Petrography and geochemistry of ferricrete near Shire, northern Ethiopia

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ABSTRACT

A detailed petrographic and geochemical study was conducted on ferricrete (laterite) developed on Mesozoic (?) ferruginous sandstone near Shire, Tigray region, northern Ethiopia. 30 rock samples were analyzed for major and minor elements and studied for petrographic details. Ferruginous sandstone overlying the Neoproterozoic low grade basement rocks dominantly contains quartz followed by orthoclase feldspar and iron oxides/hydroxides as cement. Residual enrichment process has resulted in the development 2-3m thick ferricrete horizon and also sub-horizons: mottled, mixed nodular and psuedo-pisolitic. Mineralogy of the ferricrete includes limonite, goethite and hematite. Arid conditions and dehydration reactions seem to have produced hematite from goethite. The ore minerals show replacement, cavity and fracture filling, remobilization and colloform textures. Si>Al>Fe is the mobility pattern observed in the ferricrete horizon though presence of secondary quartz and kaolinite are also common. Development of ferricrete is related to the climatic condition that existed during Eocene and is comparable with similar deposits in Arabian Nubian Shield (ANS).

Key words: Ferricrete, Laterite, Ferruginous sandstone, Shire, Tigray, Northern Ethiopia, ANS.

1. INTRODUCTION

In Ethiopia, minable iron deposits reported so far are very few. Three different types of deposits are reported from Ethiopia, though small in size. They include magmatic iron (Fe-Ti type) of Precambrian age from Bikilal, Melka Arba areas, banded iron formation (BIF type) of Precambrian age from Koree, Gordoma, Chago areas, and lateritic (also gossan related) iron deposits (residual type) from Melka Sedi, Garo, Gato, Billa, Gambo, and Gammalucho areas. Among them, Garo, Dombova and Melka Sedi (in Kaffa) are the biggest about 12.5 mt each in terms of reserve. Metals associated with iron in these deposits are mainly Mn, Au, Pt, Ni, Co etc (Tadesse, 2006). Bikilal deposit is dominated by apatite and followed by magnetite and ilmenite etc. The mineable reserve of apatite in the deposit is about 181 mt with a grade of 3.5% (P_2O_5)and iron ore of 58 mt with a grade of 41.65% total iron (Wondafrash, 2010; Tadesse, 2006).Occurrence of laterite (ferricrete) deposits are also reported in Tigray region, northern Ethiopia e.g.1) occurrence of pockets of lateritic deposits near Shire (Ebrahim, 2011) overlying ferruginous sandstone; 2) development of thin lateritic cover on Enticho Sandstone of Paleozoic age near Wukro and Sinkata; 3) Negash iron deposit near Wukro as cavity filling in Neoproterozic metalimestone by the younger remobilized lateritic material possibly related to iron-rich Paleozoic Enticho Sandstone (Gebresilassie et al., 2012);and 4) presence of iron–rich bands within Adigrat Sandstone of Mesozoic age near Wukro, Hawzein, Dugum, Adigrat etc. At present among the reported iron deposits of lateritic type are the major resources in terms of tonnage (>100mt) and hence are attracting attention of companies like Ezana Mining Company PLC (EMD) and Universities like Mekelle University to conduct research. Present paper is the result of one such effort on ferricrete near Shire, northern Ethiopia.

