MINERALOGICAL STUDIES OF WEATHERED PEGMATITE AROUND KITIBI-IWOYE, SOUTHWESTERN NIGERIA

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ABSTRACT

Weathering profile of pegmatite around Kitibi-Iwoye and Awo mining sites is heterogeneously composed of primary and secondary mineral constituents. Weathered materials obtained from nine dug pits and pegmatite samples were studied with a view to gaining insight into the mineral assemblages constituting the weathered materials. This was achieved by describing the field, petrographic and mineralogical features of the pegmatite and its weathered components. Effect of weathering on the pegmatitic parent rock leading to the evolution of secondary minerals was as well investigated. The authors are not aware of any previous investigation existing in these aspects in the study area.

This study involved geological mapping of the study area. Representative samples of pegmatite were collected for microscopic examination. Unconsolidated weathered mass obtained from the Saprolite and B-horizon was air dried. The loosened mass was sieved and screened to remove organic components and detrital quartz. The pulverized samples were analysed using X-Ray Diffractometry (XRD) technique in the Department of Geological Sciences, University of Cape Town, South Africa.

The Northeastern-Southwestern (NE-SW) trending pegmatites intruded into migmatite gneiss, banded gneiss, diorite and granite. Petrographic studies revealed primary constituent minerals such as K-feldspar, quartz, plagioclase, muscovite, biotite and opaque minerals in the pegmatite. Secondary minerals obtained are illite, kaolinite and goethite. Occurrence of ordered and well crystalline kaolinite was facilitated by weathering of feldspathic, micaceous and accessory minerals as shown by X-Ray Diffractometric studies. Kaolinite was the main secondary mineral while illite and goethite occurred in subordinate amount. This study generally showed moderate to intense degree of weathering.

Key words: Weathering profile, pegmatite, secondary minerals, detrital quartz, kaolinite,

Introduction

Pegmatite is one of the major sources of industrial minerals such as optical quartz, ceramic and dental feldspars, fluorite, biotite, muscovite, refractory spodumene, beryl and tourmaline. These industrial minerals when found in commercial quantity served as raw materials in the manufacture of abrasive, glass, pharmaceutical, paint, rubber, tile and electrical appliances (Okunlola, 1998; Adekoya *et.al*, 2003; Garba, 2003 and Okunlola and Ogedengbe, 2003). Functional application of pegmatite was further described to encompass important source of a broad spectrum of hi-tech metals with general long-range technological potential such as Li, Rb, Cs, Be, Ga, Sc, Y, REE, Sn, Nb, Ta, U, Th and Hf (Androne, *et al*, 2008). Pegmatite at its incipient form was transformed into new component through alteration. End products of weathering (regolith or residual bodies) consist of laterite, clay bodies, fragmented quartz, micas, feldspars, iron bearing and accessory minerals. Regolith also provides cover for the underlying bedrock or parent rock.

Pegmatite of the study area forms an integral part of Ibadan-Oshogbo pegmatite field (Okunlola, 2006). Economic minerals such as beryl, tourmaline, tantalite, feldspar, transparent quartz and kaolinite have been extracted from Awo mining site. Unlike other fields that have been extensively studied, few published works such as that of Akintola, *et al*. (2011) and Adetunji, *et al*. (2016) were reported on pegmatite of Ibadan-Oshogbo field. None of the previous studies addressed mineralogical composition of the weathered profile and pegmatite using X-ray diffraction studies. According to Graham *et al* (1993), weathered mass forms a transition zone between overlying soil component and underlying parent rock. The transition zone retained the rock fabric with obviously altered groundmass. Sample collection is desirable at this zone because the texture, structure and fabric of the parent crystalline rock are preserved (Stolt and Baker, 1994).Stolt and Baker (1994) further noted that lateral and vertical components of the weathering profiles displayed variability from different sampling points. This variability was related to structure, fabric, composition and grain size of the bedrock. According to Velde (1992), rock-atmosphere interface and high temperature silicate minerals become unstable due to change in chemistry of their environment. The new product referred to as clay minerals are extremely fine grained and easily distinguished from coarse grained minerals such as quartz and feldspar (Chipera and Bish, 2001). Clay minerals are described by Schulze (2005) as particulate matters with exceedingly small grain diameter of < 0.002 mm ($<2\mu m$) that crystallize in a sheet-like crystallographic habit in aqueous environment of the earth surface. These crystalline particles were formed by chemical alteration of rock-forming primary minerals such as feldspars, muscovite, biotite, olivine, pyroxene and amphibole (Carroll, 1974). This process involving aqueous-solution occurred at low-temperature and low-pH conditions (Cygan and Tazaki, 2014).Pavich *et al.* (1989) stressed that alteration was driven by reactions with meteoric water which infiltrated into rock fractures and created pathways into the joints and cleavages thereby causing outward weathering of the rock and later producing heterogeneous mass of weathered and relatively fresh rock.

Weathered materials from exposed road cut around Kitibi-Iwoye and Awo were studied so as to identify various primary and secondary minerals and to determine the extent to which hitherto pegmatite had been weathered. This study was achieved by describing the field, petrographic and mineralogical features of the pegmatite and its weathered components that were restricted to two neighbouring villages of similar geological units.

Mapping Technique and Sampling Methodology

The study area was mapped on a scale of 1:10,000. Rock outcrops within the precincts of the exposed weathering profile were sampled and studied for their textural and mineralogical features. Weathered mass developed on parent rock were collected at the saprolite zone using hand auger. The samples were preferentially selected because of relatively high content of clay in them. Bulk samples collected from this zone were free of humus and organic components. In most cases, depth of saprolite from the surface is usually between 10 and 12 meters therefore sampling and description of regolith proved to be difficult. Hence, samples were purposefully collected at road cuts and mining pits of the study area. Nine weathered samples and four fresh pegmatite samples were collected for studies. The weathered samples were air dried for 72 hours to ensure that lumps of clay were free from dampness. Undesirable crystalline silica minerals, organic matter and impurities were removed from the clay so that experimental results were attributed to clay alone. Hand specimens of parent rock were selected for petrographic and mineralogical studies. In the laboratory, rock samples were disaggregated in a jaw- crusher with tungsten carbide jaw blades and subsequently milled to fineness in a tungsten carbide ball-mill. Rock samples were very difficult to collect within the mining pits or road cuts due to their poor exposure at the surface. However, outcrops of pegmatite around the precinct of the road cut and pits were taken as representative samples.

