Available online at http://www.ifgdg.org

Int. J. Biol. Chem. Sci. 17(4): 1778-1789, June 2023

ISSN 1997-342X (Online), ISSN 1991-8631 (Print)

International Journal of Biological and Chemical Sciences

Original Paper http://ajol.info/index.php/ijbcs http://indexmedicus.afro.who.int

Influence of the parent rock nature on the mineralogical and geochemical composition of ferralsols used for sedentary agriculture in the Paleoproterozoic Franceville sub-basin (Gabon)

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Received: 23-01-2023 Accepted: 24-06-2023 Published: 30-06-2023

ABSTRACT

The aim of this study was to assess the influence of parent rock nature on the mineralogical and geochemical properties of ferralsols used by sedentary subsistence farmers in the Proterozoic Franceville sub-basin of Gabon. Thus, soils developed from cherts, black shales and sandstones were investigated for their mineralogical composition and their heavy metal contamination of topsoil using the X-ray diffraction (XRD), and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). Results show that the dominant mineralogical assemblage is made of quartz, illite, kaolinite and smectite, and this is reflected in the major-element chemistry which include essentially SiO_2 (46.4 - 89.2%), Al_2O_3 (4.3 - 19.8%) followed by Fe_2O_3 (0.7 - 15.3%), with highest amounts of SiO_2 and lowest amounts of Al_2O_3 and Fe_2O_3 found in soils developed from sandstone. The geochemical data revealed some doleritic intrusions through the chert formations with highest values of Fe_2O_3 and TiO_2 in the overlying soils. Results indicated serious health concern associated with a geogenic source of As, Ba, Cd, Cu, La, Pb, Rb, Th and U in soils developed from cherts and black shales. Consequently, only the uncontaminated soils developed from sandstone could be appropriate for smallholder farming communities.
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Keywords: Ferralsol, mineralogy, geochemistry, heavy metals, Francevillian basin, Gabon.

INTRODUCTION

Ferralsols that usually dominate in the intertropical regions of the word are leached soils enriched in iron and aluminum and lessly in silica and all major cation. Generally, ferrasols are characterized by relative accumulation of stable primary minerals, quartz, and the secondary minerals including clay assemblage dominated by kaolinite, gibbsite and ferric hydrates. These minerals are controlling the soil chemical composition (Galinha et al., 2010). In the tropical sub-Saharan Africa, several research findings indicated that environmental factor such as parent material, topography, climate, vegetation and anthropogenic perturbation, significantly influence the variability of soil properties (Umali at al., 2012; Kassawmar et al., 2018). In Gabon, the soils developed on granite in central and northeastern of the country, are classified as Xanthic Ferralsols and ferralic Cambisols, while soils developed in the arid southeast are classified iron-rich Plinthosols and the soils developed along the

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DOI: https://dx.doi.org/10.4314/ijbcs.v17i4.38

coast are classified ferralic Arensols and Calcaric Fluvisols (Wade et al., 2019). In this study, typical minerals and their significantly influence on the geochemical composition of ferralsols were investigated at local scale of the Franceville region under humid tropical climate.

