Mineralogical and Geochemical Characterization of Clay and Lacustrine Deposits of Lake Ashenge Basin, Northern Ethiopia: Implication for Industrial Applications

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ABSTRACT

The paper tries to characterize and evaluate clay, lacustrine and diatomaceous earth deposits of Lake Ashenge basin, near Koram, northern Ethiopia and comment on its industrial implications. The country rocks are dominantly basalts and basaltic agglomerates overlain by minor amounts of rhyolite and ignimbrite. Sedimentary deposits, clays and associated sediments include 1) intercalations of lacustrine diatomaceous earth, other lacustrine and clays with channel deposits (gravel, pebbly sand and silt); 2) intercalations of diatomaceous earth, peat and clays with channel deposits exposed; and 3) intercalations of clay with channel deposits.

X-ray diffractometer analysis of clay samples indicates kaolinite as a dominant clay mineral among others. On the basis of the abundance of different minerals, the clays are subdivided into four groups, 1) Kaolinite (K), 2) Microcline-Kaolinite (MK), 3) Muscovite-Kaolinite (MuK), and 4) Muscovite-Microcline-Kaolinite (MuMK). Other minor mineral phases include quartz, vermiculite, low-high albite, calcite and calcite magnesia. Diatomaceous clays are almost free from kaolinite. Kaolinite, being the dominant clay mineral varies from 6% in light brown to 77% in light grey clays. Al_2O_3 and SiO_2 dominate the clay geochemistry among other oxides and based on the Al_2O_3 content, the kaolinite variety is subdivided into highAl_2O_3 (16-21 wt %) and lowAl_2O_3 (8-13 wt%) types. Higher Al_2O_3 and similar SiO_2 and Fe_2O_3 values in clays compared to the source basaltic rocks are related to the topography, mineralogy and climatic conditions that exist in the area. Compared to the low grade kaolinite type (about $56*10^6$ tones), diatomaceous earth variety ($77.3*10^5$ tones) is relatively of good quality with high SiO_2 content.

Key words: Clay and lacustrine deposits, Kaolinite, Diatomite, Lake Ashenge, Tigray, Ethiopia.

1. INTRODUCTION

The term "clay" refers to a naturally occurring material composed primarily of fine-grained minerals,<2µm (esd equivalent spherical diameter), which is generally plastic at appropriate water contents and will harden when dried or fired (Guggenheim & Martin, 1995). The term "clay" is applied both to materials having a particle size of less than 2 microns and to the family of minerals that has similar chemical compositions and common crystal structural characteristics (Velde, 1995). Although clay minerals belong to phyllosilicate group, clays may also contain other minerals which may impart plasticity. Clays may be composed of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate, and metal oxides. Clay minerals are seldom mono-mineralic and have no genetic significance, as it is used for residual weathering products, hydrothermally altered products, and sedimentary deposits (Murrey, 2007). These minerals occur under a fairly limited range of geologic environments which include soil horizons, continental and marine sediments, geothermal fields, volcanic deposits, and weathering rock formations. In general, they form where rocks are in contact with water, air, or steam and the type of clay however is controlled by the composition of pre-existing rock mineralogy.

Prolonged and extensive weathering alters the primary rock forming minerals to clay minerals and under favorable conditions leads to the development of clay deposits of economic interest. For example bentonite, primarily composed of montmorillonite, used as light- drilling mud; and also used in ceramic industry. The weathering processes involve physical disaggregation and chemical decomposition that changes the original rock forming minerals to clay. Weathering on different rocks is uneven, and products of many stages of breakdown are found in the same clay sample. Clay minerals are determined by their chemical composition, layered structure and size. Clay minerals can be categorized into four subgroups: (1) kaolinite; (2) smectite (montmorillonite, saponite); (3) mica (illite), and (4) chlorite (Shichi and Takagi, 2000; Nayak and Singh, 2007; Burhan et al., 2010).

In Ethiopia, clay and lacustrine sediments are found in many parts of the Ethiopian rift valley as well as in smaller depressions/basins on the Ethiopian highlands. They are found in association with Tertiary-Quaternary sediments on top of the stratigraphic records. However, comprehensive studies are not yet been taken up on these clays and associated lake sediments in terms of mapping, characterization, quality and quantity. The growing demand for mineral exploration and the mineral resource utilization for speedy development of the country, efforts are being made to outline the areas potential for mineral resources for detailed studies and exploitation. Present paper is an outcome of one such effort conducted in and around Ashenge Lake area to study the clay and lacustrine deposits in terms of their distribution (space and time), mineralogy, geochemistry, quantity etc.

1.1. The Study Area

The Lake Ashenge is located in the southern zone of Tigray Region, 160 km south of Mekelle city and is bounded by UTM E550000-580000m and N1385000-1400000m (Fig. 1). It is one of