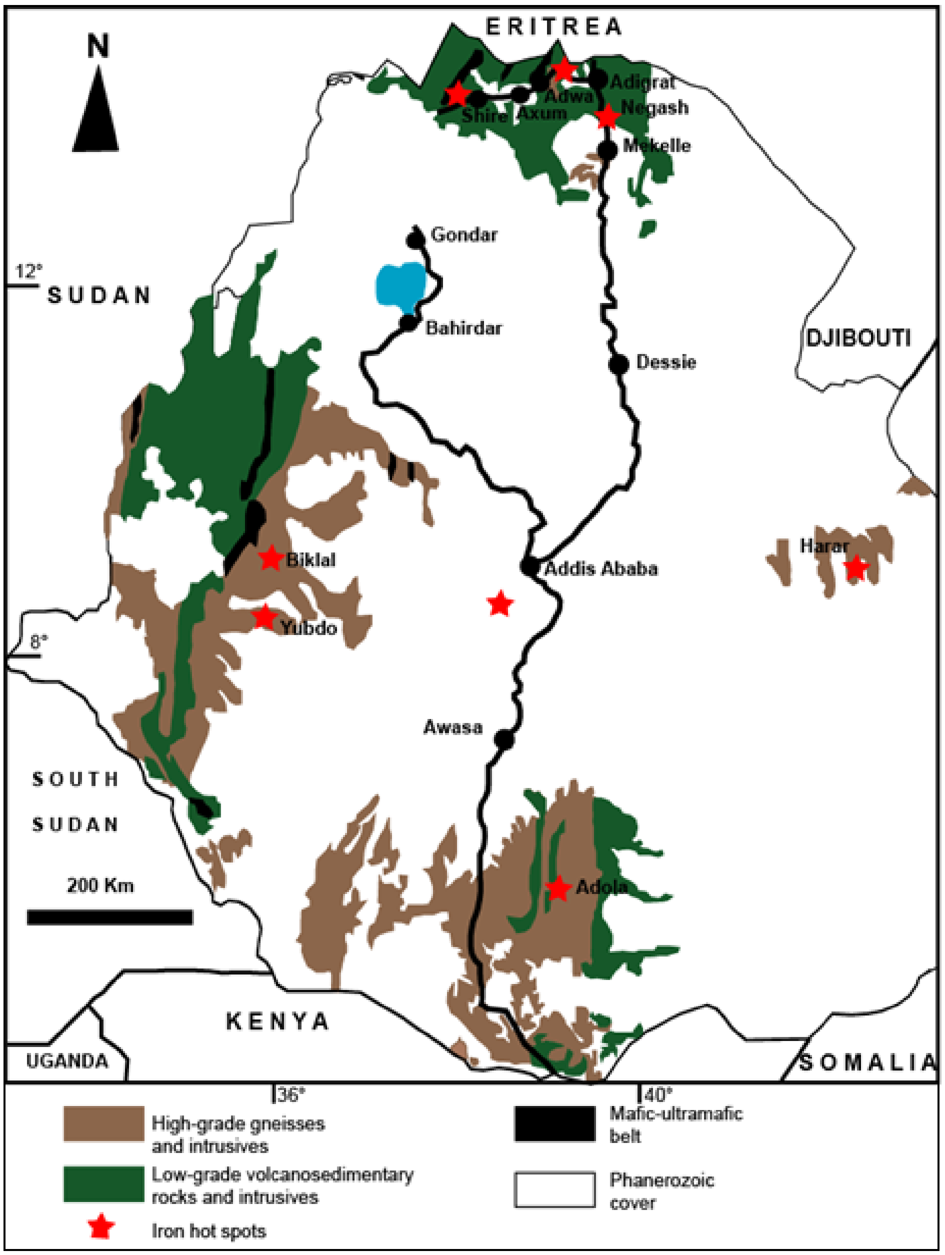

Figure 1. Map of part of Ethiopia and east Africa showing some of the iron occurrences including the Shire area (after Mengesha et al.,1996).

2. GEOLOGICAL SETTING

2.1. Regional Geologic Setting

Northern Ethiopia forms part of southern Arabian-Nubian Shield (ANS) and consist of Precambrian low-grade volcanic, volcano-sedimentary, mafic and ultramafic rocks of ophiolitic character and are intruded by syn- and post-tectonic plutonic rocks (Tadesse, 1997). The rocks have experienced different phases of deformation. The tectonic structures include the fold-thrust domains with associated shear zones of predominant sinistral sense of shear which are attributed to major collision orogeny during the amalgamation of the Arabian-Nubian Shield (Tadesse et al., 1999). The basement Precambrian rocks are divided into: (i) the metavolcanic/volcaniclastic dominated Lower Tsaliet Group (~850 Ma; Teklay, 1997), (ii) metasedimentary rocks containing Upper Tambien Group (835-740 Ma, Alene et al., 2006; Avigad et al., 2007), (iii) Dolomite dominated Didikama Formation, and (iv) younger diamictites and metasandstone/conglomerate containing Negash diamictites and Shiraro molasses (Avigad et al., 2007). The intrusive felsic plutons (syn- and post-tectonic granitoids) ranging in age from 800 to 520 Ma have altered the Precambrian rocks and acted as source of heat for the hydrothermal fluids that resulted in base metal and gold mineralization in the region (Tadesse et al., 1999; Asfawossen et al., 2001; Kuester et al., 2009; Bheemalingeswara et al., 2012).

The basement are overlain by sedimentary rocks of Paleozoic (Enticho Sandstone and Edaga Arbi Tillite), Mesozoic (Adigrat Sandstone, Antalo Limestone, Agula Shale and Ambaradom Sandstone in upward stratigraphic order) and volcanic flood basalts of Cenozoic age (Beyth, 1972; Kazmin, 1978; Mengesha et al., 1996; Tadesse, 1997). Location of the areatogether with Precambrian basement rocks, Phanerozoic cover (mostly sedimentary and volcanic rocks) and iron hot spots are shown in figure 1.

2.2. Geology of the study area

It forms part of lithostratigraphy of NW Tigray and are dominarted by low grade Tsaliet Group rocks and Mesozoic sedimentary rocks (Fig. 2). Tsaliet Group consists of metavolcanic (MV) rocks of mafic to intermediate composition. They are intruded by younger granitic plutons and overlain by Mesozoic sedimentary rocks. The sedimentary rocks are dominated by ferruginous sandstone with thin bands of siltstone and claystone. Ferricrete is a conspicuous unit in the area developed on ferruginous sandstone (Ebrahim, 2011) which is related to Adigrat Sandstone (Tadesse, 1997). Alluvial deposits mostly on sedimentary rocks present in northern and eastern parts of the area (e.g. about 2m thick in the May-Imblay River valley). Development of hexagonal / polygonal mud cracks filled with fine sand and with downward tapering are also common. The Shire area is well connected by asphalt road from Mekelle via Adigrat-Axum (about 300km). Also it is accessible through Indesillassie-Gondar main road and towards NW through Shire Indesillassie-Kisadgaba-Maihanse all-weather road. The area is characterized by arid to semi-arid weather condition with gentle to flat slopes.

