbsite. Kaolinite and quartz were the dominant components ranging from 82 to 92 wt % with >60 wt % kaolinite. The non-clay minerals constituted <18 wt % in all the samples with Ti-bearing mineral, anatase, Fe-bearing minerals, goethite and hematite dominating. Gibbsite was present mainly in minor amounts. The formation of gibbsite could be either through neoformation from the weathering of feldspars which are primary minerals in basalt or by progressive dissolution of kaolinite through desilication under intense weathering (Schaefer et al., 2008). The dominance of kaolinite coupled with gibbsite is indicative of high degree of weathering of the soils (Kanket, 2006). The presence of anatase, goethite, and hematite could be attributed to the relative accumulation by weathering of mafic minerals rich in Ti and Fe (Wiriyakinateekul et al., 2010). The Al and Fe oxide minerals will have great influences on the fertility particularly on P sorption dynamics in the soils (Hart et al., 2003). In addition, they are important in the retention of plant nutrient elements against leaching under high rainfall (Gilkes and Prakongkep, 2016).

The minerals present in clay fractions developed from granite were kaolinite, quartz, plagioclase feldspar, muscovite/illicite, chlorite, and actinolite. Kaolinite dominated the clay minerals (>24 wt %) with chlorite present in minor amounts. The non-clay minerals constituted >69 wt % in all the samples. The presence of a greater percentage of weatherable minerals could be associated with low chemical weathering due to low rainfall regime around Matoks area based on the climatic zone (Conradie, 2012). Further dissolution of the associated weatherable minerals will aid the release of nutrient elements to plants (Gilkes and Prakongkep, 2016).

Quartz was the dominant mineral (>27 wt %) followed by kaolinite in clay fractions developed from arkosic sandstone. The non-clay minerals constituted >69 wt % with weatherable minerals like muscovite and microcline present. The prevailing arid climate around Sagole area (Conradie, 2012) could not have allowed intense weathering of the primary minerals to form kaolinite.

The average abundances of kaolinite from this study which ranges between 23 and 75 wt % were lower than the average values obtained for kaolinites in Thai (95 wt %) and Brazilian (85 wt %) soils (Kanket, 2006). This could be attributed to the more advanced soil developmental stage in the latter by leaching and oxidation associated with greater moisture regime (Kheouruenromne and Sudhijprakarn, 1984; Kanket, 2006).

4.1.1. Kaolinite crystallinity and dehydroxylation temperature

X-ray diffraction-based determination of soil kaolinite crystallinity cannot be successfully used in studying these soil kaolinites since almost pure kaolin samples with little or no impurities is required for such an exercise (Hughes et al., 2009). Hence, the IR spectroscopy-based approach was applied in determining the soil kaolinite crystallinity.

Characteristic bands at 3691-89, 3669, 3651, and 3619 were represented by some soil kaolinites developed from granite and arkosic sandstone (MAT1 20–50 cm and MAT2 20–50 cm) showed very weak or no influence at the bands typical of kaolinites. These observations according to the IR empirical (IR-E) approach (Madejova et al., 1997; Vaculikova et al., 2011) which relies on the presence of the kaolinite stretching bands (3691/3689, 3669, 3651/3650, and 3619), the soil kaolinites can possibly be grouped into two classes; partially ordered and poorly ordered. The first class is represented by some soil kaolinites developed from granite and arkosic sandstone which are MAT1 0–20 cm, MAT2 0–20 cm, and SA1 0–20 cm, respectively (Table 3a). The IR spectra of those developed from basalt and granite (MAT1 20–50 cm and MAT2 20–50 cm) belong to the second class because of the absence of the typical kaolin bands.