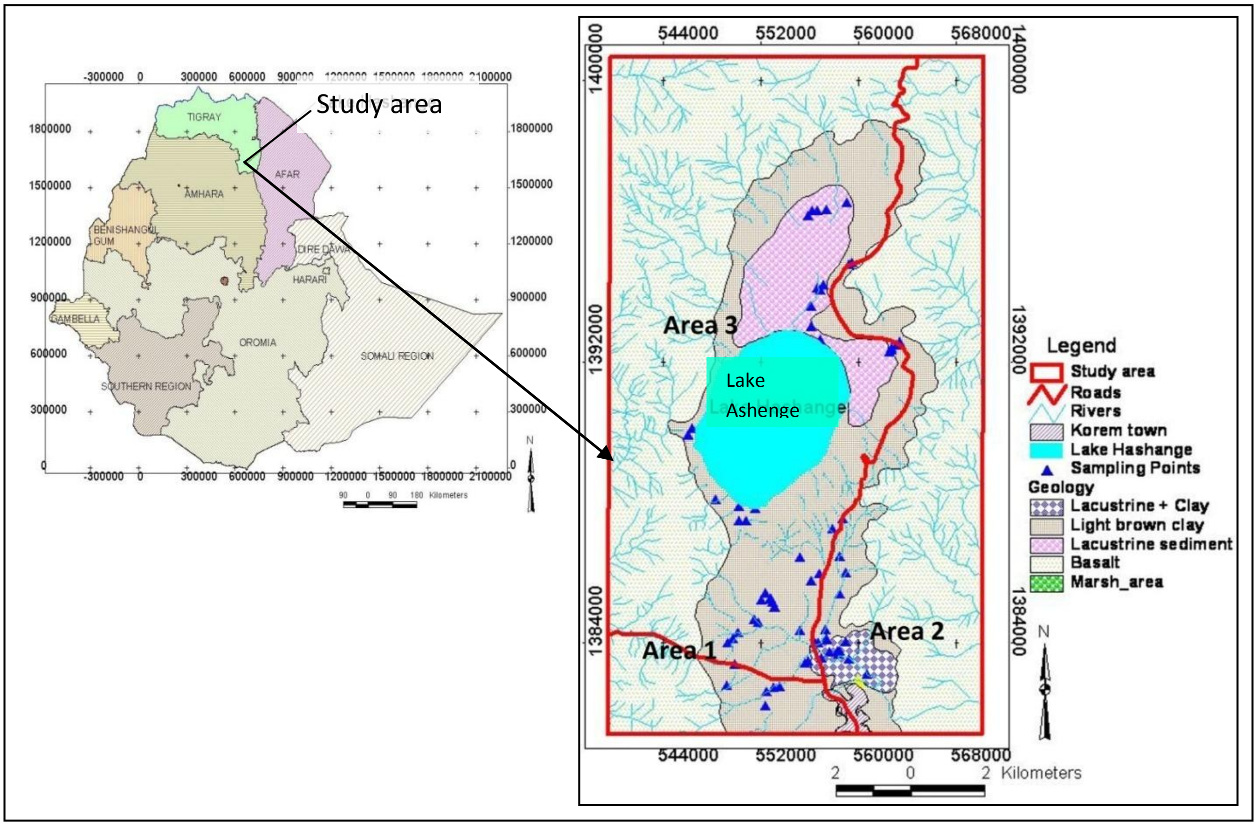


Figure 1. Location and geological map of Lake Ashenge.

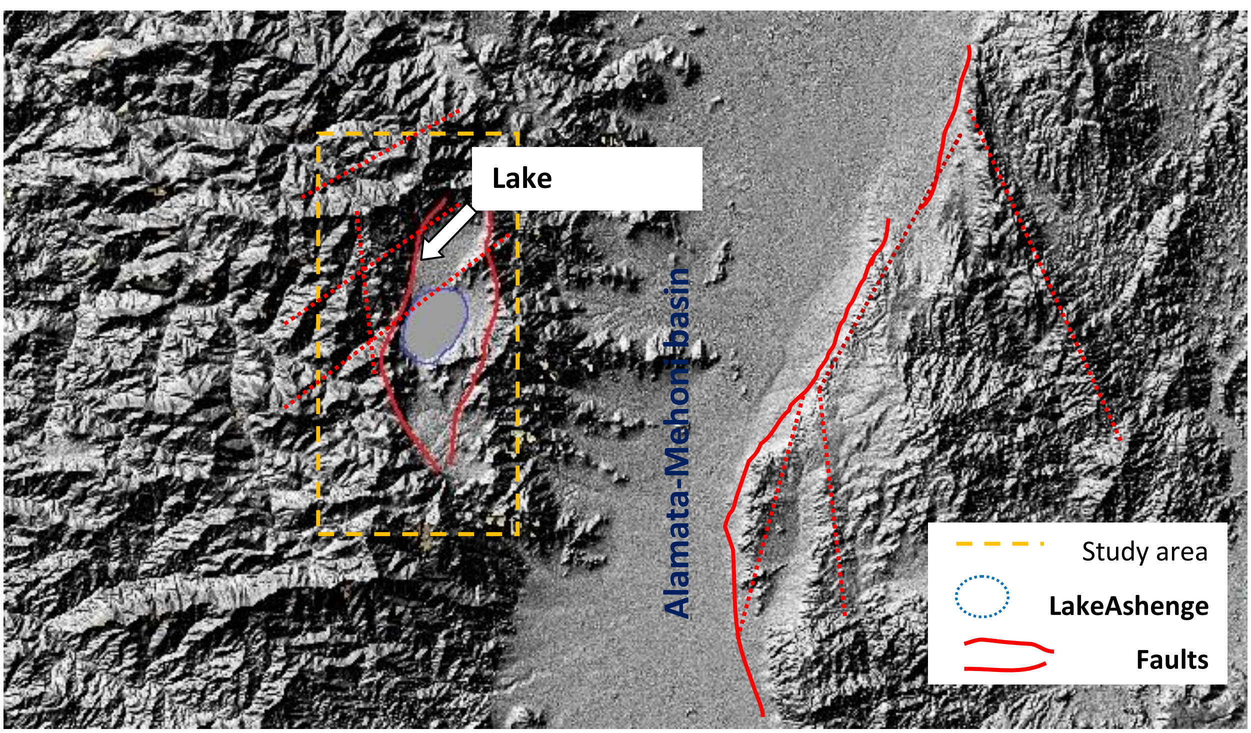


Figure2. Digital Elevation Model (DEM 30m resolution) of Lake Ashenge and the surrounding Alamata-Mehoni basin.

the highland lakes of northern Ethiopia situated at an elevation of 2450 m above mean sea level. Meteorological data collected for the last 28 years (1976-2005m) was obtained from the nearby Korem Meterological Station, 9 km south of Lake Ashenge. As most of the Ethiopian highlands, the lake basin is characterized by biannual nature of precipitation with a mean annual precipitation of 979 mm summer rains mostly between June and September. Mean monthly air temperature varies from 13-19°C.

Lake Ashenge lies in a faulted graben of mid-Tertiary flood basaltic sequences (Marshall et al., 2009). The basin is bounded by NNE-SSW faults producing escarpments running sub-parallely in the eastern and western margins, finally tapering and closing in the southern and northern margins of the lake basin (Fig. 2). Similar structural depression features are observed north of Lake Ashenge basin around Korem, Maychew, Ayiba and Adihisho areas. The lake catchment is characterized by sparse drainage pattern, where most of the major intermittent streams are aligned i.e. NW-SE of the lake and the marsh areas.

2. GEOLOGICAL SETTING

2.1. Regional Geology

Ethiopian geology mainly comprises of Precambrian metavolcano-sedimentary basement (17%), Paleozoic-Mesozoic sedimentary (22%), and Cenozoic-Quaternary dominantly volcanic and minor sedimentary rocks (60%). Weathering of these rocks has produced eluvial and alluvial deposits that form the Quaternary cover. Some of these have resulted in the development of commercially viable clay deposits present on the valley floor and inter-mountain depressions derived from the Ethiopian Flood basalts of the Plateau (Pik et al., 1998), as basin fill and cover sediments on the underlying bed rocks. The basin fill sediments are composed of unconsolidated material ranging from gravel to clay and lacustrine sediments. At Lake Ashenge the clay deposits forms the cover over NW Ethiopian Flood basalt sequences, predominantly basaltic rocks (Kabeto, 2010).