Gabon has the second largest forest among countries of the Congo basin, and 88.5% of its 267.700 km^2 area is covered by the dense equatorial evergreen forest; the remainder (in southeast and southwest) being consisted of savannas (6%) cropland (2%) and flooded broadleaved forest (3%) (Sannier et al., 2014). Gabon has a contrasted basement geology from east which is largely made of metasedimentary and metaigneous rock, to west dominated by a mosaic of carbonate and non-carbonate rock minerals (Thiéblemont et al., 2009). The lithology of Franceville region, located in southern east of Gabon, is largely made of metasedimentary rock of the ~2.1 Ga Paleoproterozoic Francevillian Basin. This Basin is filled with a volcanic-sedimentary succession and divided into four sub-basins, including Franceville, Booué, Okondja and Lastourville (Bouton et al., 2009). The pioneer investigations carried out in Franceville sub-basin have highlighted several Mn deposits localized on plateau-like topographic highs in Moanda and Franceville area (Guauthier-Lafaye and Weber, 2003; Bouton et al., 2009). The Francevillian basin occurs in an area of about 42 000 km² located under very distinct landscapes: forest-savanna mosaic, rain forest and savanna with colonizing forest (Makaya Mvoubou et al., 2012). Ferralsols are the most representative and have good physical properties but are chemically poor soils (Mabicka et al., 2021). Concerning the Franceville region, many ferralsols are used for shifting cultivation. About soil fertility, the geochemical and mineralogical composition of soil has significant implications. However, in several African countries, solid urban waste and chemical products are brought to fertilize the top layer of agricultural soils (Agueh et al., 2015; Ye et al., 2020). This pratice leads to the heavy metal contamination in the food chain via cultivated plant product, thus compromising the population health. In effect, some heavy metals, such as Cu, Zn, Fe and Mn, are essential soil micronutrients required by living organisms in trace amounts for biological metabolic processes, and other heavy metals like Cd, Pb, Cr, Hg and As are non-essential for the growth of living organisms. But, all heavy metals are hazardous to human health as they easily bio-accumulate via the food chain due to soil-to-plant transfer of metals (Ali et al., 2019). Given this problem, a better knowledge of the state of soil contamination remains essential for natural resource protection and for environmental protection (Ye et al., 2020; Aduayi-Akue et Grandi, 2014; Yehouenou Azehoun Pazou et al. 2020; Kouakou et al., 2019). If data on heavy metal contents and their behavior in plants are available in other African countries, heavy metal contents were not investigated on the top soil layer at Franceville Gabon, despite anthropogenic and agricultural activities throughout studied region. Thus, the aim of this study was to assess the mineralogical and geochemical compositions depending on the parent rock in order to estimate soil nutrients and possible source of plant contamination that are potentially hazardous to human and animal life in the Franceville region.

MATERIALS AND METHODS

Location and geological setting

The Paleoproterozoic Francevillian basin, located in southeastern Gabon (Figure 1-A), is composed of four intracratonic sub-basins: Booué, Lastourville, Okondja, and Franceville. The basin is filled of 1.0 to 2.5-km-thick siliciclastic sedimentary succession, commonly referred to as the Francevillian Group (Bouton et al., 2009). These sediments bed uncomfortably on the Archean crystalline basement within the west Congolese craton. The Francevillian Group is divided into five lithostratigraphic formations, labeled FA, FB, FC, FD and FE, from de oldest to the youngest. The lower formation, FA, is dominated by fluviatil conglomerates and sandstones. The topmost part of the FA formation is marked by post-depositional formation of U ore deposits in association with bitumen (Guauthier-Lafaye and Weber, 2003; Bankole et al., 2016). The overlying marine FB formation is subdivided based on the lithostratigraphy into FB1 member, mainly characterized by greenish shales and manganese-rich black shales (Reynaud et al., 2017), followed by FB2 member characterized by massive sandstones frequently intercalated by black shale layers, and black shales with siltstones interbedded (Reynaud et al., 2017). The overlying FC formation consists of shallow marine deposits of massive dolostones and cyanobacteria-hosting striomatolitic cherts with intercalation of black shale beds. The FD formation is composed of trangressive marine black shales with interbedded volcanic tuffs, while the uppermost FE formation contains arkosic sandstones (Thiéblemont et al., 2014).

The top layers of soil profiles developed from different parent rocks in the Franceville sub-basin were investigated. Specifically, the top layer of ferralsol profiles were developed from sandstones, black shales and cherts of FA, FB and FC formations, respectively. The Franceville region is characterized by a colonising forest / savanna mosaic, an annual rainfall of 1,800 mm and an average monthly temperature which varies between 21 and 28°C. The main soil types of Franceville result from a strong weathering, under the hydrolysis processes; this leads to the rapid destruction of weatherable minerals in FA (sandstones), FB (black shales) and FC (cherts) formations and massive neogensis of news minerals, clays and ferric hydrates.

Soil sampling

The top layer of soil profiles developed from sandstones (Ssa), black shales (Sbl), and cherts (Sch) in Franceville sub-basin were sampled at 0-20 cm depth (Figure 1-B). The main soils properties previously studied by Guichard and Lavaud (1980) and Mabika Obame et al., (2021) were summarized in Table 1. Generaly, the soil pH is moderately acid (4.1 to 4.9) and poor in organic matter (OM) content (3 à 6%). Additionally, the mean C/N values less than 25 were in accordance with those observed in Gabon regions. In Franceville region, investigations carried out from 187 soil samples confirm that the top layer of soil profiles were chemically poor, with an acidic pH (Mabika Obame et al., 2021). However, the soil parameters seem to be influenced by the parent rock nature. According to soil texture, the soil from the sandstone formation (FA) is sandy-clay, thus giving it good porosity and friability, favoring the root penetration, whereas the two soils from black shales (FB) and cherts (FC), respectively clay-loam and clay, show a strong compactness limiting the root penetration inside the aggregates (Table 1). The high cation exchange capacity (CEC) observed in soils developed from black shales (13 to 17.5 me/100 g) compared to soils from cherts (9.5 to 12.3 me/100 g) and sandstone (5 to 12 me/100 g) can be attributed to his higher smectite clay and organic matter contents (Table 1). Moreover, the illite / kaolinite association in soils from sandstone and black shales formations reflects the intensity of kaolinization, while its absence in soils from chert formation indicates a ferrallization process.