2.2.1. Basement rocks

The basement rocks exposed in many parts of the area are dominated by metavolcanics and show foliated (mafic variety) and massive (intermediate variety) nature. Massive variety is exposed in the south and south western part and foliated variety in the central part around MayDumu of the study area. The rocks form rugged and ridge topography in the SW part of the study area with moderate to steep tilt towards NW. Quartz veins are common in these rocks possibly related to the pale gray to pink colored intrusive post-tectonic granite known as Shire granite which is exposed in the northern part of the study area (Tadesse, 1997).It is dominated by coarse (>3mm) orthoclase feldspar and quartz and with development of kaolinite along the intrusive contact.

2.2.2. Ferruginous Sandstone

It shows red color due to high content of iron and is intercalated with bands of claystone/siltstone. Tadesse (1997) interpreted it equivalent to Adigrat Sandstone. It covers large area, overlies unconformably the Precambrian basement rocks and is characterized by flat lying morphology on both sides of gorgesand is undergoing erosion. In the west side of the study area the rock shows angular unconformity with MV unit making it to have an outlier feature. It varies in thickness from about 30-35m in SW to 10m in NE and shows a gradational contact with the overlying lateritic unit (Fig.3).The sandstone is thick, bedded and reddish brown in color having medium to coarse grain size quartz as dominant mineral and followed by orthoclase feldspar and iron hydroxides as cement. Alteration of feldspars to kaolinite is seen at many places and being soft it is eroded leaving depressions on the top of the profile. The resistant quartz minerals remain in situ and show alignment fabric indicating sedimentary process (Fig.3A & B). Development of secondary structures such as cracks and joints common in sandstone which are later filled by iron hydroxides and chert (Fig. 3C). In the northern part, there are small patches of pink colored thinly laminated siltstone beds showing conchoidal fracture.

Structures like faults, foliations, folds are common in the basement rocks compared to sandstone and related ferricrete. The latter commonly show structures like primary bedding, fractures and cross bedding especially in sandstone unit. The fractures are dense, dip vertically, show north-south and east-west trend and are filled by quartz, chert and iron oxides.

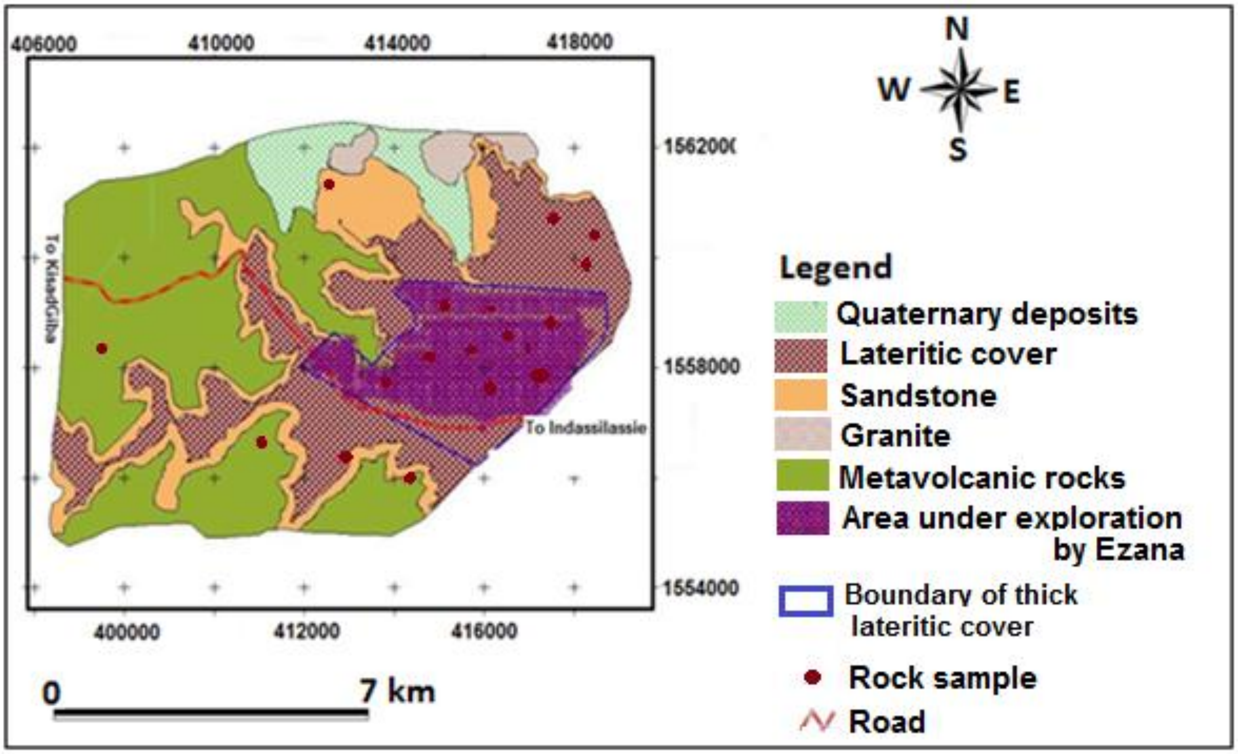

Figure 2. Geological map of the study area.