Weathered samples were pulverised using motorised agate mortar and pestle. The powder was uniformly spread as a thin film of smooth flat surface on glass slide with rectangular slit. Uneven surfaces reduce the intensity of low angle peaks during X-ray absorption. Samples were densely packed and leveled with the upper surface of slide. Ideally, the powdered specimen contains numerous randomly oriented grains so that the crystallites (powdered samples to be analyzed) are at different diffraction angles when the beam of the X-ray strikes them. Mineralogical studies were accomplished using X-ray Diffractometric (XRD) method in the sample preparation laboratory, Department of Geological Sciences, University of Cape Town. X-ray diffraction patterns of clay minerals and pegmatite were obtained using PANanalytical PW 3830 X-ray generator system operated at 40 kV and 25 mA with Cu (Kα) radiation (λ = 1.542A$^{\circ}$). All the samples were scanned from 5 to 75 degrees using a step size of 0.51° 2θ and the counting time is 0.02 second. Identification of phases is based on positions of the lines (in terms of degrees 2θ).The peak angles and spacing obtained were compared with the values of Joint Committee on Powder Diffraction Standards (JCPDS, 1974) and database files of International Center for Diffraction Data (ICDD) which contains reference patterns for more than 70,000 crystalline forms.

Results

Field description of pegmatite bodies and characteristics of weathering profile

The study area is located within the southwestern part of the map (Fig. 1). Thick vegetation protected the regolith which spread over a distance of about 30 meters long and thickness of about 12 meters deep (Figs 2 and 3). These physical parameters and mineral assemblages were similar throughout the sampling points but clay content differs from one sampling point to the other. At the bedrock, lateral component of the profile showed an increasing variability when compared to its vertical component. Weathering profile of road cut at Kitibi-Iwoye and Awo mining pits consists of four different horizons with diagnostic features (Figs. 2, 3 and 4). The topmost horizon is the organic matter horizon or O-horizon. This layer forms above the mineral soil due to deposition of litter of dead plant and animal matter. Plant roots also extend from this zone into weathered rock by penetrating the soil matrix or following rock fractures. This horizon contains >20% organic material by weight and fragmented quartz which are resistant to weathering. A-horizon lies directly below O-horizon. In some parts of the study area, this horizon consists of lateritic soil which is reddish brown in colour. The horizon contains accumulation of organic matter and root of living plant that imparts dark brown or black colour to the soil. B-horizon lies below A-horizon and consists of upper lateritic soil which contains muscovite, quartz and clay materials and the lower layer of weathered pegmatite is rich in kaolinised feldspar, smoky quartz, large sheets of muscovite, beryl and tourmaline. C-horizon (Saprolite zone) lies on top of the parent rock. Saprolite is clay-rich, soft, friable and composed of disintegrated rock formed in place by chemical weathering. The C-horizon consists of mottled brown feldspar, quartz, and pale brown muscovite. Cores of Saprolite at C-horizon and parts of B-horizon were collected at designated intervals for mineralogical studies.

Petrography and modal mineralogy of pegmatite

Modal composition of constituent minerals in pegmatite is shown in Table 1. The pegmatite showed uniform texture and mineralogy which is characteristically coarse grained and composed of quartz, feldspar, muscovite and biotite. Varying amount of accessory minerals such as tourmaline and beryl also occurred in the pegmatite (Fig. 4). Growth of large crystals witnessed in these pegmatites is attributed to complex chemistry of the solution which reached its climax in the last stage of magmatic differentiation (Quirke and Kramers, 1943; Cameron, *et al* 1949). Biotite is generally in shade of brown and green (Fig. 4). Biotite and muscovite often occur in parallel intergrowth where crystals of muscovite sometimes enclose an inner crystal of biotite. The mining site yielded large sheets of muscovite which are sometimes tainted due to presence of rare metals. Muscovite occurred in a quantity that is sufficient to render its mining profitable.

In thin section, quartz occurred as irregular, colourless and anhedral to subhedral crystals with low relief. Hand specimen of plagioclase appeared as colourless to whitish crystals with clearly visible cleavage (Fig. 4). It appeared as grayish to black in colour and sometimes with white striations under cross polarised light. Opaque minerals occurred as black grains with high relief. Microcline is the dominant mineral in pegmatite, its appearance resembles plagioclase but it is distinguished by its pink colour in hand specimen. In thin section, it appeared as colourless to grayish crystals with tartan twinning (Fig. 4). In some portions of the thin section it assumed a cloudy appearance due to alteration.