Soil analyses

The soil samples used in our study were air-dried and 63µm-sieved. The mineral composition of soil samples was studied by means of X-ray diffractometry (XRD). Samples were scanned on a Bruker D8 Advance diffractometer using Cu-Kα radiation and LynxEye positive sensitive detector in 2 - 70° 2 Theta range at the Department of Geology of the University of Tartu in Estonia. The quantitative mineralogical composition of the samples was interpreted and modeled by using the Rietveld algorithm-based program with an accuracy within approximately ±3 wt.%, as described by Hillier (2003).

The concentrations of major elements SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, Na_2O, K_2O, MnO, SO_3 and P_2O_5 in soil samples were analysed using a X-ray fluorescence (XRF) Rigaku Primus II spectrometer on fused lithium tetraborate glass disks, using a PANalytical MagiX Pro PW2540 spectrometer at the Department of Geology, University of Tartu (Estonia). The major elements were reported in weight percent (wt.%) with a detection limit of 0.01 wt.%. Loss on Ignition (LOI) was determined after heating the samples to 950°C in a furnace for 30 minutes.

The metallic compositions of the pulverized soil samples were determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES) and inductively coupled plasma–mass spectrometry (ICP-MS) by a method adapted from Briggs (2002). The sample was decomposed using a near-total three-acid (nitric, hydrofluoric, and perchloric) digestion at a temperature between 125 and 150ºC.

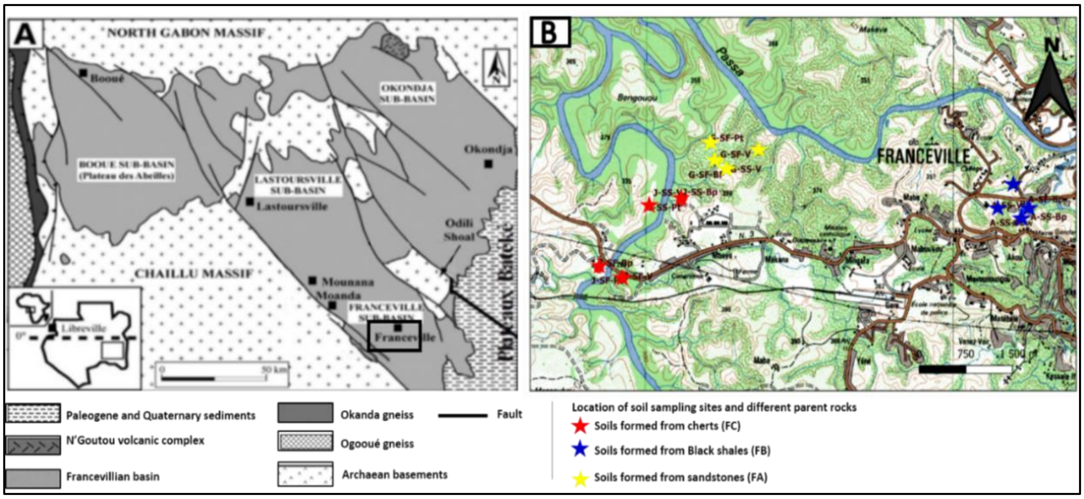

Figure 1: (A) Geologic map of the Paleoproterozoic Francevillian basin with included sub-basins, and (B) the location of soil sampling sites of the study areas.

Table 1: Parameters of arable soil layer of Franceville region form different parent rocks.