The IR numerical (IR-N) approach for the soil kaolinites correspond to partially ordered structures based on the IR-N classification (Table 3b). The IR-N classification corresponds well with the first class from IR-E. However, the discrepancy between IR-N and the second class of IR-E could be due to Fe³⁺ substituting for Al in the octahedral sheet of the kaolinite.
4.2. Geochemical characteristics

4.2.1. Major oxides

The average values and ranges of the major oxide concentrations are given in Table 4. The clay fractions in soils developed from basalt have higher Al2O3 (24.57 wt %) and lower SiO2 (35.66 wt %) and SiO2/Al2O3 ratio (1.45) mean values relative to those obtained developed from granite and arkosic sandstone (Table 4). This is harmonious with the mineralogy, since the clay fractions in soils developed from basalt have more kaolinite than the other clay fractions in soils developed from granite and arkosic sandstone. LOI was highest in clay fractions in soils developed from basalt. This could be attributed to the higher percentages of kaolinite, goethite, and gibbsite with chemically bound water in their matrices (Beuria et al., 2017). The mean SiO2/Al2O3 ratios for the clay fractions were greater than the value of 1.38 for Thailand oxisols and 1.16 for Brazilian ultisols (Table 4).

The variation in the SiO2/Al2O3 ratios suggest different degree of weathering. Soils with lower ratios have experienced higher degree of weathering relative to those with higher ratios (Schaefer et al., 2008). This is consistent with the earlier observations from the mineralogy of the clay fractions.

The TiO2 and Fe2O3 were present in all the clay fractions but highest in those developed from basalt (Table 4). This reflects the mafic nature of basalt with more ferromagnesian minerals (Baioumy, 2014). In addition, Fe2O3 mean values for clay fractions developed from basalt and granite were comparable to those obtained for Thailand oxisols and ultisols, respectively (Table 4).

The lowest levels of CaO, MgO, K2O, and Na2O were obtained for clay fractions developed from basalt with lower percentages of weatherable minerals relative to other clay fractions. In addition to differences in the rainfall regimes in the study areas earlier mentioned, the observation also reflects the stability of the minerals to alteration. As such, minerals in basalt with higher crystallisation temperatures alter faster to more stable secondary minerals relative to minerals in granite and arkosic sandstone with lower crystallisation temperatures (Naqvi, 2013; Ibarra et al., 2016).

4.2.2. Trace elements

The average values and ranges of trace elements in the clay fractions are presented in Table 5a. The clay fractions developed from basalt contain higher amounts of Sc, V, Co, Ni, and Cu whereas, clay fractions developed from granite have higher concentrations of Zr. Clay fractions from arkosic sandstone derived soils contain higher concentrations of Cr, Rb, Ba, Pb, Th, and U.
Table 5b. Non-carcinogenic hazard index (HI) based on the average trace element concentrations in clay fractions (0–20 cm) developed from different Parent rocks in Limpopo Province, South Africa.

|     | Basalt | Granite | Ark St |
|-----|--------|---------|--------|
|     | HQ inh | HQ derm | HQ inh | HQ inh | HQ inh | HQ inh |
|     |       |         |       |       |       |       |
| Children |  |  |  |  |  |  |
| Cr  | 1.14E+00 | 1.60E-01 | 8.61E-03 | 1.31E+00 | 8.13E-01 | 1.14E-01 | 6.14E-03 | 9.33E-01 | 1.58E+00 | 2.21E-01 | 1.19E-02 | 1.81E+00 |
| Ni  | 7.83E-02 | 8.12E-04 | 1.25E-03 | 8.04E-02 | 4.52E-02 | 4.68E-04 | 7.22E-04 | 4.64E-02 | 5.24E-02 | 5.43E-04 | 8.37E-04 | 5.37E-02 |
| Zn  | 2.90E-03 | 4.06E-05 | 2.99E-07 | 2.94E-03 | 1.98E-03 | 2.77E-05 | 1.42E-07 | 2.01E-03 | 2.78E-03 | 3.89E-05 | 2.00E-07 | 2.82E-03 |
| Pb  | 3.98E-02 | 7.43E-04 | 2.85E-06 | 4.06E-02 | 8.07E-02 | 1.51E-03 | 5.77E-06 | 8.22E-02 | 1.23E-01 | 2.29E-03 | 8.77E-06 | 1.25E-01 |
| Co  | 7.97E-04 | -       | 7.97E-04 | 1.61E-03 | -       | 1.61E-03 | 1.61E-03 | 2.45E-03 | -       | -       | 2.45E-03 | 2.45E-03 |
| Cu  | 8.25E-02 | 7.14E-04 | 5.50E-06 | 8.25E-02 | 1.00E-02 | 8.70E-06 | 6.70E-07 | 1.01E-02 | 1.35E-02 | 1.16E-05 | 8.98E-07 | 1.35E-02 |
| Total | 1.35E+00 | 1.61E-01 | 9.87E-03 | 1.52E+00 | 9.53E-01 | 1.16E-01 | 6.86E-03 | 1.08E+00 | 1.77E+00 | 2.24E-01 | 1.28E-02 | 2.01E+00 |