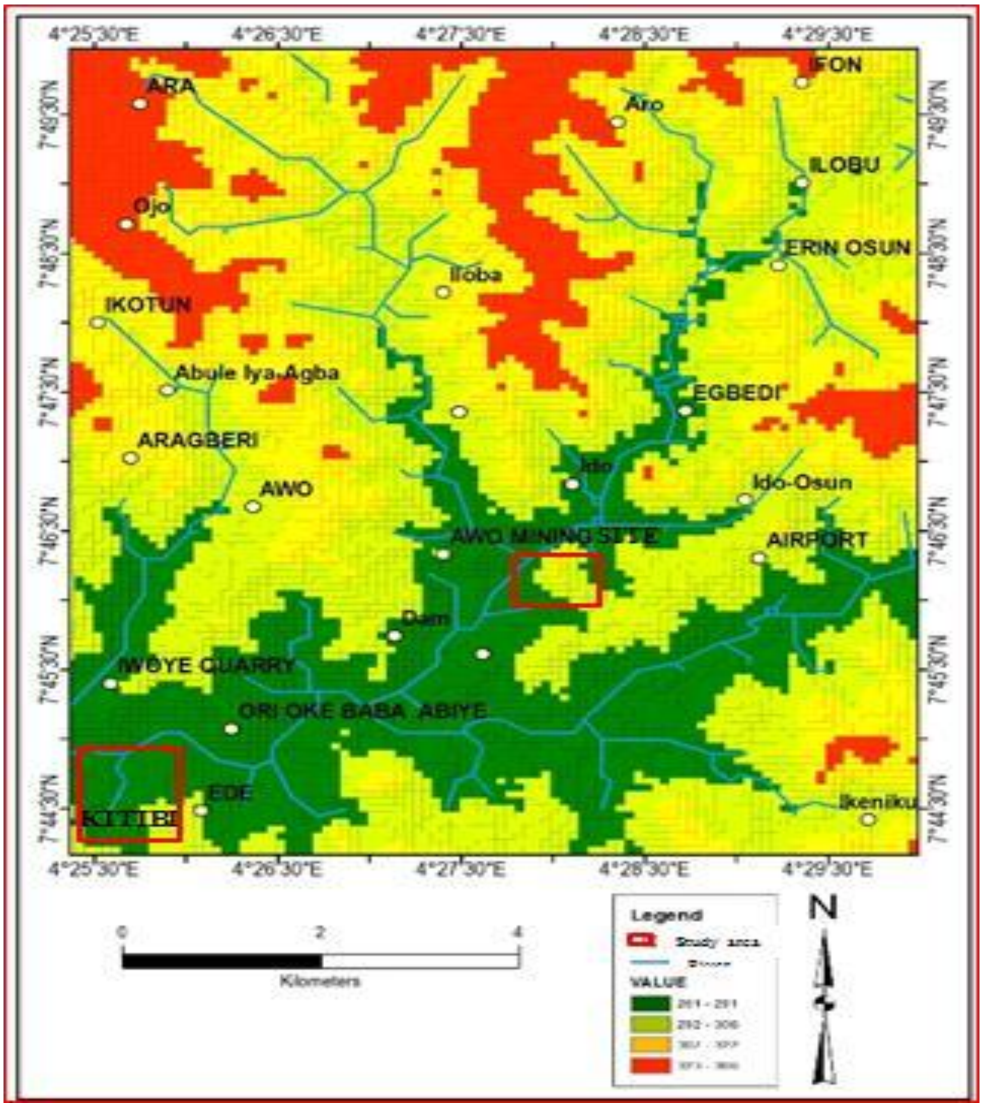

Fig. 1: Drainage, topographical and location map of the study area

Fig. 2: Collection of samples from a section of weathering profile at Kitibi-Iwoye