2.1.1. The NW Ethiopian Flood Basalt Sequences

During Tertiary time, Ethiopia-Kenya-Yemen were under fire due to the deep mantle plume (Afar and Kenya) activity and volcanism was robust and the early works of Berhe et al. (1987)

and others classified the Ethiopian volcanics into four Formations of different ages (60-20 Ma): Ashenge basalt, Ayiba basalt, Alaje basalt and rhyolite and Terma Bere Formations. However, such subdivision is avoided as the new data by Hoffman et al. (1997) suggests 30 Ma (mid-Tertiary) age for the NW Ethiopian Trap series dominated by alkali basalts. Pik et al. (1998) have classified these 30 Ma alkali basalts (NW Ethiopian Flood Basalts) into three distinct groups based on the trace element and Ti concentrations: low-Ti basalts (LT), high-Ti1 (HT1) basalts and high-Ti2 (HT2) basalts. They have recognized a suite of ‘low-Ti’ (LT) basalts restricted to the northwestern part of the province assumed to be derived from depleted mantle. Alkali basalts found to the south and east of the province on the other hand show higher concentrations of incompatible elements and more fractionated REE patterns and related to the so-called ‘high-Ti’ basalts (HT1 and HT2), which are exposed in the Lake Ashenge area (Fig. 3). Recently, Kabeto (2010) have further studied the geology and geochemistry of the flood basalt sequences including the study area and subdivided the volcanic piles in to six sequences with a preserved thickness of ~ 2 km. Out of six, four sequences (Sequence 2 to 5) are present in Lake Ashenge area.

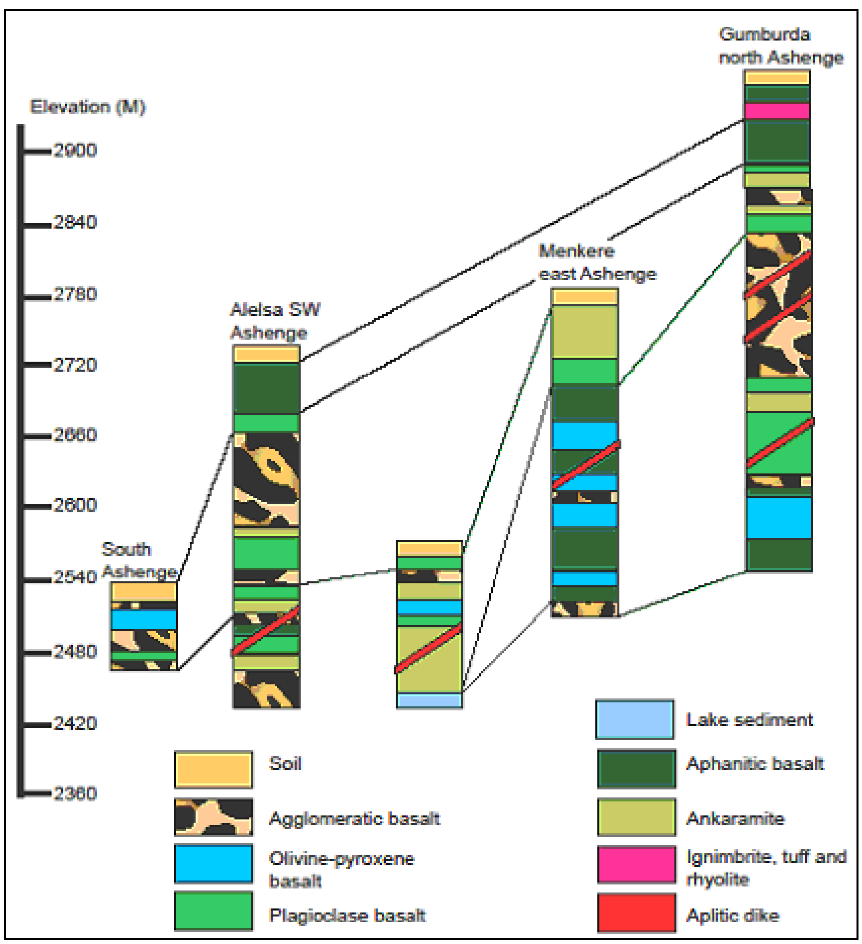


Figure 3. Columnar sections of the basaltic sequences, Ashenge Lake area.

2.2. Geology of the study area

The geology of the study area comprises of basaltic sequences, light brown clay, clay and lacustrine sediments intercalations, and lacustrine sediments (Fig.1). The volcanic sequences in the area exhibit different degrees of weathering but more intense towards the central plain areas of the basin. Geotectonic-related features are like brittle deformation in volcanic rocks common in this area. Recently formed Quaternary sediments of fluvio-lacustrine origin overlie the basaltic rocks.

2.2.1. Basaltic sequences

The detailed log section of Ashenge volcanics is shown in figure 3. The volcanic successions in the region reveal six cycles, referred as sequences by Kabeto (2010). Out of six, sequences 1-4 are related to mafic-agglomerate volcanism (exposed between 1800-2900m a.s.l), in which basanites and alkaline basalts and transitional ankaramites occupy the base (sequences 1, 2 and 3) followed by silica-rich tholeiitic to transitional sequence 4. This is followed by sequence 5 of mafic-felsic volcanism (2900-3450m) and is covered by tholeiitic to transitional basalts of sequence 6 (3450-3780m); and represent the last stage of flood basalt volcanism in the eastern part of NW Ethiopian plateau flood basalts. The upper three sequences extend upto Shire through Hagereselam, Adigrat and Axum areas in the west, in Ashenge area, sequence 2, 3, 4, and 5 are exposed. These are different varieties of stratified volcanic rocks (of mainly basaltic composition) including (aphanitic and porphyritic basalts, picritic basalts, agglomeratic basalts, pyroxene-olivine phenocryst-rich basalts/ankaramites, plagioclase-pyroxene-olivine phenocryst-rich basalt and plagioclase-rich basalt (Fig. 3).

3. METHODOLOGY

Fieldwork was conducted in three phases in the area to obtain required data. Initially many field traverses were taken on selected ridges and columnar sections where rocks and thick sediments are better exposed were examined. Detailed geological/stratigraphic logs were prepared for selected sections where the clay and associated sediments show better exposures. 65 sediment samples about 0.5 Kg each were collected, out of which 21 representative samples were selected for clay minerals analysis using X-ray Diffractometer (XRD)and 11 for major, minor and trace element geochemical analysis using X-ray Fluoroscence Spectrometer (XRF). In most cases, XRF is coupled with XRD to determine the chemical and mineral compositions of clay samples (Ehinola et al., 2009). Both XRD and XRF analyses were done in Ethiopian Geological Survey Geoscience Central Laboratory, Addis Ababa. Samples were ground in a clean agate mortar to obtain minus 10µm size. The powder sample is filled and pressed in a specimen holder and pushed into the goniometer chamber of XRD machine (BRUKER AXS, D8 Advanced). The machine was set at operating voltage of 35KV and ampere of 40mA and run from 4 to $64^{0}2\theta$. It was run according to the DIFFRAC^{plus}2000 software package instructions and the diffractogram with 2θ versus peak intensities were obtained. The values for 'd' were calculated accordingly and processed using the EVA /search match/ program from DIFFRAC ^{plus} 2000 software package for mineral identification and quantification. The data is given in table 3. In the case of XRF, the sample pellets prepared by combining the binding material were analyzed for major and minor oxides and trace elements. The data is given in tables1 and 2.