2.2.3. Ferricrete

It is about 2-3m thick, developed on ferruginous sandstoneas part of weathering/ lateritization and extensively exposed in the study area. The vertical section exposed in the quarry site (416000 and 1558000m, Fig. 2) shows the transformation with gradational contact from source ferruginous sandstone to iron-rich ferricrete (horizon) and also sub-horizons within ferricrete. Ferricrete varies in thickness from 3m to less than a meter particularly in the northern part. At places it is absent because of its removal due to erosion and filling the depressions and gentle slopes downstream.

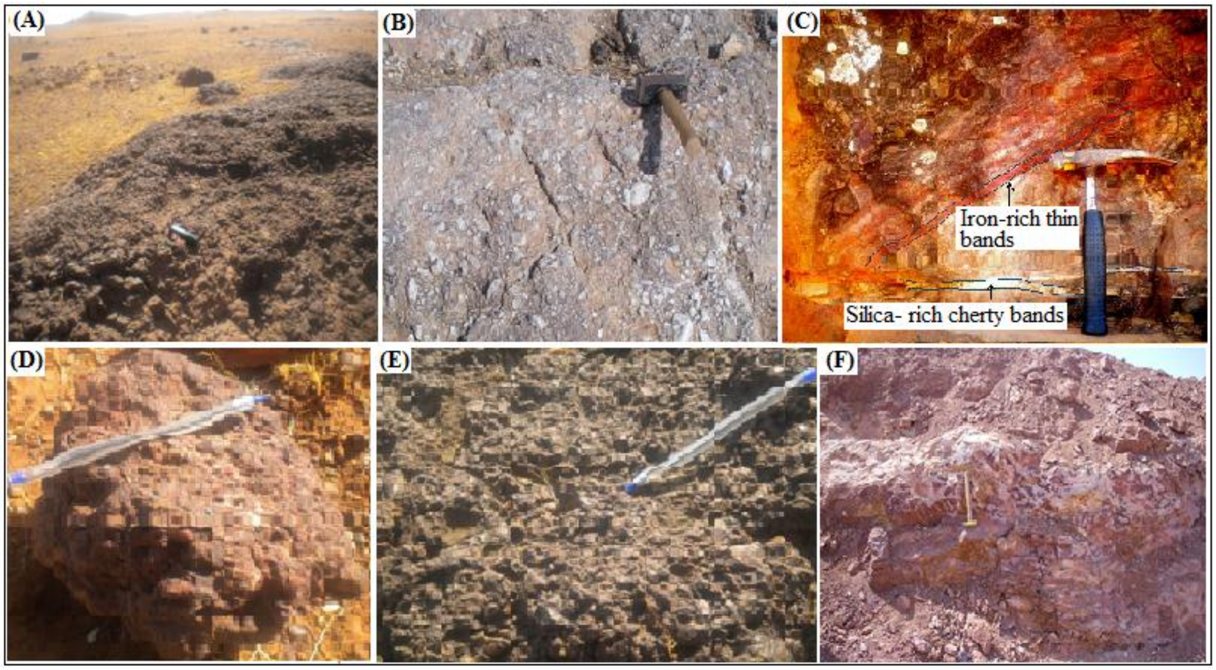

Figure 3. A) Dark brown colored ferricrete on top of ferruginous sandstone, B) weathered ferruginous sandstone with white colored aligned quartz minerals, C) fresh ferruginous sandstone with thin iron and silica –rich bands, D) and E) pseudo-pisolitic texture in ferricrete, and F) kaolinite development in ferricrete.

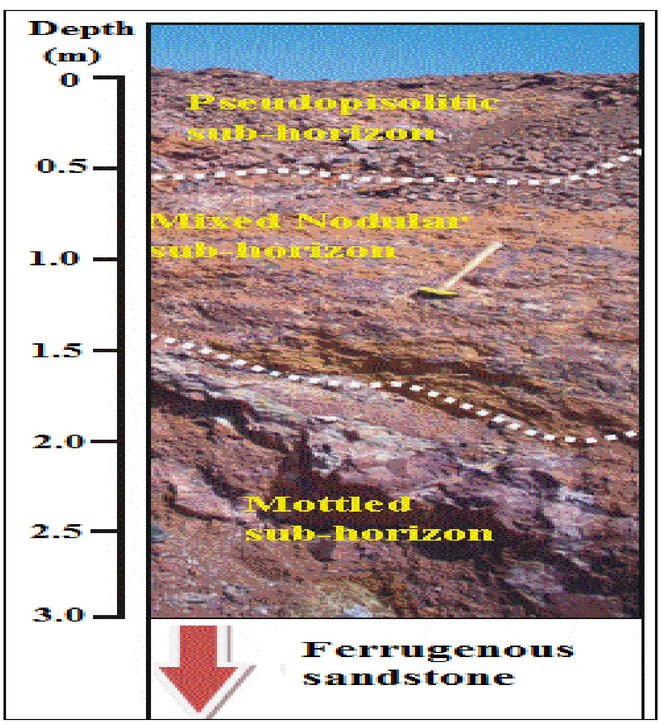

Figure 4. Ferricrete profile showing different sub-horizons in the ferricrete from quarry exposure.