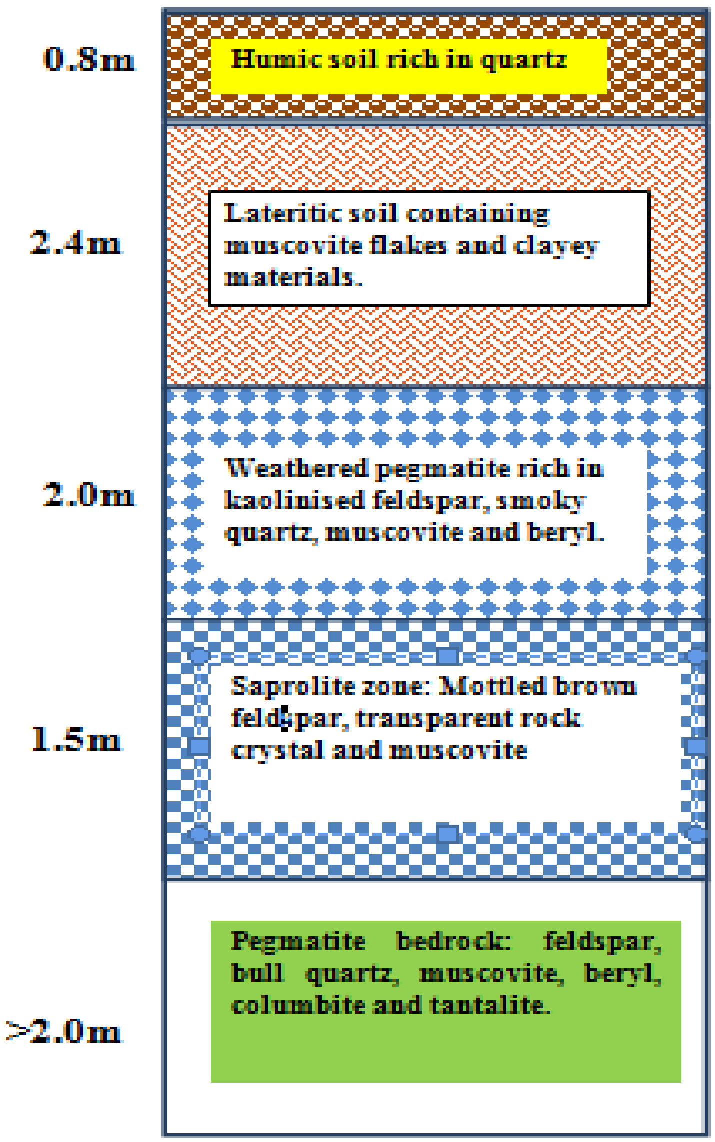

Fig. 3: Sketch of weathering profile at the road cut and mining pit

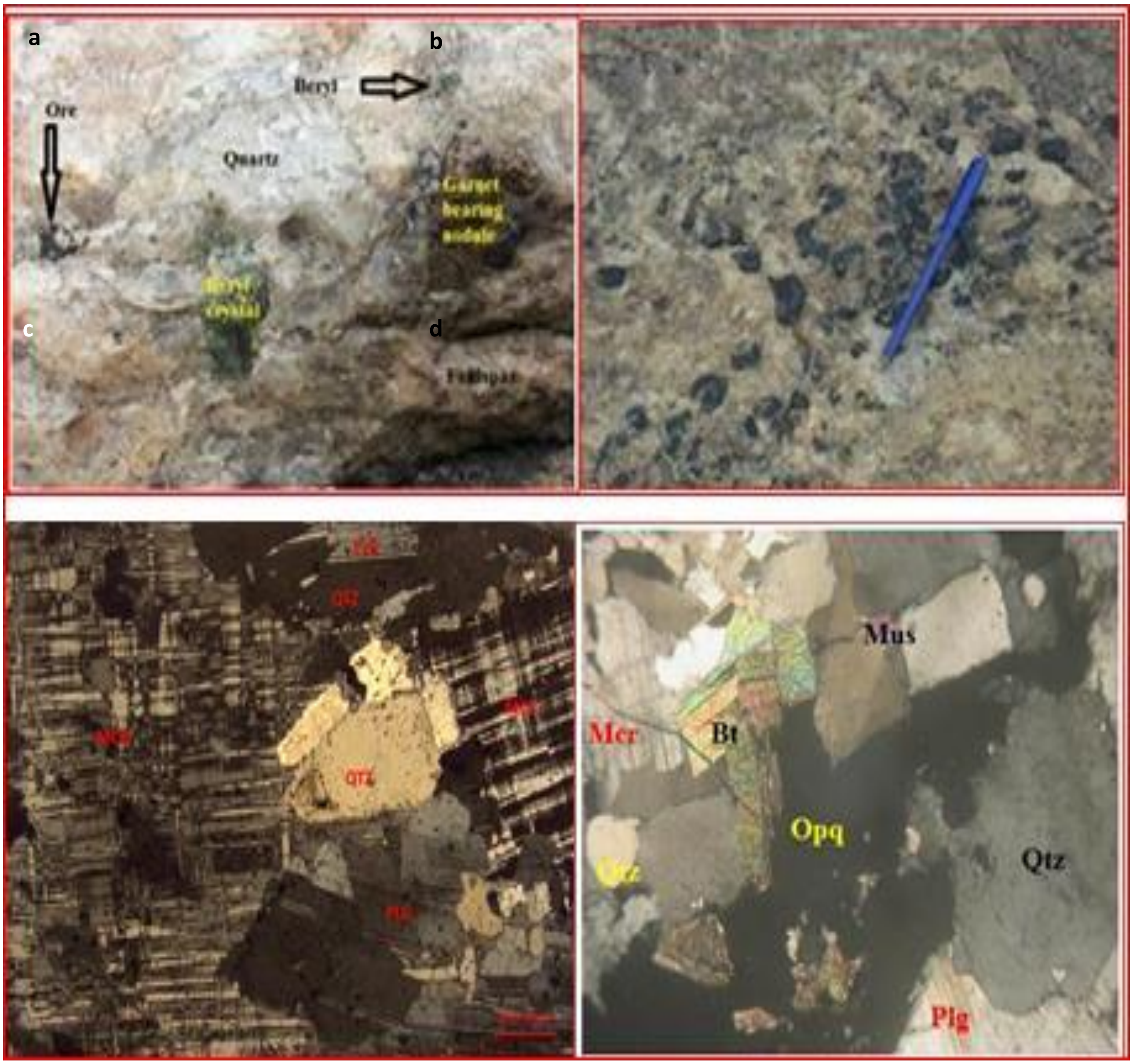

Fig. 4: (a) Beryl crystal embedded in feldspar-rich pegmatite (b) Tourmaline bearing pegmatite (c) Photomicrograph of pegmatite showing subhedral crystals of plagioclase (PLG) and quartz (QTZ) in matrix of microcline (MCR). Cross polarized light x2.5 (d)Photomicrograph of pegmatite showing quartz (Qtz), microcline (Mcr), plagioclase (Plg), muscovite (Mus), biotite (Bt) and opaque minerals (Opq). Cross polarized light. x2.5

Table 1: Modal composition (vol %) of pegmatite around the study area

Minerals	L1	L2	L3	L4	Mean
K-feldspar	29	35	33	33	33
Plagioclase	23	21	20	23	22
Quartz	22	20	15	22	20
Muscovite	11	13	12	10	12
Biotite	10	07	10	07	08
Accessories	05	04	05	05	05
TOTAL	**100**	**100**	**100**	**100**	**100**

Discussion

X-ray diffraction patterns of quartz- feldspar-muscovite-rich pegmatite and quartz-muscovite-illite-kaolinite-rich weathered samples from the study area are shown in Figs.5 to 10. Primary minerals such as albite, anorthite, microcline, quartz, muscovite, biotite and accessory minerals were identified in the pegmatite (Fig. 5). Phases such as clay minerals (kaolinite and illite), quartz, phlogopite, muscovite and goethite were identified in the weathered mass (Figs. 6 to 10).According to Jelitto, *et al* (1993), local equilibrium conditions and variation in composition of solutions over a prolonged weathering are responsible for variation in mineral assemblage. Local variation in mineral composition of altered and weathered components as witnessed in the study area also followed similar trend.