Table 1. XRF analysis data for major and minor oxides in clay and sediment samples (wt.%).

Sample	***SiO_2***	***Al_2O_3***	***Fe_2O_3***	***CaO***	***MgO***	***Na_2O***	***K_2O***	***TiO_2***	***P_2O_5***	***MnO***	***SO_3***	***CO_2***
A1S9	84.22	2.66	2.31	0.93	0.52	<0.01	0.31	0.45	0.041	0.02	0.13	12.1
A1S10	26.02	1.92	2.52	34.42	1.39	<0.01	0.36	0.68	0.14	0.05	0.23	33.1
A2S8A	47.06	19.09	15.5	3.31	1.42	0.13	0.63	3.36	0.257	0.14	0.01	10.6
A2S8B	46.35	20.89	15.22	1.78	2.02	<0.01	1.15	2.19	0.24	0.16	0.00	22.3
A2S10A	46.56	15.88	16.83	2.51	3.54	0.39	2.1	4.55	0.374	0.20	0.01	8.5
A2S12B	64.29	13.02	7.9	2.15	1.73	1.25	3.79	0.94	0.171	0.23	0.02	6.4
A2S13A	66.98	8.4	9.99	1.53	3.8	<0.01	1	2.09	0.204	0.09	0.01	8.5
A3S12A	52.15	1.88	1.79	21.5	1.33	<0.01	0.31	0.31	0.124	0.05	1.36	21.3
A3S12B	18.93	0.96	1.12	41.8	1.32	<0.01	0.14	0.31	0.117	0.06	0.06	35.7
A3S21	64.22	11.93	7.71	2.84	0.81	3.18	5.09	1.07	0.173	0.21	0.04	4.58
A2S6AS	63.25	12.32	7.77	2.56	1.02	4.6	4.95	1.59	0.203	0.14	0.02	3.8

Table 2. XRF data for trace elements in clay and sediment samples (ppm).

Sample no	***V***	***Cr***	***Co***	***Ni***	***Zn***	***Ga***	***Rb***	***Sr***	***Nb_2O_5***	***Ta_2O_5***
A1S9	174	150	11	21	108	<5	8	50	67	99
A1S10	108	76	10	13	103	<5	12	606	96	<1
A2S8A	199	384	43	61	146	24	17	256	144	<1
A2S8B	174	98	39	65	134	43	29	247	281	<1
A2S10A	346	105	54	32	65	131	14	300	114	<1
A2S12B	178	53	17	33	146	33	91	150	233	<1
A2S13A	255	150	32	65	131	14	29	166	<1	<1
A3S12A	92	19	11	8	113	9	6	384	<1	<1
A3S12B	46	26	<5	7	98	<5	<5	772	<1	6

A3S21	79	<5	18	8	139	27	156	106	357	<1
A2S6AS	123	53	26	7	133	26	100	232	297	<1

Table 3. Clay and other minerals (%) based on XRD data, LakeAshange basin.

S.No.	***Sample No***	***Kaolinite***	***Microcline***	***Muscovite***	***Quartz***	***Calcite Magnesia***	***Vermiculite***	***Calcite***	***Albite High***	***Albite Low***
1	A2S10A	34.4	58	-	7.6	-	-	-	-	-
2	A3S15	30.7	57.3	-	12	-	-	-	-	-
3	A3S6	33.9	-	-	7.4	-	-	-	58.7	-
4	A2S13	73.1	-	-	-	-	26.9	-	-	-
5	A3S21	32.3	48.4	-	9.7	9.6	-	-	-	-
6	A2S12A	30.7	-	59.9	8.3	-	1.2	-	-	-
7	A2S1	21.6	38.7	-	5.1	-	-	-	34.6	-
8	A2S6AS	76.9	-	-	23.1	-	-	-	-	-
9	A3Sd	30.7	-	60	-	-	1.2	8.7	-	-
10	A2S13B	24.8	-	66.2	9	-	-	-	-	-
11	A2S8B	76.9	-	-	-	-	23.1	-	-	-
12	A1S4	37.4	55.2	-	7.4	-	-	-	-	-
13	A2S10B	14.8	22.2	33	4.5	4.4	-	-	-	21.1
14	A1S3	29.2	58.9	-	-	11.8	-	-	-	-
15	A1S10	30	58	-	-	-	-	11.9	-	-
16	A2S11	16.3	-	45	5.7	-	-	5.6	27.4	-
17	A3S20	5.7	35.4	51.3	7.5	-	-	-	-	-
18	A3S13	8.7	-	24.1	67.2	-	-	-	-	-
19	A3S12A	-	-	-	49.8	50.2	-	-	-	-

4. RESULTS AND DISCUSSION

4.1. Clay and associated Lake sediments

It is well known that the type and the proportions of individual clay minerals in sediments are linked to the sediment supplying source rocks, weathering conditions on the land and transportation mechanisms (Biscaye, 1965; Liangbiao and Liu, 1999). Weathering products from the different volcanic units are the sources of the clay and lacustrine deposits in the area. The volcanic rocks in the study area are strongly weathered and easily washed out during rainy seasons and entered the basin during the last 17000 years (Marshall et al., 2009). The majority of the silt- and sand-sized sediment is deposited in the streams draining to Lake Ashenge, whereas clay-sized sediments are dispersed dominantly in the central parts of the basin.

For convenience, the study area is divided in to three (Fig. 1): Area 1, around the Lake basin, Area 2, around northeast of Korem town, and Area 3, around northwest of Korem town. The clays and associated sediments and logs are discussed accordingly as Area 1 (Ashenge); Area 2 (NE Korem) and Area 3 (NW Korem) (Fig.4).

Generally, the sediments in the Lake catchment and surrounding areas vary from purely lacustrine origin like white diatomaceous earth, and light brown to black clays intercalated with conglomeritic and rarely cross and graded bedded fluvial channel sand deposits of variable sizes. Most of the lake catchment area is covered by the extensive recent black cotton soil, upto 4 m thick. Hence, lacustrine and clay sediment exposures in most localities are found in wider river channels and gullies (Fig. 4, Area1). The thickness of these sediments is found exposed in a river cut in the western margin of the basin ranging upto 30m and show presence of successive units of light brown, fine-grained clay beds (0.5-2m thick), and intercalated with successive channel deposits of conglomeratic sand beds (~ 8m thick) (Fig. 4). The clays typically show soapy property, slicken slide nature, plastic character and at places reacts with dilute HCl indicating presence of carbonate minerals and in some sections as calcrete.