Ferricrete horizon is mostly massive and shows reddish brown color due to high content of iron oxides (Fig. 3D & F). The top part occurs as loose material showing pisolitic texture and is heavily coated with iron oxides. Coarse quartz generally remains the major part of pisolite (Fig. 3E). The pseudo-pisolites are widely distributed throughout the ferricrete together with limited development of kaolinite (Fig. 3F) indicating variation in lithology locally. Different horizons observed in the vertical section and their variations from bottom to top are shown in figure 4.

0 - 0.5m → iron crust with pseudo-pisolite sub-horizon
0.5 - 1.5m → nodular and mixed nodular sub-horizon
1.5 - 3.5m → mottled sub-horizon

Mottled sub-horizon is represented by weathered part of ferruginous sandstone (saprolith) in which the primary sedimentary structures are preserved and locally intercalated with siltstone.Quartz with minor feldspar dominate the rock with iron oxide/hydroxidesfilling the fractures (discordant and concordant). It consists of nodular type quartz grains with few mm to cm size and rounded to sub-rounded shape. The grains are cemented by brown-red iron oxides and slightly indurate dark red ferruginous and clay matrix. Intercalation of white clay developed due to the alteration of feldspars with iron oxides is common. The purple red nodular structure is not abundant in the bottom of the mottled sub-horizon but increase very rapidly upward and form a dense framework in the upper part in the section resulting pseudo-pisolitic sub-horizon. It is followed by the development of mixed mottled and nodular sub-horizon(Fig.4).

Mixed mottled sub-horizon is characterized by the breakdown of nodular structures into smaller size spherical, irregular or concretionary shapes with increasing coating by brown color iron oxides. Compared to other sub-horizons, banded nature of iron oxide cement is common (Fig. 4).This sub-horizon is followed by <1m thick pseudo-pisolitic sub-horizon which is characterised by presence of pisolites, occur as independent and welded variety. The nucleus, mainly quartz, is coated by iron oxides with varying thickness. The rounded and sub-rounded red/brown color pisolites grows thicker due to coating and strongly indurated and welded together producing pseudo-pisolite and colloform textures. With time, the welded ones are breaking down producing independent pisolites which get eroded and accumulated in the stream channels. Occurrence of independent pisolites or welded variety seems depend on the varying degree of fragmentation and oxidation (Fig.4). Though, the iron-rich cement strongly binds the rounded to sub-rounded pisolites but at places, it becomes cellular type due to removal of cement.

3. METHODOLOGY

30 rock samples were collected randomly from the field outcrops taking into account the lithologies present and variation within the lithologies particularly ferricrete and sandstone. Out of 30 samples, 5 each are from metavolcanic, intrusive granite and ferruginous sandstone rocks and 15 from ferricrete (both lateral and vertical). Selected samples were chosen for petrographic and geochemical analysis. 5 rock samples were chosen for thin section preparation (2 from metavolcanics and 3 from ferruginous sandstone) at Geological Survey of Ethiopia, Addis Ababa. 9 samples from ferricrete were chosen for polished sections preparation at Department of Earth Science, Mekelle University. Petrographic studies were conducted using transmitted and reflected light microscopes in the petrology laboratory of Department of Earth Science at Mekelle University..

10 rock samples were chosen from ferricrete and sandstone for geochemical analysis. The rock samples were powdered upto minus 200mesh at EMD laboratory. After homogenization and coning and quartering, about 100gmof rock powder each were submitted to central laboratory at the Geological Survey of Ethiopia for major and minor element analysis using XRF. The analyses were carried out on pressed pellets using rock standards as reference and control the accuracy of the data. Data is given in table 1. Apart from these data, 16 surface and borehole samples unpublished XRF data of ferricrete from Ezana Mining Company are also used in the discussion related to geochemical mobility patterns of mobile and immobile elements.

4. RESULTS AND DISCUSSION

4.1. Petrography of ferruginous sandstone and ferricrete

Fine to medium grained ferruginous sandstone typically shows red color in thin section. It is mainly composed of irregular, sub-rounded to angular shaped quartz grains (~70%), orthoclase feldspar (~10%)and ferruginous oxides as cement (~ 20%) (Fig.5). Quartz shows low relief and low birefringence but does not show wavy extinction.Iron oxide/hydroxides serve as a binding material (cement) between mineral grains and rock fragments and seems to have remobilized during the chemical weathering process (Fig.5).