X-ray diffraction of feldspar-rich pegmatite

Phases such as quartz, albite, anorthite, microcline, phlogopite and kaolinite were recognised in X-ray diffraction pattern of pegmatite (Fig. 5). Presence of kaolinite in the diffractogram indicated that phases such as microcline, albite, anorthite, and muscovite have been affected by weathering (Fig. 5). Comparative examination of phases identified in thin section showed presence of quartz, microcline, plagioclase, muscovite, biotite, tourmaline, beryl and opaque minerals while the diffractogram revealed phases such as quartz, microcline, albite, anorthite, phlogopite, and kaolinite. In XRD, plagioclase had been distinguished into albite and anorthite while K-feldspar recognised was microcline. The dark mica which was identified as biotite in thin section was recognised as phlogopite in the diffractogram (Fig. 5). According to Carroll (1974), biotite is trioctahedral mica whose composition varies between Mg-rich variety (phlogopite) and Fe-rich (siderophyllite) end members. Therefore, biotite identified on the field and under the microscope was recognised by the X-ray diffraction patterns as phlogopite which is the Mg-rich end members. Kaolinite identified in the pegmatite showed that most of the primary constituent minerals had been passing through a transition phase into their corresponding secondary minerals.

Following the approach of Goldich (1938) ranking of stability in various rock forming minerals to weathering, anorthite is the least resistant phase thus becoming the first constituent mineral to undergo alteration. The next phase to be altered was albite, followed by biotite, but microcline was more resistant while quartz is the most resistant to weathering. Sequence of weathering from least to most resistant rock forming mineral is anorthite < albite < biotite < microcline < muscovite < quartz.

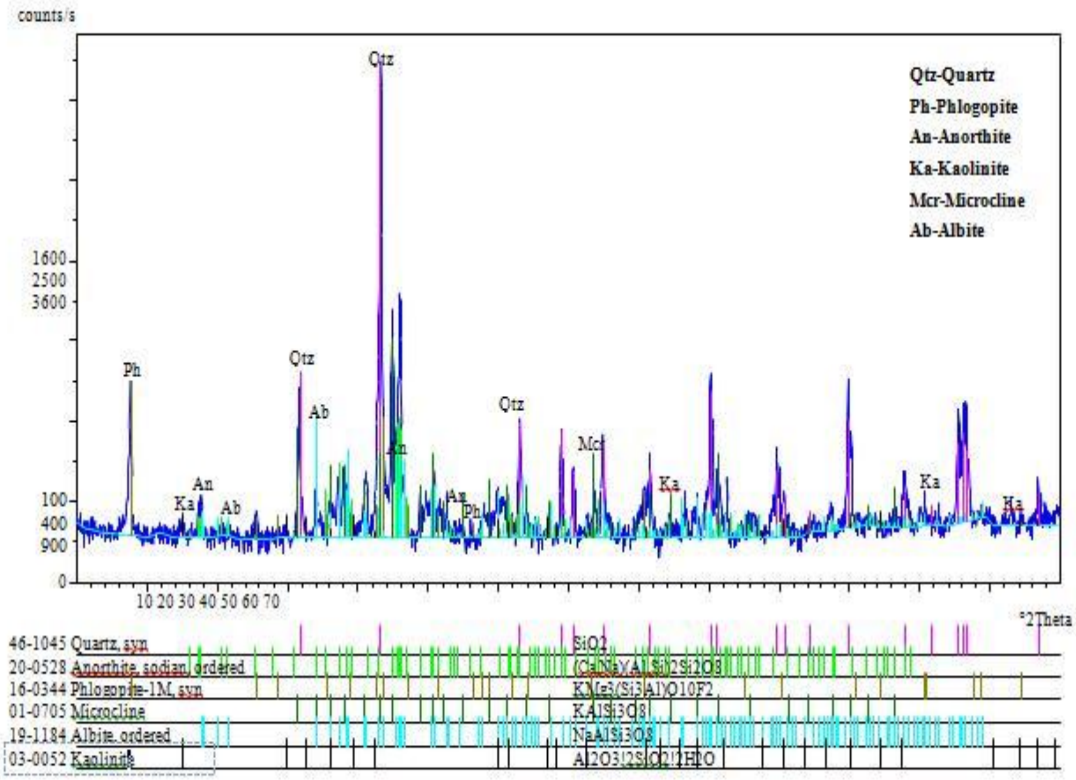

Fig. 5:X-ray diffractogram of feldspar-richpegmatite comprising albite (Ab), microcline (Mcr), anorthite (An), quartz (Qtz), phlogopite (Ph), and kaolinite (Ka) in the mineralogy. X-ray generator system operated at 40 kV and 25 mA with Cu (Kα) radiation (λ = 1.542A°)

X-ray diffraction of illite/kaolinite-rich weathered samples

Diffraction patterns of kaolinite are characterised by several intense peaks in samples analysed. Incomplete alteration leads to the formation of kaolinised feldspar but upon complete alteration kaolinite appeared as a chalky white and friable mass with earthy luster (Klein and Hulburt, 1985). Fig. 6 showed X-ray diffractogram of kaolinite that was free from impurities as there are no other phases occurring in the sample. Alteration can be said to be complete as appearance of kaolinite marks the terminal stage of all weathering processes. Phases recognised in Fig. 8 are quartz, kaolinite and illite. Kaolinite is the dominant phase as shown in the diffraction pattern. Illite which is subordinate to kaolinite formed the transitional phase between clay minerals and muscovite (Wahlstrom, 1955 and Carroll, 1974). Portion of the site where illite was collected contained large sheets of muscovite which had been broken into smaller particles by physical weathering until they become clay sized fractions. Illite is K-poor and SiO_2-rich than muscovite. Deficiency in K^{2+} is due to replacement by Ca and Mg (Klein and Hulburt, 1985). Kaolinite in this sampling point is still undergoing alteration due to the presence of illite. Diffraction patterns of illite and muscovite are similar but their intensities differ. Intensity of illite is relatively stronger than muscovite. XRD patterns of phlogopite, illite and muscovite are noteworthy because they were characterized by sharp and weak peak intensities. Generally, micas are nonexpandable, 2:1 layered silicates in which one layer of alumina octahedral was sandwiched between two layers of silica tetrahedra (Carroll, 1974). Their non-expandability is caused by charge balance between the non-hydrated interlayer cations (typically K^+) and the high layer charges. Phlogopite was characterised by broader peak intensity but illite is composed of broad and weak intensities whereas muscovite is characterised by narrow and weak intensities. Variation in diffraction pattern of micas described the degrees to which they have been altered. Muscovite had been extensively altered followed by illite whereas phlogopite maintained its unique mineralogical features. Phlogopite displayed high crystallinity, illite is moderately crystalline while muscovite is poorly crystalline. It could be inferred that muscovite contributed to kaolinisation within the weathered profile more than phlogopite and illite. In addition, muscovite had been undergoing transformation of non-exchangeable cations by hydrated exchangeable cations. According to Deer, *et al*. (1992), muscovite with chemical composition of K_2Al_4 $[Si_6Al_2O_{20}]$ $(OH, F)_4$ has a layered structure of aluminum silicate sheets. The sheets are weakly bonded together by layers of K^+ which produced perfect cleavage of muscovite. The X site of the muscovite which is a site for Al has been occupied by Ba and Na whereas the Y site has been replaced by Mg, Cr and V resulting into the new chemical formula for muscovite (K, Ba, Na) 0.75 (Al, Mg, Cr, V)2 (Si, Al, V) $4O_{10}(OH, O)_2$ as shown in Fig. 7.The silvery white colouration has been changed to dull brown. From the diffraction pattern in Fig. 8, muscovite is still undergoing weathering which proceeded through illite and hydromuscovite to kaolinite by losing K^{2+} and increasing the H_2O and SiO_2 concentration. Feldspathisation and muscovitisation were mainly responsible for the genesis of kaolinite in the study area, but contribution of accessory minerals such as beryl and tourmaline to alteration is minimal.