4.1.1. Lake Ashenge area

The sediment sequence in Ashenge area is exposed between 2455 to 2495 m and subdivided into the lower and upper sub-units. The lower sub-unit is characterized by intercalations of diatomaceous earth and light brown clay and channel deposits and exposed below 2480 m altitude. The maximum exposed thickness of this sub unit is found at the base of a river cut valley within the swampy area of the Lake (Fig.4, Area 1) and NW and NE of Korem areas. Together with this sub-unit, there are thin beds of peat deposits, deep black colored and loose sediments rich in organic matter (Fig. 4, Area 2). These peat beds have a maximum thickness of 30 cm, and seem laterally restricted to the present day marshy areas located close to the vicinity of the Lake.

The diatomaceous earth and white lacustrine is extensive further towards the south and south eastern parts of areas outside the present day lake line. Its thickness varies from a few cm up to 6 m, thickening towards the lake center (Fig. 4, Area 1). It is intercalated with fossiliferous (gastropod shells& broken fragments) dark and muddy beds. They consist predominantly of sediment types, mostly calcareous diatomaceous earth and calcareous mud and at places changes to diatomaceous clay. Based on the reaction with dilute HCl, diatomaceous sediments exposed in the area are categorized into two, non-reactive and reactive. The reactive ones not only indicate presence of carbonate minerals but also show high CaO and low SiO_2 contents. They too grade to diatomaceous clay, which are microcline-kaolin, type (Tables 1 & 2). The non-reactive on the other hand are SiO_2 -rich and with very low CaO contents (Table 2). This sediment is thinly laminated and floats on water being very low in specific gravity. Clays in the area generally vary in color from light brown to brown, dull grey to grey, and dark brown to black. All these sediment exposures are overlain by the recent soils of about 10 to 20 cm thick.

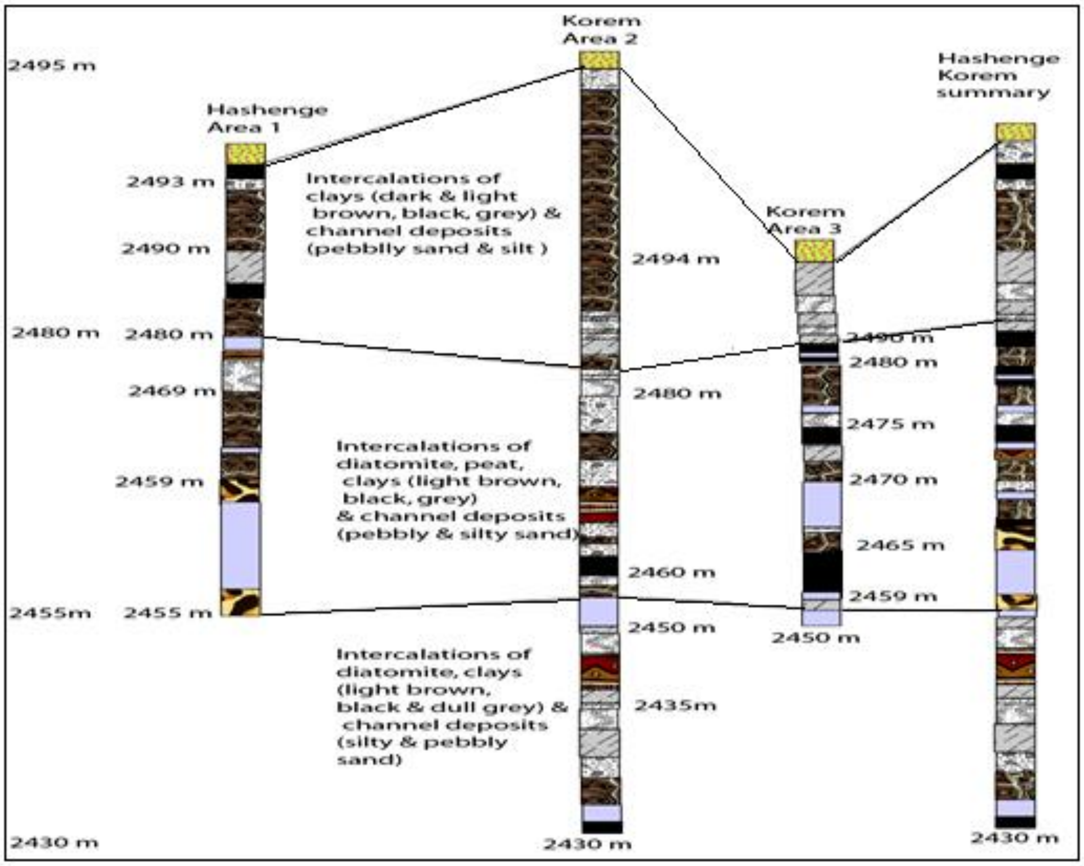


Figure 4. Columnar sections of Ashenge (Area 1);NE of Korem (Area 2);NW of Korem (Area3) and summary of Area 1, 2 & 3 sections [Scale =1 meter; numbers below the section and given in the left side indicate elevation/altitude above mean sea level in meters].

The light brown to brown clay layers are the second abundant in the lower sub-unit (Fig. 4). This is the clay-dominant sediment found in the area. The clay shows slicken slide surfaces with typical conchoidal fractures and also plasticity. It is dominant in the Korem than the Ashenge basin. Presence of secondary carbonate (calcrete) and organic materials and sub-rounded pebbles though rare are also common within the fractures resulting in higher loss on ignition in geochemical analysis. The channel deposit materials are immature, poorly sorted, ranges in sizes from the fine silt to a very coarse boulder (pebbly). The boulders are commonly rounded to sub-rounded. Laminations of sand, silt and coarse materials ranging in thickness from cm to few 5 m are common and the profiles rarely show upward coarsening.