Parameters	**Soil from cherts (Sch)**	**Soil from black shales (Sbl)**	**Soil from sandstone (Ssa)**
Granulometry %			
clay	43.5 - 44	38 - 43	25.5 - 29
loam	20.3 - 20.6	41 - 43	3 - 6
sand	25 - 25.3	6 - 7	15 - 40
Texture	Clay	Clay loam	Sand clay
Organic matter(OM) %			
OM total	3 - 5	3.2 - 6	3
C/N	16.6 - 18.8	11.6 - 16	~ 18.4
pHeau	4.7 - 4.9	4.1 - 4.2	4.4 - 4.8
CEC (me/100 g)	9.5 - 12.3	13 - 17.5	5 - 12
P_2O_5 total (%)	0.85 - 0.95	0.5 - 0.6	0.3
Fe_2O_3 total (%)	9.1 - 9.3	3 - 3.6	3.5
Clay minerals content (%)	Kaolinite (~ 56.5), goethite (16.3), gibbsite (5)	Illite (25.2), kaolinite (13.6), smectite (7.1), goethite (2.7), gibbsite (1.9)	Kaolinite (20.5); illite (13), goethite (4), residues (60.5)

Sources: Guichard and Lavaud, (1980); Mabika Obame et al. (2021).

Legend: OM: Organic matter; C: Carbon; N: Nitrogen; CEC: Cation exchange capacity.

RESULTS

Mineralogical characteristics

The percentages of the various minerals found in the studied soils are presented in Table 2. The main minerals present in soils developed from stromatolitic cherts (Sch) were quartz (22.7 to 49.9 wt.%), kaolinite (11.8 to 55.5 wt.%), illite/k-mica (16.9 to 20.7 wt.%), goethite (2.4 to 17.9 wt.%), smectite (0.7 to 10.8 wt.%), halloysite (5.2 to 6 wt.%) and anatase (1.3 to 2.6 wt.%) (Table 2). Kaolinite and quartz were the dominant components. The non-clay minerals constituted < 21 wt.% in all samples with Fe-bearing mineral, goethite dominating. Both Sch_03 and Sch_04 soil samples show greater amounts of kaolinite (35.9 - 55.5%), goethite (8.8 - 17.9%) and anatase (1.3 - 2.6%).

In soils developed from black shales (Sbs), quartz and illite/k-mica were the dominant minerals (>32 wt % each) followed by kaolinite (7.7 to 19.5 wt.%), smectite (5.4 to 12.1 wt.%) and halloysite (4.6 to 5.6 wt.%) (Table 2). The non-clay minerals, including essentially goethite, gibbsite and hematite, constituted < 9 wt.% in all samples. Gibbsite was present mainly in minor amounts (1.8 to 2.8 wt.%).

Soils developed from sandstones (Ssa) were mainly composed of quartz, illite/k-mica, kaolinite, and goethite. Quartz was the dominant mineral (78.8 to 85 wt.%), followed by kaolinite (7.8 to 9.1 wt.%) and illite (7 to 8.9 wt.%) (Table 2). Here, non-clay minerals included trace Ti-bearing mineral, anatase, and Fe-bearing minerals. These later constituted < 3.2 wt.% in all the samples. Goethite were present mainly in minor amounts.

Major oxides

The average values of the major oxide concentrations are given in Table 3. The soils developed from sandstone (Ssa) had higher SiO_2 (85.4 to 90.6%) and lower Al_2O_3 (2.5 to 5.7%) amounts, and SiO_2/ Al_2O_3 ratio (15.4 to 35.7) values were greater compared to those obtained with soils developed from cherts and black shales. The Al_2O_3, Fe_2O_3 and TiO_2 values were higher in both soils developed from cherts and black shales (Table 3). In these two last soils, Loss on ignition (LOI) was higher than in soils developed from sandstone. The variation of the SiO_2/Al_2O_3 ratios in soils formed from cherts and black shales (2.4 to 4.4) indicated a higher degree of weathering, compared to soils formed from sandstone (15.4 to 35.7) (Table 3). The soil sample developed from cherts number 3 (Sch_03) presented higher contents of kaolinite, goethite, and anatase, and a more advanced hydrolysis intensity (SiO_2/Al_2O_3 = 2.4), compared to all the other samples in this study ($SiO_2/Al_2O_3 > 3$). The lowest levels of CaO, MgO, K_2O, MnO and Na_2O were obtained for soils developed from sandstone.

Fe_2O_3 was strongly correlated with TiO_2, Al_2O_3, MnO and P_2O_5 (r = 0.97, 0.65, 0.93 and 0.76; respectively). The results indicated a very strong positive correlation between TiO2 and Fe_2O_3 (r = 0.97), and MnO (r = 0.97) and Al_2O_3 (r = 0.59). Significant positive correlation between SiO_2 and quartz content (r = 0.98) was observed in all soil samples, whereas significant negative correlation (- 0.93) was obtained between SiO_2 and Al_2O_3 (Table 4). The Na_2O content was positively correlated with Al_2O_3 and MgO with correlation coefficients of r = 0.63 and 0.95, respectively (Table 4), suggesting that Na was mainly associated with silicate minerals.