Occurrence of quartz is common throughout all the samples as a result of its resistance to weathering and because it is a common mineral in almost all crustal rocks. X-ray patterns show that peak intensities of quartz were broad and sharp. Although there are minor quartz peaks in the diffractogram.

X-ray diffraction pattern of goethite revealed narrow peak intensities at 18 2θ, the trend became more manifest at 20 2θ up to 73 2θ for samples represented by X-ray diffraction pattern shown in Fig. 9. The diffractogram trend was very similar for goethite because they bear mineralogical similarities to each other as evident in the X-ray diffraction patterns (Figs 9 and 10). Such similarities were ascribed to the fact that they were derived from the same parent rocks that have undergone the same rate of weathering. Goethite is found in oxidizing conditions as a weathering product of magnetite that occurred in laterite and clay minerals. The X-ray diffraction patterns show well crystalline and ordered kaolinite. Kaolinite is the principal phase in Fig. 9as shown in the reference pattern and peak intensities of the diffractogram.

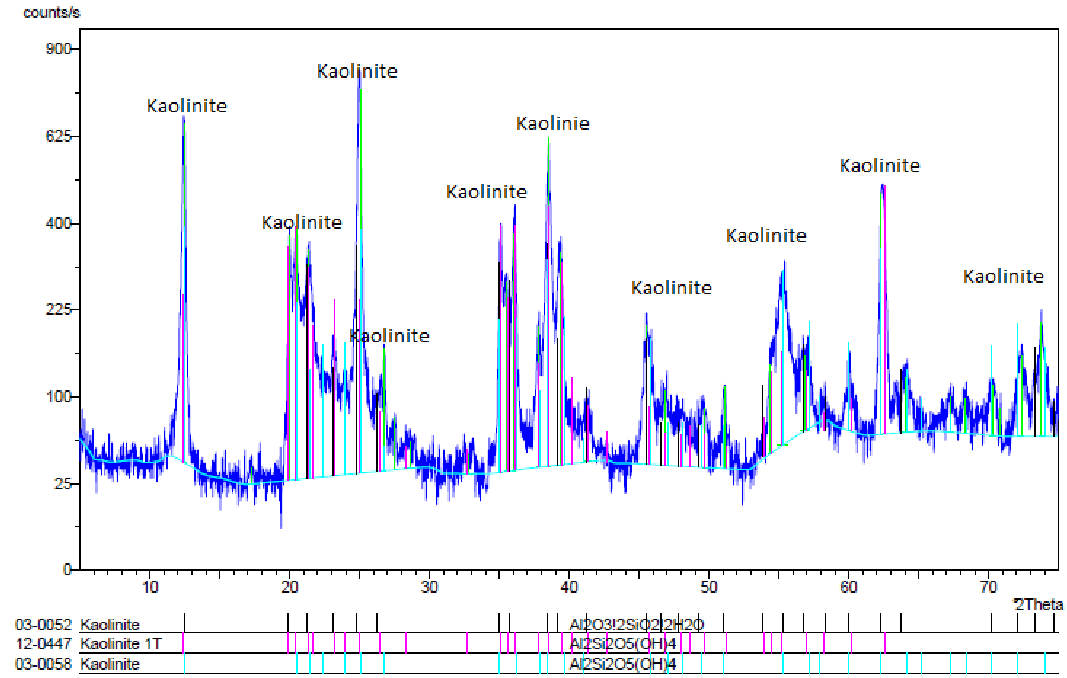

Fig. 6: X-ray diffractogram of kaolinite-rich weathered profile at Kitibi- Iwoye road cut