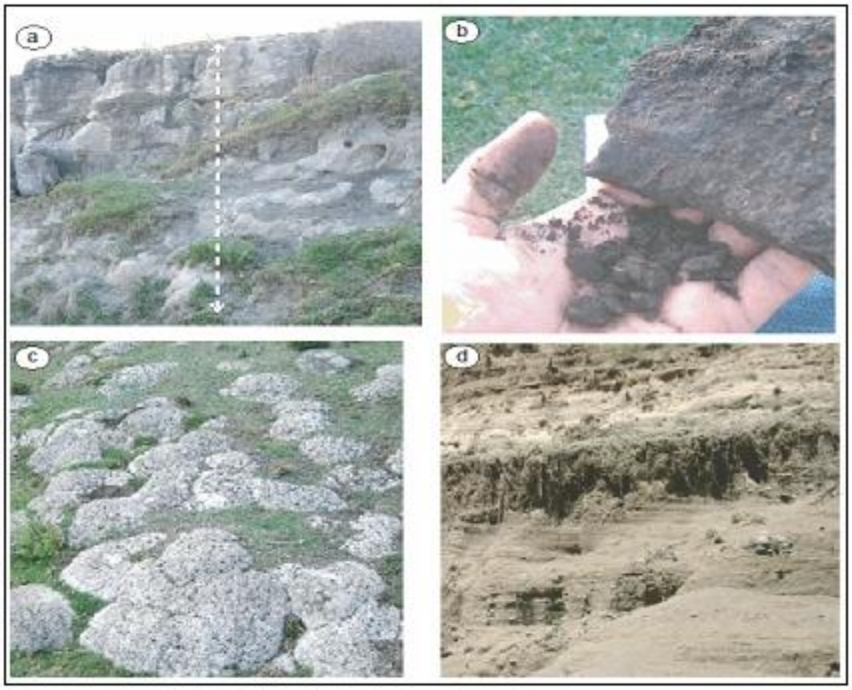


Figure 5. Field photo showing (a) thick lacustrine sediment, diatomaceous Lake sediment, (b) organic material rich sediment, peat at the base of the same section, (c) stromatolite around Lake Ashenge (south eastern part), and (d) light grey and light brown clay layers above the channel sand deposit NE of Korem town.

The upper unit dominantly consists of light brown, dark and dull grey clay and is exposed between 2480 m and 2495 m. In most log sections, the lower portion of the upper unit is characterized by pebbly sand and dull grey clay layer intercalations (Fig. 5). At places black clay layer also overlie this unit. Stromatolites are observed in the northern parts of the Lake between 2450 to 2495 m a.s.l. The stromatolite colony with size up to 1m are grown on basalt boulders and bed rocks indicating the paleoshore line of the lake and mimic the circular to semi-circular shape of the basalt boulders and beds (Fig. 5c). The white colored stromatolite domes are calcareous in composition, actively reacts with diluted HCl. The stromatolite columns about 2m in size relatively occur at higher elevation, 2465m. They seem to have grown on jointed basalt rocks and sometimes woods of tree. The stromatolite colonies and diatoms are known to be important in terms of interpretation of past lake level, and environmental as well as hydrological conditions (Marshall et al., 2009). The exposure of these shallow water stromatolite colonies at a higher elevation, ~30 m higher than the present day lake level is an indication that the lake shore was at a higher elevation than the present level. The lacustrine sediments intercalating with clays are dated to be around 17000 years (Marshall et al., 2009).

4.1.2. NE Korem area

Columnar sections made around north and northeastern parts of Korem town (Fig 4, Area 2). Here the sediment is subdivided in to three: Lower, Middle and Upper sub-units. The lower part is similar to that of Ashenge basin area, however, the lacustrine and clay deposits are exposed at about 2430 m much below the Ashenge basin area and are thinner. The middle sub-unit is dominantly intercalation of light brown clay and channel deposit (gravel, pebbly sand and silt). At places, the color of the sub-unit becomes light grey to dull (Fig. 4, Area 3). This sub-unit is exposed between 2460 and 2480 m elevations and has thin black clay layer at its base. At about 2480m the channel deposits form the base of the upper light brown clay sub-unit. The upper sub-unit is dominated by the light brown clay (Fig. 4, Area 2) and is as thick as 5 m and is overlain by pebbly sand to clay intercalations.

4.1.3. NW Korem area

Columnar section made around northwestern part of Korem town (Fig 4, Area 3). The sediment log sections indicate lower and upper units. The lower unit comprises of lacustrine sediments, light brown clay and black clay intercalations with rare pebbly sand clay intercalations and the upper unit with intercalation of light brown to dull grey clay with few layers of pebbly sand and clay intercalations.

The summary of the logs in figure 4 indicates comparison of the dominant clays and associated diatomaceous and other sediments in the three areas. It is possible to generalize that the clays and associated sediments can be grouped into three sub-units from base to top. Sub-unit 1 is intercalations of clays (commonly dull grey) diatomaceous earth and channel deposits (silty and pebbly sand) exposed from between 2430 m and 2455 m. The sub unit is exposed on surface only in Korem area. Sub-unit 2 is intercalations of diatomaceous earth, peat, clays (commonly light brown) and channel deposits (commonly sand and silty sand) exposed between 2455 m and 2480 m. Peat is only exposed in Ashenge area and diatomaceous earth is not observed in Korem area 2 within 2455 m to 2480 m elevations. Rather, there channel deposit and light brown clays intercalate. Black clay predominates in Area 3. Sub-unit 3 is exposed between 2480 and 2495 m. Clays (light to brown and dark & black) and channel deposits intercalations form the top section in this area. Light brown and dark brown clays dominate Area 2 and Area 1, respectively. Lack of lacustrine sediments above 2480 m suggests the highest Lake level at Ashenge is around 2480 m. This is also in confirmation with the observation of stromatolite at 30 meter above the current lake level (Marshall et al., 2009).

4.2. Mineralogy and chemistry of the clays and associated lake sediments

XRD data show the presence of kaolinite as major mineral. Based on kaolinite and other associated minerals the clays subdivided into four types (Table 3 & Figs. 6, 7a, b, c, & d): 1) Kaolinite (Kal), 2) Microcline-Kaolinite (Mc Kal), 3) Muscovite-Kaolinite (Mu Kal), and 4) Muscovite-Microcline-Kaolinite (Mu Kal McK). However, considering XRD patterns and the intensity peaks, it is observed that clays samples A2S6AS, A2S8B, and A2S13 (all from Area 2) are the richest clay in kaolinite whereas the Mc Kal clay sample (from the three areas) is the second richest in kaolinite. However, the third (Mu Kal) and fourth (Mu Kal Mc) varieties are poor in kaolinite. Other associated minor minerals include quartz, vermiculite, albite, calcite and calcite magnesia (Table 3).