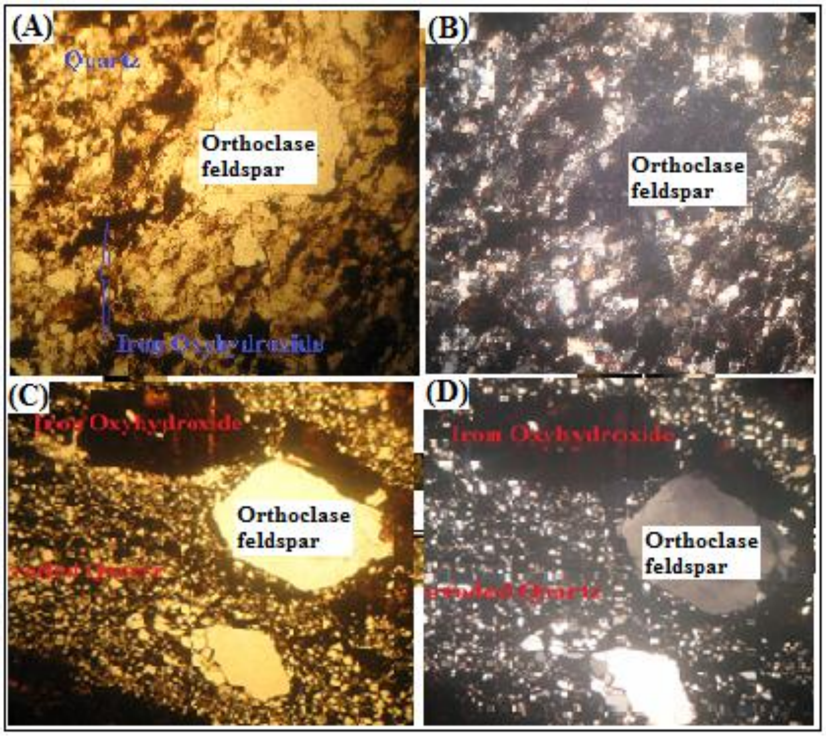

Figure 5. This section of ferruginous sandstone showing quartz and orthoclase feldspar (A& C, PPL; and B& D; XPL (40x)).

Thin sections from mottled ferricrete sub-horizon show presence of about 60% quartz. Sub-rounded to roundedgrains are mostlycorroded and affected by later developed cracks. Majority of the grains are coated with iron oxides and show brownish red color. There are few fresh grains exhibiting nocracks. These fresh quartz grains are considered to besecondaryin originproduced by dissolution of primary quartz grains and reprecipitation. The polished sections under reflected light microscope show presence of hematite, goethite and limonite. Hematite shows light yellow color and is weekly anisotropic. Interestingly, hematite does not show any alteration, on the contrary, goethite shows transformation to hematite (Fig. 6). Hematite is fine-grained, fracture filling and occupies intra-granular and inter-granular space. It produces colloform banding around the nodules. Development of cracks and cavities produced due to removal of kaolinite and dissolution of quartz are filled by iron oxide/hydroxide. Its gradual enrichment and evolution facilitated development of various iron minerals such as limonite, goethite and hematite. Presence of chert as lenses, fracture filling and irregular bodies in sandstone and ferricrete is related to the dissolution of primary quartz and precipitation (Figs. 5 and 6).