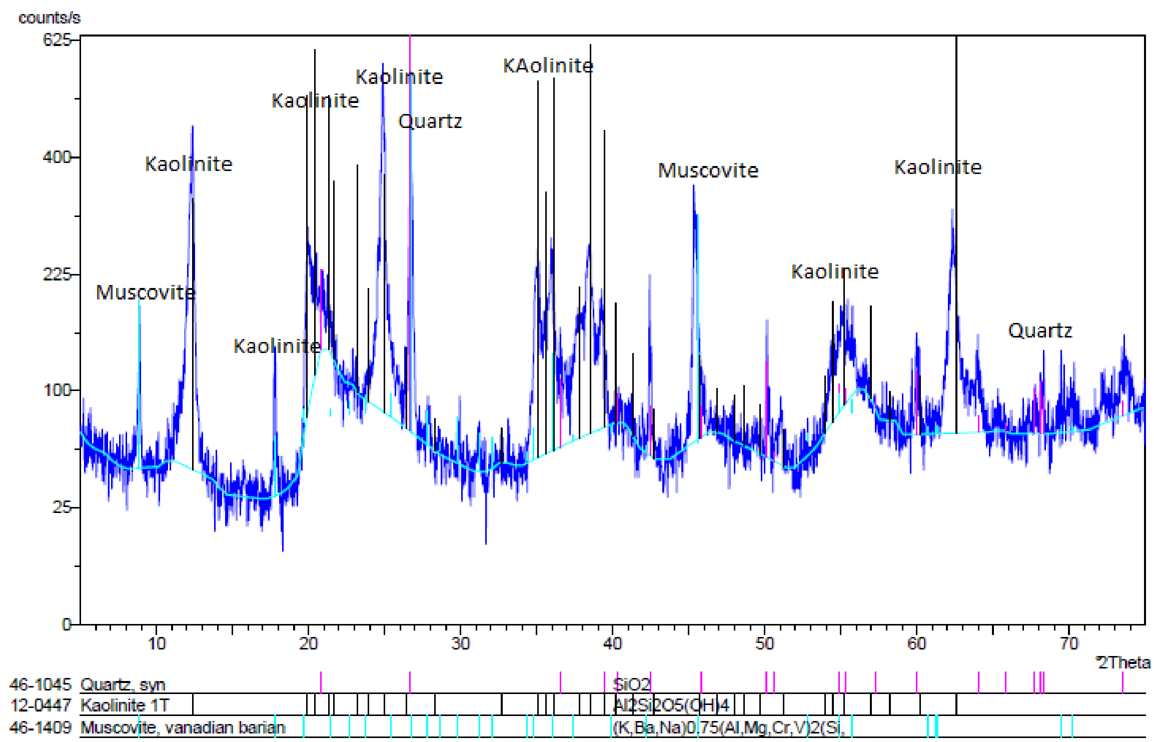

Fig. 7: X-ray diffractogram of kaolinite, quartz and muscovite (CL5)