The clay fractions developed from basalt were enriched in Sc, V, Cr, Cu, and Zr, respectively, relative to Thailand oxisols whereas, those developed from granite were enriched in all the trace elements compared to Thailand Ultisols except for Th (Table 5a). This could be attributed to the presence of other weatherable and accessory minerals in the clay fractions from this study. The retention of appreciable proportions of trace elements in the clay fractions has significant implications for soil fertility and geochemical exploration (Kanket et al., 2005).

The average AF values for selected trace elements in the respective parent rocks are presented Table 5a and Figure 3. The trace elements generally show preferential enrichment in the clay fractions (except for Co, Zn, and Pb for clay fractions in soils developed from basalt) relative to the bulk soils.

Higher adsorption capacity in the clay fraction (finer fraction) due to greater surface area per unit of mass have been reported to have caused the preferential partitioning (Wong et al., 2006; Luo et al., 2011; Gomes et al., 2016). Lower AF average values obtained for clay fractions in soils developed from basalt relative to those developed from granite and arkosic sandstone could be due to the presence of lower percentage of weatherable minerals in them (Acosta et al., 2011). Trace element accumulation sequences in the clay fractions were Ni > Cr ≈ Cu > Pb > Zn > Co, Cr > Ni ≈ Zn > Cu > Co > Pb, and Cr > Zn > Ni > Cu > Co > Pb for those developed from basalt, granite, and arkosic sandstone respectively.

The average non-carcinogenic HI for children and adults are presented in Table 5b and Figure 4a. Ingestion pathway was the main means of exposure to the trace elements for both children and adults. The average HQ contributions through oral ingestion accounted for between 88.20 to 88.70 % and 83.80–84.50 % to the total average HI for children and adults, respectively in the clay fractions from basalt, granite, and arkosic sandstone.
Table 6. REE concentrations (ppm) of clay fractions developed from different Parent rocks in Limpopo Province, South Africa and for average Upper Continental Crust (UCC).