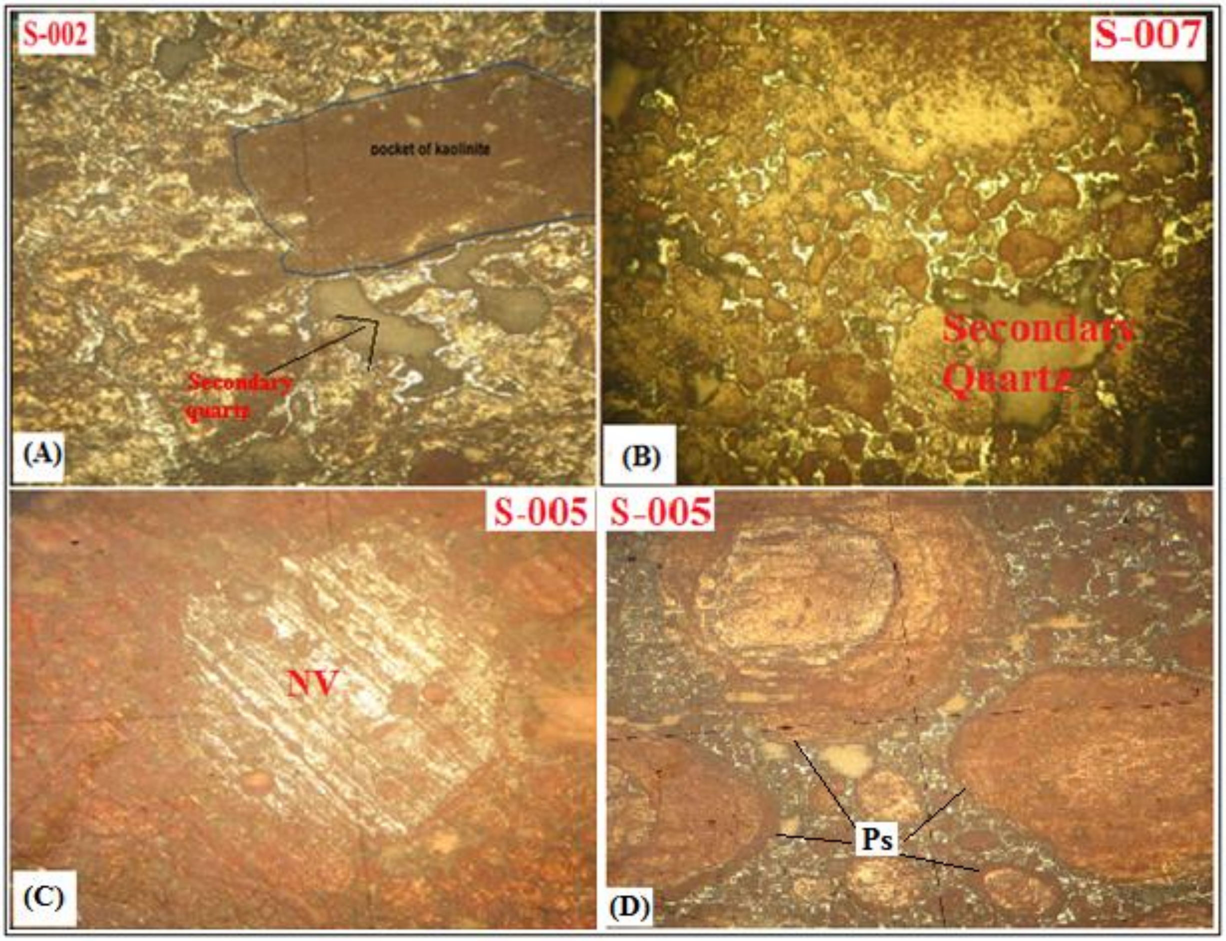

Figure.6. Microphotographs polished sections from A) mottled sub-horizon, showing hematite development around kaolinite, secondary quartz and inter-granular space (PPL, 40x); B) mixed nodular sub-horizon, showing inter-granular filling by hematite (PPL, 100x); C) nodular variety; showing thin hematite-rich bands within the sandstone lithic fragment suggesting in-situ modification and concentration (PPL, 100x); and D) pseudo-pisoliticsub-horizon, showing development of pisolites and fine grained hematite in the matrix and around pisolites (PPL, 100x). ***Note***: Ps: pseudo-pisolite; and NV: Nodular variety.

The samples from transition zone (mottled to nodular sub-horizon) indicate remobilization and accumulation of iron oxides/hydroxides. Apart from filling the voids, iron hydroxide-rich fragments which are common in this zone show development of hematite. Fine bands/layers of hematite are common in addition to fracture filling textures (Fig.6). Many quartz grains show corrosion effects and gradually become rounded and produced nodular structures. Secondary quartz is common. Macroscopically recognizable purple-red nodular variety of hematite remains the principal ore mineral in these transformations in this zone. Association of this nodular variety (NV) with residual zones of the simple mottled variety defines the iron crust with mixed sub-horizon. Brown-red nodules with yellowish brown rings haves changed to brown pseudo-pisolites with banded outer shells. The rings developed in a centripetal way at the expense of the cores in the nodules (Fig.6). This evolution proceeds as follows: isolation of scales of opaque matrix from the core; diminution of these scales of matrix as soon as the outer shell develops; obliteration of the micro-porosity observed in the core; and replacement of the opaque matrix by hematite. Such changes have resulted in the development of white and brown alternating bands in the pisolites (Fig. 6; Ebrahim, 2011).

Table.1. Range of major and minor oxide values for ferricrete and ferruginous sandstone.

Major oxides	***Ferruginous Sandstone (wt. %)***	***Ferricrete (wt. %)***
SiO_2	74	22-39
Al_2O_3	13	16-25
Fe_2O_3	8	30-50
K_2O	0.05	0-0.5
TiO_2	0.37	0.7-2
P_2O_5	0.036	0.1-0.7
MnO	0.0159	0-0.3

Table. 2. Correlation matrix for major oxides in ferricrete (a total of 16 surface samples).

	Fe_2O_3	$Al_2O_3+SiO_2$	SiO_2	Al_2O_3	$Al_2O_3+Fe_2O_3$
Fe_2O_3	1				
$Al_2O_3+SiO_2$	-0.940	1			
SiO_2	-0.892	0.952	1		
Al_2O_3	-0.735	0.776	0.545	1	
$Al_2O_3+Fe_2O_3$	0.951	-0.856	-0.899	-0.491	1

4.2. Geochemistry of ferricrete

Major and trace element data for ferruginous sandstone and ferricrete are presented in table 1.Among the major oxides, Fe_2O_3 shows higher, Al_2O_3 almost remains the same. SiO_2has lower values in ferricrete compared to the source ferruginous sandstone. SiO_2 values vary from 74 to17 wt%, Fe_2O_3 8 to 63 wt% and Al_2O_3 13 to 11 wt%. Iron and silica contents show significant variation in concentration compared to Al value, which remain almost constant in both sandstone and ferricrete. Correlation matrix (Table 2) indicates negative relationship for iron with Si and

Al; and positive relationship though not very strong between Si and Al. Relatively higher mobility of Si compared to Al is related to secondary quartz produced due to dissolution of primary quartz (Si), its removal and precipitation (Fig. 6A) compared to kaolinite (Al) which is partially removed by erosion not by dissolution (Fig. 3F).