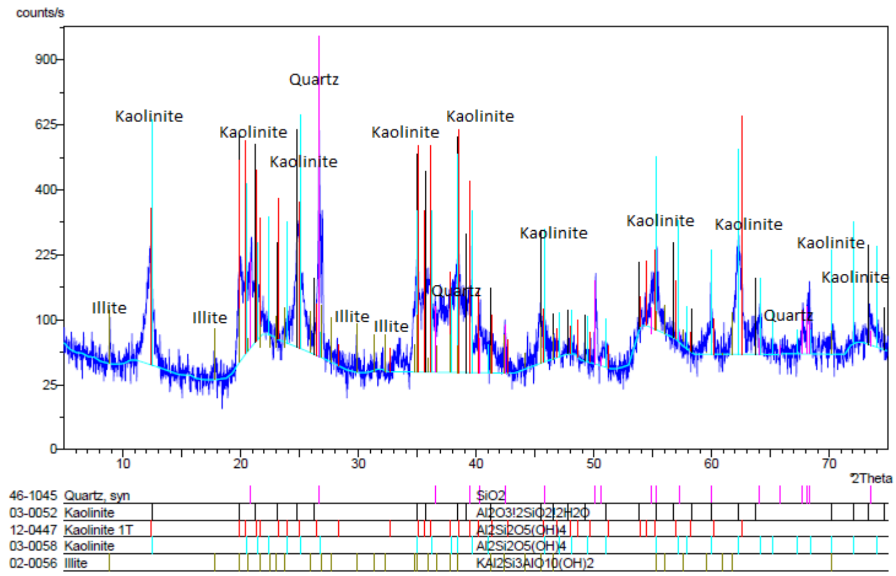

Fig. 8: X-ray diffractogram of kaolinite, quartz and illite

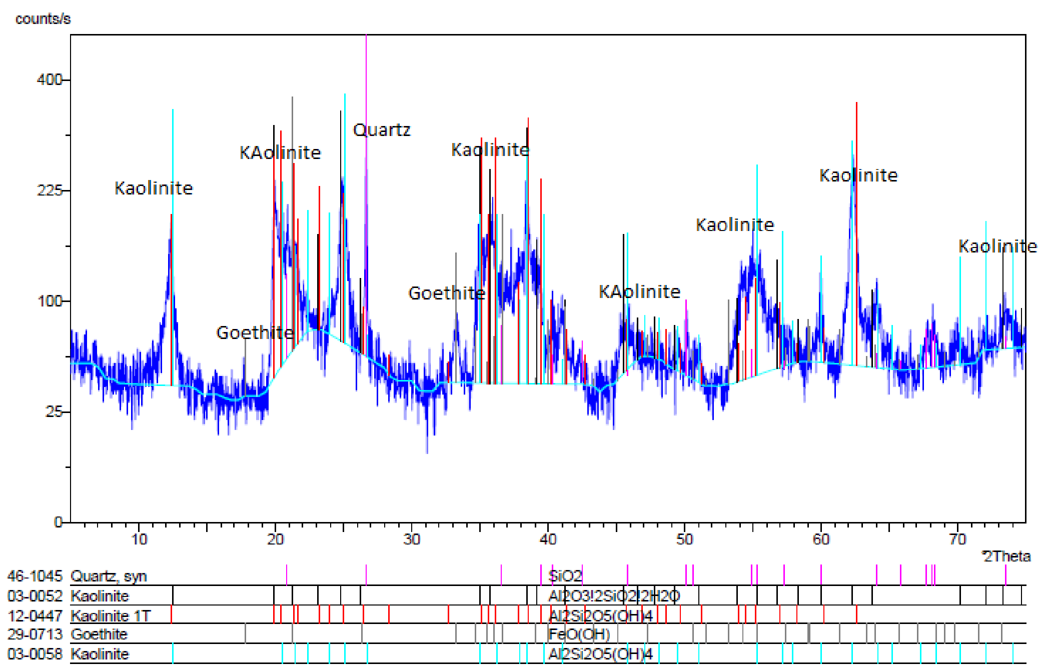

Fig. 9: X-ray diffractogram of kaolinite, quartz and goethite

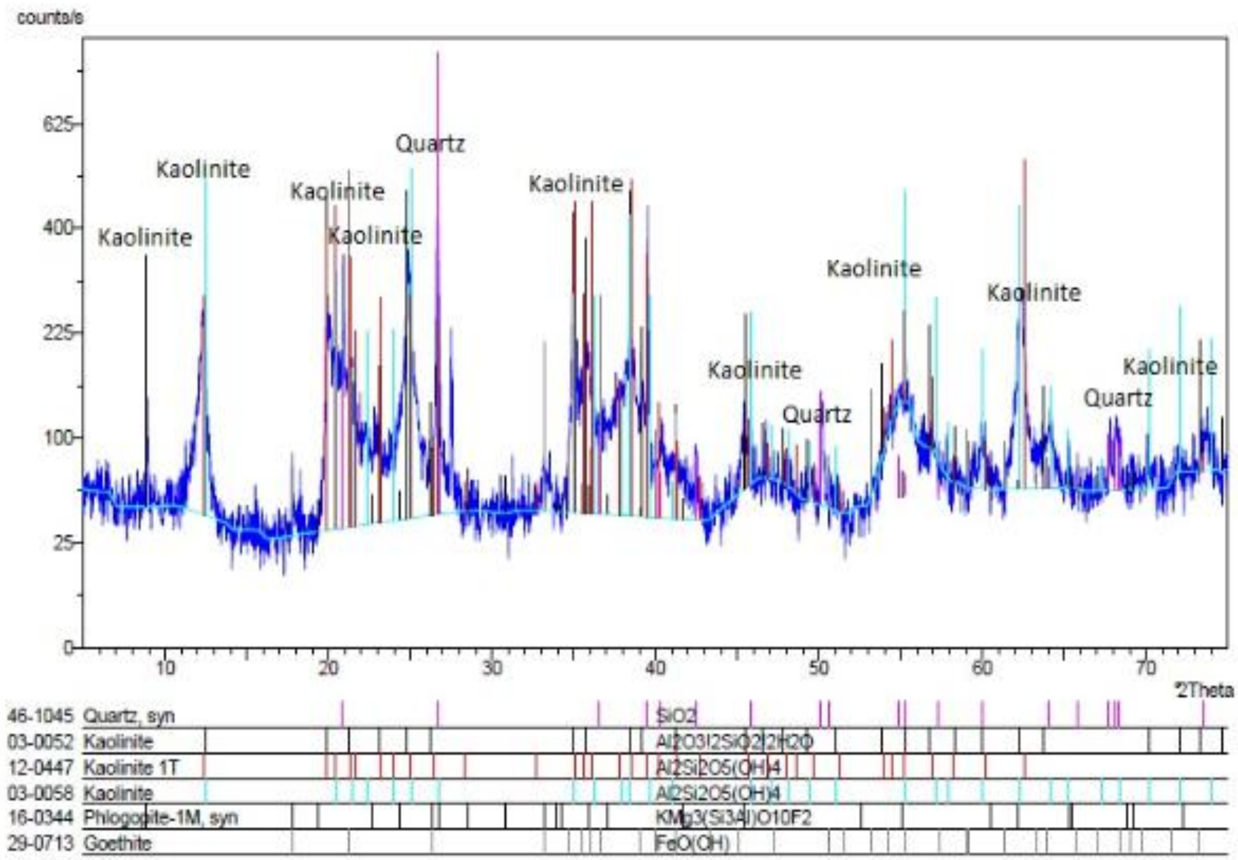

Fig. 10: X-ray diffractogram of kaolinite, quartz, phlogopite and goethite (CL3)

Table 2: Summary of the mineralogy obtained from X-ray diffractogram

S/No	Nature of sample	Location	Mineralogy
CL1	Pegmatite	Awo mining site	Quartz, Anorthite, Microcline, Albite, Kaolinite, Phlogopite
CL2	Weathered mass	Awo mining site	Kaolinite
CL3	Weathered mass	Awo mining site	Quartz, Kaolinite, Illite
CL4	Weathered mass	Kitibi-Iwoye	Quartz, Kaolinite, Muscovite
CL5	Weathered mass	Kitibi-Iwoye	Quartz, Kaolinite, Goethite
CL6	Weathered mass	Kitibi-Iwoye	Quartz, Kaolinite, Phlogopite, Goethite

Conclusion

The pegmatite is composed of quartz, feldspar, muscovite, biotite with varying amount of accessory minerals such as tourmaline and beryl. X-ray diffraction patterns of quartz- feldspar-muscovite-rich pegmatite further identified primary minerals such as albite, anorthite, microcline, quartz, muscovite, biotite and accessory minerals.

Phases such as clay minerals (kaolinite and illite), quartz, phlogopite, muscovite and goethite were identified in the weathered mass. Sequence of weathering from least to most resistant rock forming mineral is anorthite < albite < biotite < microcline < muscovite < quartz.

Appearance of muscovite, illite and kaolinite at various sampling points signified moderate to intense degree of weathering which were caused by topography, fluid-rock interaction, moisture content, nature and composition of the rock undergoing weathering. Occurrence of muscovite heralded its successive transformation to hydromuscovite, illite and kaolinite. Appearance of goethite in the weathered mass revealed the presence of magnetite as the primary mineral of the parent rock. The X-ray diffraction patterns generally showed well crystalline and ordered kaolinite which is the principal phase as shown in the reference pattern and peak intensities of the diffractogram.

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