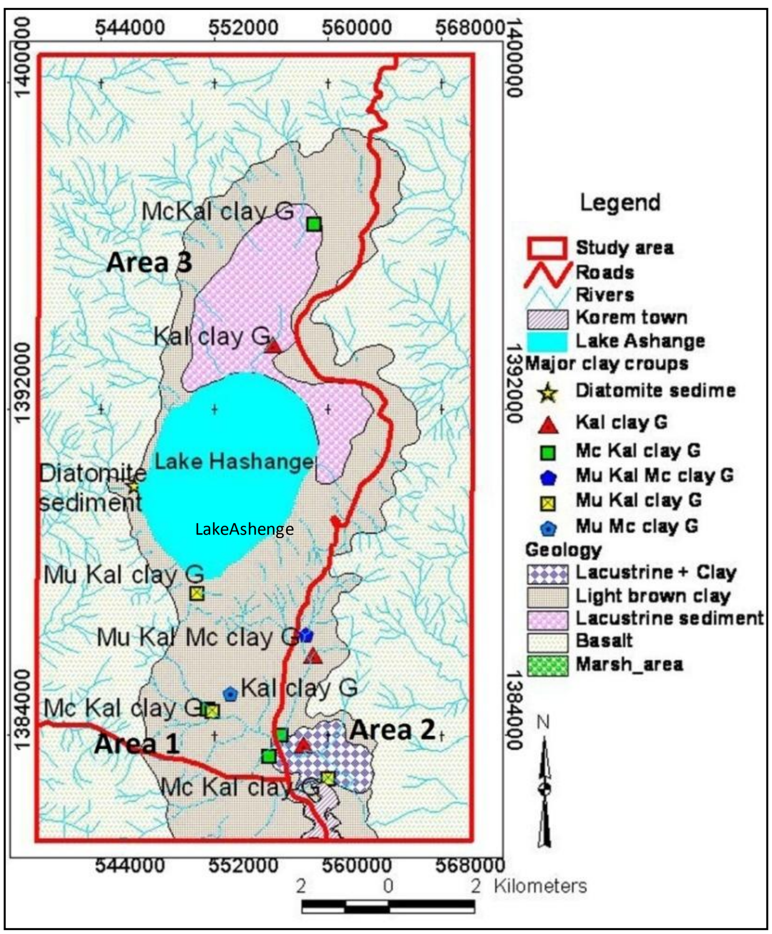
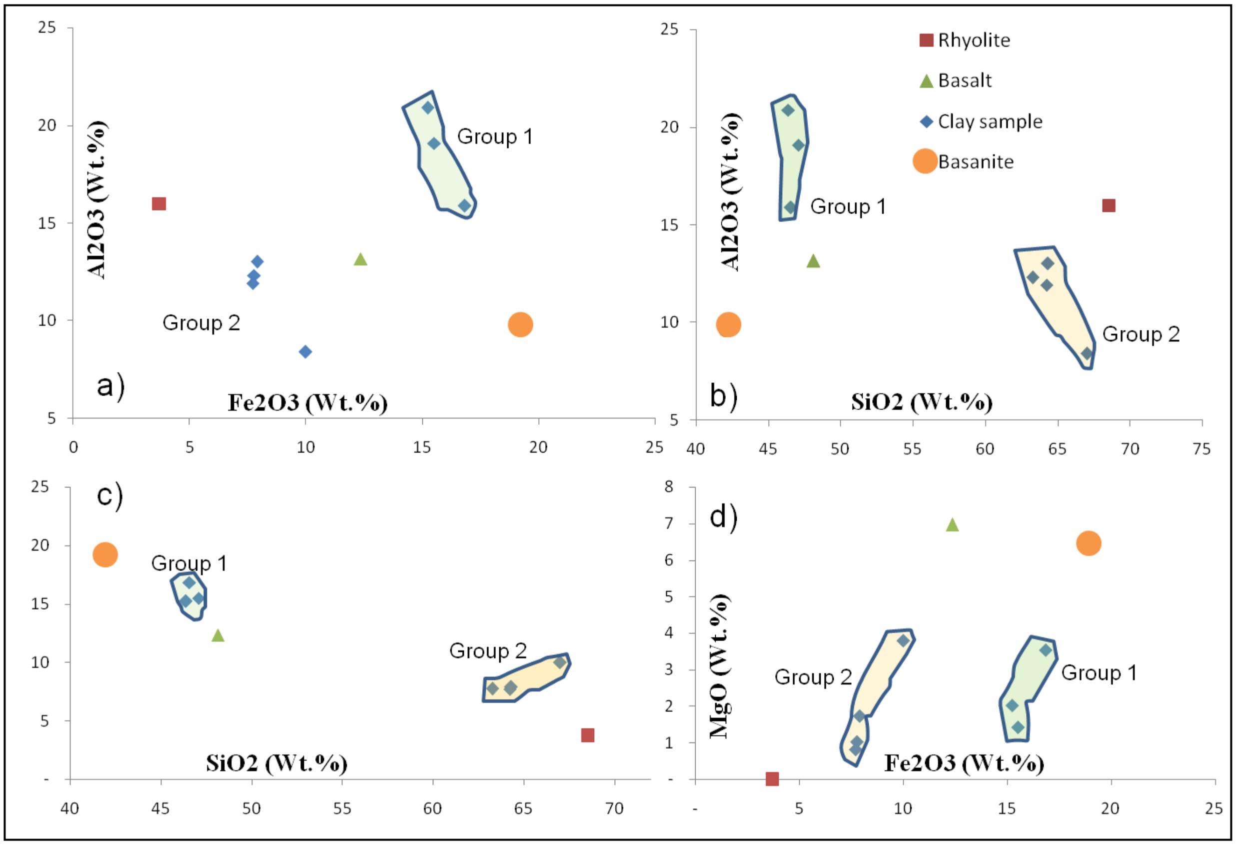


Figure 6. Distribution of clay and associated minerals in and around Lake Ashenge area.
Data suggests that there is no significant aerial variation in the mineralogy of the sediments. However, samples taken from Area 2 have the highest kaolinite contents and relatively pure compared to the impure variety from Area 3. Compared to Saudi Arabia and Nigerian clays (Mohsen and El-maghraby, 2010; Aref and Rong, 2009; Ehinola et al., 2009), the Ashenge clays are low-kaolinite variety (Table 3). The kaolinite content in the area varies from 6 to 77% whereas in the Saudi Arabia's deposit it varies from 40%to 84%. The associated minerals, quartz, montmorillonite, albite and hematite reported in Saudi Arabia and Nigeria clays is similar to the clays of the study area but the relatively high content of the quartz and calcite in some clay samples affects the kaolinite contents and makes it impure (Tables 1 & 3). The diatomaceous earth samples analyzed by XRD (A1S9, A3S12A and A1S10) show two types, with clay and without clay. The sample A1S9 is silica-rich diatomite and the other two are calcareous varieties of diatomaceous clays (Table 1).

XRF data (Tables1 and 2) for major and trace elements for Ashenge clay and diatomaceous earth samples indicate predominance of $Al_2O_3$and SiO_2oxides and followed by Fe_2O_3, CaO, MgO, TiO_2, K_2O and Na_2O. The remaining oxides are present in trace amounts. On the basis of XRD, XRF and field observation it is clear that diatomaceous clays have the highest CaO concentrations and low Al_2O_3 and Fe_2O_3 contents compared with other clays (Tables 1 & 2). The CaO contents indicate the calcareous sediment input, whereas the low Al_2O_3 concentrations are due to lower intensity of alterations of the rocks into clays. Among different types of clays, kaolinite and MK clays as expected show low SiO_2 content except samples A3S21 and A2S6AS (Table 1) and high Al_2O_3. On the other hand, MuK clays show higher SiO_2 and lower Al_2O_3values.