Sulphur oxide (SO_3) showed high positive correlation with SiO_2 (r = 0.81) and negative correlations with Al_2O_3 (r = - 0.66), Fe_2O_3 (r = - 0.78), TiO_2 (r = - 0.79) and MnO (r = - 0.72) (Table 4). The significant positive correlation between LOI and Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO and MnO (r = 0.88, 0.76, 0.76, 0.62, 0.59, and 0.65, respectively) (Table 4) confirmed that the main contributors to LOI were clay minerals and oxides of Fe and Ti. The highest LOI value obtained for Sch_03 soil sample developed from a doleritic intrusion in cherts confirmed highest kaolinite, goethite and anatase contents in this soil sampled from the basaltic rock.

Trace elements

The trace elements data are shown in Table 5. Soils developed from sandstone contained the lowest concentrations of all heavy metals, compared to soils developed from cherts and black shales. In soils developed from sandstone, As, Ba, Cd, Co, Cr, Zn, La, Mn, Ni, P, Pb, Sc, Sr, Th and U concentrations were generally lower than that of the average composition of upper continental crust (UUC) as revealed by Rudnick and Gao (2014); indicating an uncontaminated soil. However, in the soils developed from cherts and black shales the As, Ba, Cd, Cu, La, Pb, Rb, Th and U concentrations were strongly higher than that of the average composition of UCC, indicating a possible anthropogenic input. Among soils with higher heavy metals concentrations than average of UCC composition, those developed from cherts, contained higher amounts of As (2.1 to 21.9 ppm), Ba (110 to 2170 ppm), Pb (16.7 to 24.3 ppm), Rb (7.7 to 98.8 ppm), Th (12.5 to 16.3 ppm) and U (2.0 to 4.3 ppm), whereas those developed from black shales were more riched in Cd (2.5 to 8.4 ppm), Cu (14.7 to 49.8 ppm) and La (35.5 to 47.5 ppm) (Table 5). Highest concentrations of As, Ba, Pb, Rb, Th and U were obtained from soil sample developed from cherts number 3 (Sch_03), collected from a doleritic intrusion located in cherts. These metal contaminated soils could be potential hazard to human health.

Table 2: The summary of mineralogical data in 12 top soils samples in the study area.

	Quartz	K-feldspar	Illite/K-mica	Smectite (Illite-Smect)	Kaolinite	Halloysite	Gibbsite	Anatase	Hematite	Goethite
Sch_01	49.9	-	16.9	10.1	13.1	5.2	tr	tr	tr.	4.1
Sch_02	47.7	-	20.7	10.8	11.8	6.0	-	tr	-	2.4
Sch_03	22.7	-	-	0.9	55.5	-	-	2.6	0.4	17.9
Sch_04	53.1	-	-	0.7	35.9	-	-	1.3	-	8.8
Sbl_01	34.7	-	24.9	12.1	19.5	5.4	-	-	1.2	2.1
Sbl_02	39.8	-	32.4	5.7	11.2	4.6	2.4	-	0.6	3.2
Sbl_03	37.5	-	33.3	5.6	11.5	5.2	2.8	tr	0.7	3.2
Sbl_04	35.0	-	37.8	5.4	7.7	5.6	1.8	tr	0.7	5.7
Ssa_01	80.0	0.8	8.3	-	8.3	-	-	-	-	2.4
Ssa_02	78.8	-	8.9	-	9.5	-	-	-	-	2.7
Ssa_03	85.0	-	7.0	-	7.8	-	-	-	-	-
Ssa_04	82.1	-	8.4	-	9.1	-	-	0.1	-	-

Legend: Sch: Soil sample from cherts; Sbl: Soil sample from black shales; Ssa: Soil sample from sandstone; _01: Soil sample number 1; _02: Soil sample number 2; _03: Soil sample number 3; _04: Soil sample number 4.

Table 3: Major oxides contents (wt %) and LOI in the studied soils samples.