| Parent Rock | Sample ID       | La   | Ce   | Pr   | Nd   | Sm   | Eu   | Gd   | Tb   | Dy   | Ho   | Er   | Tm   | Yb   | Lu   |
|-------------|----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Basalt      | S1 0-20 cm     | 16.74| 39.46| 4.01 | 17.25| 4.32 | 1.26 | 4.34 | 0.76 | 4.83 | 0.97 | 2.71 | 0.42 | 2.89 | 0.41 |
|             | S1 20-50 cm    | 12.18| 37.43| 2.73 | 12.14| 2.80 | 0.90 | 3.06 | 0.58 | 3.53 | 0.77 | 2.18 | 0.33 | 2.29 | 0.36 |
|             | S1 50-100 cm   | 15.01| 55.16| 3.74 | 16.16| 4.41 | 1.18 | 4.01 | 0.67 | 4.78 | 0.96 | 2.87 | 0.43 | 3.11 | 0.46 |
|             | S2 0-20 cm     | 9.75 | 26.60| 2.23 | 10.30| 2.47 | 0.73 | 2.76 | 0.54 | 3.05 | 0.68 | 1.93 | 0.29 | 2.26 | 0.35 |
|             | S2 20-50 cm    | 7.69 | 22.47| 1.78 | 7.90 | 1.75 | 0.67 | 2.15 | 0.38 | 2.54 | 0.55 | 1.77 | 0.26 | 1.94 | 0.29 |
|             | S2 50-100 cm   | 6.12 | 23.29| 1.39 | 6.08 | 1.33 | 0.44 | 1.63 | 0.30 | 2.05 | 0.48 | 1.44 | 0.24 | 1.74 | 0.26 |
| Average     |                | 11.25| 34.06| 2.64 | 11.64| 2.84 | 0.86 | 2.99 | 0.54 | 3.46 | 0.74 | 2.15 | 0.33 | 2.37 | 0.36 |
| Granite     | MAT1 0-20 cm   | 47.39| 89.83| 10.09| 39.85| 7.07 | 1.04 | 5.37 | 0.73 | 4.10 | 0.78 | 2.10 | 0.35 | 2.71 | 0.41 |
|             | MAT1 20-50 cm  | 44.82| 84.16| 9.58 | 37.95| 6.56 | 1.10 | 5.11 | 0.70 | 3.62 | 0.72 | 2.13 | 0.32 | 2.37 | 0.42 |
|             | MAT2 0-20 cm   | 61.99| 120.35|13.27| 52.15| 9.61 | 1.67 | 6.98 | 0.98 | 5.39 | 1.12 | 3.01 | 0.45 | 3.17 | 0.56 |
|             | MAT2 20-50 cm  | 56.78| 106.60|12.56| 49.50| 8.60 | 1.46 | 7.02 | 0.88 | 5.03 | 1.01 | 2.91 | 0.50 | 3.50 | 0.52 |
| Average     |                | 52.52| 100.24|11.37| 44.86| 7.96 | 1.32 | 6.12 | 0.82 | 4.53 | 0.91 | 2.53 | 0.41 | 2.94 | 0.48 |
| Ark. Sst.   | SA1 0-20 cm    | 76.25| 146.15|16.32| 64.00| 11.62| 1.73 | 8.82 | 1.24 | 7.31 | 1.42 | 4.06 | 0.64 | 4.42 | 0.66 |
|             | SA2 0-20 cm    | 67.29| 125.97|14.70| 59.15| 10.65| 1.92 | 8.14 | 1.15 | 6.69 | 1.26 | 3.63 | 0.52 | 3.69 | 0.59 |
|             | SA2 20-50 cm   | 65.74| 123.53|14.78| 57.80| 10.85| 1.89 | 8.34 | 1.14 | 6.37 | 1.35 | 3.50 | 0.48 | 3.62 | 0.55 |
| Average     |                | 69.76| 131.88|15.27| 60.32| 11.04| 1.84 | 8.43 | 1.18 | 6.79 | 1.34 | 3.73 | 0.55 | 3.91 | 0.60 |
| UCC         | Average        | 30   | 64   | 7.1  | 26   | 4.5  | 0.9  | 3.8  | 0.64 | 3.5  | 0.8  | 2.3  | 0.33 | 2.2  | 0.3  |

1. McLennan (2001).
minerals in the parent rocks took place under suboxic conditions since minerals formed in equilibrium withoxic marine waters are likely to show a negative Ce anomaly (Jeans et al., 2000; Arslan et al., 2006).

5. Conclusion

The study revealed that the dominant clay mineral in the clay fraction was kaolinite with highest percentage in clay fractions developed from basalt. Other minerals present were quartz, plagioclase, microcline, muscovite/illite, anatase, goethite, hematite, gibbsite, chlorite, and actinolite. The percentage of weatherable minerals present in clay fractions were in those developed from granite and arkosic sandstone which accounted for the greater amounts of CaO, MgO, K2O, and Na2O relative to clay fractions developed from basalt. The interaction between parent rock influence, climate, and intensity of weathering played a major role in explaining the variations in the mineralogy and geochemistry of the clay fractions of the soils in the study area. The crystallinity based on FTIR showed that the soil kaolinites were partially to poorly ordered. The clay fractions of the soils in the study area. The crystallinity based on rock in Additional information

Declarations

Author contribution statement

O. O. Oyebanjo: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

G. E. Ekosse: Performed the experiments; Contributed reagents, materials, analysis tools or data. Wrote the paper.

J. O. Odiyo: Contributed reagents, materials, analysis tools or data.

Funding statement

O. Oyebanjo was supported by the University of Venda (S999). G. E. Ekosse was supported by the National Research Foundation (ZA) (CPRR UID 91559).

Data availability statement

Data associated with this study has been deposited at UNIVERSITY OF VENDA LIBRARY https://univendspaced.univen.ac.za/handle/11602/1 519.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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