Though relatively, Al_2O_3, SiO_2 andFe_2O_3 are almost similar to Saudi Arabia white, red and grey and Nigerian clays, differ from the ideal kaolin and pure kaolin from UK and Saudi Arabia (Mohsen and El-maghraby, 2010; Aref and Rong, 2009; Ehinola et al., 2009) (Table 3). The Ashenge samples are characterized by high content of Fe_2O_3, TiO_2 and MgO indicating the dominant source basaltic rocks compositions. Relatively high content of Fe_2O_3 might explain the brownish color of the clay samples. The Al_2O_3 contents of the unweathered basaltic rocks (basalt and basanite) in the region is less than in the kaolinite clays, however, SiO_2 and Fe_2O_3 contents in clays are similar to that of the basaltic rocks and felsic rocks in the region (Kabeto et al., 2009;

Kabeto, 2010). Plots shown in figure 7, further suggest two distinct groups in the Ashenge clays, with high-Al_2O_3 and low-Al_2O_3 contents. The low-Al_2O_3 clay samples have high SiO_2 and low Fe_2O_3 concentrations, whereas the high-Al_2O_3 clays have low SiO_2 and high Fe_2O_3 contents. However, both types have similar MgO contents (Table 1& Fig. 7d). The low-Al_2O_3 might be attributed to the higher sand content in the samples, as indicated by the gritty feel of the samples



(Atsbeha, 2011).

Figure 7. Plots of major elemental data of Ashenge clays compared with basalt, basanite and rhyolitic rocks in the area (Kabeto, 2010; Kabeto et al., 2009).

Group 1, high-Al_2O_3 clays are generally plotted closer to the basalt and basanite sample fields and group 2, low-Al_2O_3 clays are plotted near the rhyolite sample field (Fig. 7a, b, c, & d). This relation seems to suggest that felsic dominant source (rhyolitic) for group 2 and mafic dominant source (basaltic rocks) for group 1 clays, Further, the clay mineral composition is controlled by the interplay between these different source rocks and the main sedimentary processes taking place in the streams and lake sediment deposition, like the size-sorting processes and bed load structures.

According to Goren et al. (2002), the typical chemical composition of diatomaceous earth is 86% silica, 5% sodium, 3% magnesium and 2% iron. The chemical analysis of the non-clay diatomaceous earth sample (A1S9, Table 1) gave the following major oxide concentrations 84.22% SiO_2, 2.66% Al_2O_3, 2.31% Fe_2O_3, 0.93% CaO, and 0.52% MgO and negligible Na_2O. This suggests the Ashenge diatomaceous earth deposits are of good quality.

4.3 Reserve estimation of the clay and associated sediments

The clay minerals and diatomaceous earth are estimated quantitatively. Estimation of industrial minerals reserves requires geological logging including drilling, geophysical techniques and reliable statistical tool (Ehinola et al., 2009; Salman et al., 2009 and references therein). At the moment our reserve estimation is based on measured exposed thickness of the deposits. Observations were made at 63 stations and 23 vertical sections prepared to delineate horizons of interest (clays and diatomaceous earth) are prepared (Figs. 1 &4). The criteria used to estimate industrial mineral reserve is based on the equation of Ehinola et al. (2009). The reserve is estimated using the below given equation where 'm' is mean thickness; 'ρ' density; and 'A' area.

$$\text{Reserve} = A * m * \rho$$

The mean thickness of the clay deposits and diatomaceous earth is calculated from the maximum and minimum values of the profiles (Table 4). Thus the tonnage is calculated from the total sum areas of each polygon multiplied by the mean thickness and the density of the materials. Accordingly, the rough estimate of the clay minerals and diatomaceous earth reserve is $56*10^6$and $77.3 * 10^5$tons, respectively. This reserve estimate is highly approximate because of lack of drilling data. Four boreholes log data of shallow wells taken from Tigray Water Work Enterprise in the study area indicate the presence of thick clays and associated sediments up to 60 m. Further, core sample 03AL3/2, 8 m thick lake sediments were collected from Lake Ashenge at 8.9 m of water depth (Marshall et al., 2009). This suggests the reserve estimation for the industrial mineral deposits in the area is the minimum.

Table 4. Approximate estimation of clay deposit reserves.

Deposit	Polygon numbers used	Maximum thickness (m)	Minimum thickness (m)	Mean thickness (m)	Area of polygon (m^2)	Volume (m^3)	Density (kg/m^3)	Reserve (ton)
Clay minerals	21	10	0.3	5.15	$4.09*10^6$	$21.1*10^6$	≈2660	$56*10^6$
Diatomaceous earth	11	4	0.2	2.1	$1.647*10^6$	$3.46*10^6$	≈2300	$77.3*10^5$

5. CONCLUSION

This preliminary characterization and evaluation of Ashenge clay and associated diatomaceous earth deposits was based on the chemical and mineralogical composition; and geological mapping and log description of the resources. Three types of clay and associated sediments are identified in the area which include: 1) intercalations of lacustrine diatomaceous earth, (lacustrine) and clays with channel deposits (gravel, pebbly sand & silt) exposed between 2430 m and 2455 m; 2) intercalations of diatomaceous earth, peat and clays with channel deposits exposed between 2455m and 2480 m; and 3) intercalations of clays with channel deposits exposed between 2480 m and 2495 m.

XRD data indicate kaolinite as the dominating clay mineral ranging from 77% to 6%. On the basis of presence of other associated minerals, the clays are grouped into four types 1) kaolinite, 2) microcline-kaolinite, 3) muscovite-kaolinite, and 4) muscovite-microcline-kaolinite. Other minor minerals noted are quartz, vermiculite, albite, calcite and calcite magnesia.XRF data of Ashenge clays suggest dominance of Al_2O_3 and SiO_2 among others. The major elements percentage in chemical composition of kaolinite is similar to some of the Saudi Arabia and Nigeria clays but differ from pure kaolinite and industrial kaolinite deposits of UK and Saudi Arabia. The Ashenge clays are low kaolinite (Al_2O_3 ~16-21%) type and needs to enhance the clay content by different treatments so as to meet various industrial applications. Fe_2O_3 provides brownish color to the clay which is otherwise white. Diatomaceous earth samples with high SiO_2 (84.22%) content is of good quality for industrial use.

Topography, neo-tectonic activities, limited transportation of the sediment and improper separation of non-clay minerals from clays seems to be the major reasons for low grade kaolinite in the area. Rough estimate of the clay minerals and diatomaceous earth reserve indicate presence of about $56*10^6$and $77.3 * 10^5$ tons respectively. The preliminary resource estimation figures suggest that the Ashenge area is a promising future target for clay mineral resource.The occurrence of non clay minerals like quartz, calcite, albite, and vermiculite and calcite magnesia in the clay sediments makes the deposit low grade. Hence, it needs to be processed using different methods of treatment so as to enhance the clay content to meet various industrial applications.

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