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	MnO	SO_3	P_2O_5	LOI950	Si02/Al203
Sch_01	68.06	15.51	4.68	0.587	0.03	0.23	0.20	1.94	0.005	0.15	0.049	9.16	4.4
Sch_02	68.86	15.69	3.60	0.756	0.03	0.21	0.27	2.27	0.007	0.15	0.057	8.90	4.4
Sch_03	46.43	19.75	**15.33**	**2.692**	0.02	0.20	0.01	0.41	0.069	0.14	0.072	**15.38**	**2.4**
Sch_04	68.48	15.96	8.03	0.924	0.01	0.16	0.01	0.16	0.015	0.15	0.035	7.06	4.3
Sbl_01	63.74	21.06	4.67	0.562	0.01	0.25	0.81	2.25	0.012	0.15	0.046	7.13	3.0
Sbl_02	66.82	19.46	4.12	0.766	0.00	0.34	1.08	1.17	0.006	0.15	0.037	6.42	3.4

Sbl_03	64.38	19.79	5.03	0.715	0.01	0.36	1.10	1.21	0.008	0.15	0.044	7.33	3.3
Sbl_04	62.47	19.65	4.25	0.682	0.02	0.34	1.25	1.23	0.013	0.15	0.056	10.38	3.2
Ssa_01	85.84	5.39	0.82	0.155	<0.01	0.16	0.01	0.57	0.001	0.15	0.012	4.02	15.9
Ssa_02	87.04	5.67	0.88	0.162	<0.01	0.16	<0.01	0.61	0.001	0.15	0.016	4.87	15.4
Ssa_03	90.63	2.54	0.72	0.192	<0.01	0.05	<0.01	0.16	0.003	0.16	0.007	2.26	35.7
Ssa_04	89.21	4.25	0.98	0.097	<0.01	0.14	0.01	0.56	0.002	0.16	0.005	3.06	21.0

Legend: Sch: Soil sample from cherts; Sbl: Soil sample from black shales; Ssa: Soil sample from sandstone; _01: Soil sample number 1; _02: Soil sample number 2; _03: Soil sample number 3; _04: Soil sample number 4.

Table 4: Correlation matrix of the major oxides in the studied soils

	Quartz	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**MnO**	**SO_3**	**P_2O_5**	**LOI950**
Quartz	1												
SiO_2	**0.98**	1											
Al_2O_3	**-0.98**	**-0.93**	1										
Fe_2O_3	**-0.75**	**-0.87**	**0.65**	1									
TiO_2	**-0.72**	**-0.84**	0.59	**0.97**	1								
CaO	0.17	-0.04	-0.57	0.03	0.09	1							
MgO	-0.74	**-0.63**	**0.80**	0.22	0.21	-0.40	1						
Na_2O	-0.53	-0.31	**0.63**	-0.17	-0.14	-0.47	**0.95**	1					
K_2O	-0.47	-0.35	0.53	-0.07	-0.07	0.38	0.51	0.38	1				
MnO	**-0.60**	**-0.74**	0.45	**0.93**	**0.97**	0.10	0.06	-0.22	-0.19	1			
SO_3	**0.73**	**0.81**	**-0.66**	**-0.78**	**-0.79**	-0.14	-0.43	-0.22	-0.17	**-0.72**	1		
P_2O_5	**-0.93**	**-0.95**	**0.88**	**0.76**	**0.76**	**0.62**	**0.59**	-0.22	0.51	**0.65**	**-0.78**	1	
LOI950	**-0.85**	**-0.92**	**0.75**	**0.87**	**0.88**	0.49	0.45	-0.17	0.27	**0.81**	**-0.85**	**0.94**	1

Table 5: Heavy metals (ppm) contents in the studied soils.

Samples	**As**	**Ba**	**Cd**	**Co**	**Cr**	**Cu**	**Zn**	**La**	**Mn**	**Ni**	**Pb**	**Rb**	**Sr**	**Th**	**U**
Sch_01	3.4	1850	1.65	1	65	16.6	22.00	32.6	53	13.8	16.7	95	54.10	12.50	2.00
Sch_02	2.1	2170	2.93	1.2	54	13.4	20.00	50.5	74	10.8	17.3	98.8	72.90	14.35	2.50
Sch_03	21.9	150	1.59	8.5	84	91.9	52.00	15.1	456	25.6	24.3	21.2	38.80	16.30	4.30
Sch_04	15.5	110	2.4	2.5	69	22.4	23.00	17.7	101	13.6	17.1	7.7	17.90	13.40	3.30
Sbl_01	5.6	1250	5.82	1	66	14.7	37.00	35.5	134	25.6	17.4	107	114.50	10.95	2.00
Sbl_02	12	410	4.1	0.9	66	48	22.00	40	64	28.8	19.4	75.7	122.00	11.65	3.90
Sbl_03	14.5	440	8.37	1	74	49.8	29.00	45.8	80	27	21.5	77.8	127.50	12.55	3.80

Sbl_04	12.4	450	2.48	1.7	73	46.9	26.00	47.5	116	26.6	23.1	76.4	135.00	11.85	3.60
Ssa_01	1.2	520	0.68	0.4	14	3.7	8.00	6	21	2.2	5.1	25.3	7.80	4.12	1.20
Ssa_02	1	550	0.5	0.5	14	3.9	7.00	10.9	27	2.3	5.7	26.6	8.70	5.01	1.40
Ssa_03	0.7	80	0.59	0.3	8	2.7	5.00	3.3	22	1.9	2.9	8.5	4.00	2.59	0.60
Ssa_04	1	380	0.71	0.4	10	4	5.00	8.4	26	1.9	3.1	18.9	4.60	2.43	0.80
UCC	*4.8*	*624*	*0.09*	*17.3*	*92*	*28*	*67*	*31*	*-*	*47*	*17*	*84*	*320*	*10.5*	*2.7*

Legend: Sch: Soil sample from cherts; Sbl: Soil sample from black shales; Ssa: Soil sample from sandstone; _01: Soil sample number 1; _02: Soil sample number 2; _03: Soil sample number 3; _04: Soil sample number 4.

DISCUSSION

Results revealed high predominance of quartz, illite/mica, kaolinite and goethite in studied soils. The same average abundances of kaolinite and goethite were observed by Guichard and Lavaud (1980) in top soils developed from cherts formation in Franceville sub-basin. Generaly, The presence of kaolinite coupled with gibbsite is indicative of high degree of weathering of the soils. The formation of gibbsite could be either through neoformation from the progressive dissolution of kaolinite through the hydrolyze process under intense weathering (Schaefer et al., 2008). However, the few gibbsite content in soils indicates low Al and Fe oxide minerals which enhanced the soil fertility by a great P sorption on soil particles (Hart et al., 2003) and on the retention of plant nutrient elements against leaching under high rainfall (Gilkes and Prakongkep, 2016). In soils developed from cherts, greater amounts of kaolinite and goethite coupled with anatase indicate doleritic intrusions from scherts formation. Indeed, at the local scale, the sedimentary formations of the Franceville sub-basin are affected by doleritic intrusions (Bouton et al., 2009) which are basic vein rocks rich in Si, Fe, Al and Ti oxides. The presence of anatase goethite and trace of hematite could be attributed to the relative accumulation by weathering of mafic minerals rich in Ti and Fe. Further dissolution of the associated weatherable mafic minerals will aid the release of nutrient elements to plants (Gilkes and Prakongkep, 2016). The mineralogical analysis defines the main stages of ferralsols evolution in the study area. According to typical minerals and paragenesis, the combination between illite, Kaolinite and oxy-hydroxides of Fe in all soils, confirms that our studied soils are mainly ferrallitic soils which result from partial hydrolysis of primary minerals by bisiallitization and monosiallitizatrion processes. The low quantities of gibbsite (1.8-2.8%) obtained only in the soils from the black shales, indicates an advanced stage of weathering by a still timid allitization process. These ferrallitic soils tend towards oxidic soils, often characterized by typical minerals which are gibbsite - ferric hydrates. However, the few weatherable minerals relative to the sandstone can explain the absence of gibbsite and less percentage of kaolinite and goethite in soil matrices (Beuria et al., 2017).

The average major oxide contents are in line with the mineralogical composition of studied soils. In the studied soils, high SiO_2 content is due to the abundance of quartz in agreement with the strong significant positive correlation between SiO_2 and quartz content ($r = 0.98$) as well as negative correlation (- 0.93) between SiO_2 and Al_2O_3. The high concentration of Fe_2O_3 may be attributed to the presence of other iron-bearing phases in the soil such as iron oxides (goethite, hematite) (Abou El-Anwar et al., 2018). The very strong positive correlation between TiO_2 and both Fe_2O_3 ($r = 0.97$) and MnO ($r = 0.97$) indicated the major role of iron and manganese oxides in

Ti distribution. Also, the positive correlation between TiO_2 and Al_2O_3 (r = 0.59) indicated that clays minerals constituted another source of Ti. The SO_3 content can result to weathering of primary sulphuric minerals such as pyrite generally present in the siliciclastic sedimentary rocks of Francevillian basin, and principally in the black shales of Francevillian B formation (Ndongo et al., 2016). During the alteration of these sedimentary rocks, S and Si were concomitantly evacuated (r = 0.81), while Al, Fe, Ti and Mn accumulated on site, which explains the strong negative correlations between these last elements precipitants and S. The variation of SiO_2/Al_2O_3 ratios suggests different degrees of weathering (Schaefer et al., 2008). Soils from cherts and black shales with lower ratios (2.4 to 4.4) have experienced relative higher degree of weathering compared to soils from sandstone (15.4 to 35.7). The Al_2O_3, Fe_2O_3 and TiO_2 contents and higher Loss on ignition (LOI) values in both soils developed from cherts and black shales compared to soils developed from sandstone could be attributed to their higher percentages in illites, smectite, kaolinite, goethite and gibbsite with chemically bound water in their matrices (Beuria et al., 2017). However, higher amounts of Fe_2O_3 and TiO_2 in soil developed from scherts formation (Sch_03 sample), compared to that of the average composition of upper continental crust (UUC) recorded by Rudnick and Gao (2003) confirm the presence of doleritic intrusions through the chert formations (FC) which constitutes the parent rock for Sch_03 soil profile. Indeed, the iron and titanium enrichment in this soil sample may be strongly controlled by the source rock composition, essentially basaltic, and riched in ferromagnesian minerals (Baioumy, 2014; Abou El-Anwar et al., 2018). Minerals in dolerite with higher crystallisation temperatures alter faster to more stable secondary minerals compared to minerals in cherts, black shales and sandstone with lower crystallisation temperatures (Ibarra et al., 2016).

Generally, As, Ba, Cd, Cu, La, Pb, Rb, Th and U concentrations in soils developed from cherts and black shales are strongly higher than that of the average composition of upper continental crust (UUC) recorded by Rudnick and Gao (2014), indicating an anthropogenic input. Metal contamination has a negative effect on soil fertility, water quality, and could be carried to human food chain causing great health risk (Lu et al., 2015; Salman et al., 2017). The enrichment in Ba, Cd, Cu and U may be, partially related to a bioconcentration of the above elements by soil organic matter such as humins. The surprising enrichment in As, Pb in the top soil may also be related to biological fixation of these elements (Agyeman et al., 2022). The enrichment in U in the studied soils from Franceville sub-basin can result from leaching during the alteration of the FA formation sandstone rocks of the Francevillian basin rich in U element (Gauthier-Lafaye and Weber, 2003). Such processes include the uptake of metals by plants, or by microbes acting as catalysts during microbial activity. Over the acid pH range recorded in this study (4.1 - 4.9), metals such as Cd, Cu and Pb are mobile and can be adsorbed by clay minerals or Fe-Mn-oxides in the form of hydroxide complexes (Yu et al., 2023).

Conclusion

This study revealed that the dominant mineral in the studied soil samples was quartz, followed by clay-minerals including illite/k-mica, kaolinite, smectite and halloysite. Other trace minerals present were goethite, gibbsite, hematite and anatase. The combination between illite, Kaolinite and Fe oxy-hydroxides in all soils indicates that the studied soils were mainly ferrallitic soils which resulted from partial hydrolysis of primary minerals by bisiallitization and monosiallitizatrion processes. However, the degree of weathering was higher in soils from cherts and black shales than in soils from sandstone, richer in quartz. The highest values of Fe_2O_3 and TiO_2 were obtained in soil samples covering doleritic intrusions through the chert formations. The presence of trace elements (As, Ba, Cd, Cu, La, Pb, Rb, Th and U) in soils developed from cherts and black shales with concentrations strongly higher than that of the average composition of UCC indicates their anthropogenic input. The potential risk of foodstuff metal contamination and hazard to human health remains higher in soils developped on doleritic intrusions from chert which present higher concentrations in heavy metals.

COMPETING INTERESTS

The authors declare that they have no competing interests.

AUTHORS' CONTRIBUTIONS

NOZA conceived the study design, sample collection and formal data analysis, reviewed the literature, wrote the first draft and proofread the final manuscript. VN and MM were implied in the sample collection, formal data analysis and manuscript revision.

All authors contributed to the article and approved the submitted version.

ACKNOWLEDGMENTS

Authors wish to thank Kalle Kirsimae (University of Tartu, Geology Department, Tartu, Estonia) for mineralogical compositions and geochemical analyses.

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