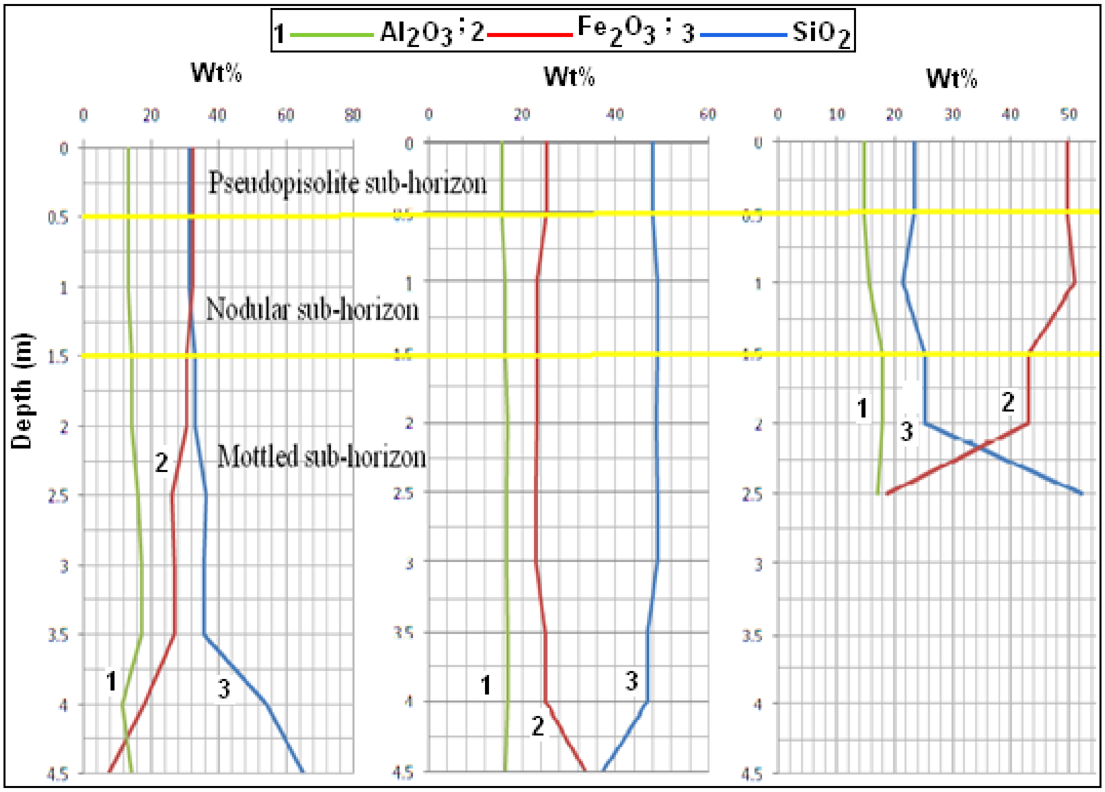

Figure 7. Variation in Fe_2O_3, Al_2O_3, and SiO_2wt% values in ferricrete with depth (test pit data from Ezana). **Note:** Lines at 0.5 and 1.5m depth indicate approx. sub-horizon boundary.

Major oxides data of three drill holes maximum about 4.5m deep passing through the mottled sub-horizon (Fig.7) indicate significant variation in both Fe_2O_3andSiO_2 concentration values between 3.25-4.25m compared to 0.25-0.5m depth. Al_2O_3 on the other hand almost remains constant with minor variation from top to bottom in the section. The sub-horizons shown in the figure 7 compare well with that of ferricrete profile shown in figure 3, which is about 3mthick and exposed in the quarry site in the central part of the study area. Since the sub-horizons thickness is more or less comparable with that of test pits (borehole) log data, it is possible to relate the elemental concentrations and their geochemical behavior along ferricrete profile. Correlation matrix (Table 2) of surface ferricrete samples data also correlate well with the test pits data. Compared to others, mottled sub-horizon varies in thickness from less than a meter to more than 3m (Fig. 7). Among trace elements, vanadium shows significant values > 1300 ppm in ferrictere compared about 300ppm in source sandstone. These values also tallies well with Ezana data in which vanadium shows values > 2500ppm. Apart from V, zirconium values range upto 222 ppm and Co upto 129 ppm (Ebrahim, 2011).

4.3. Development of ferricrete

Petrographic together with field data indicate that ferruginous sandstone forms the source for the development of ferricrete as part of lateritization and residual enrichment. Different sub-horizons noted in the ferricrete profile based on mineralogy and textures compare well with the laterites (ferricretes) reported elsewhere developed on ferruginous sandstone (Nahod et al., 1977; Tardy and Nahod, 1985; Ramakrishan and Tiwari, 2006; Ramanaidu et al., 1996).

4.3.1. Ferruginous sandstone to mottled sub-horizon

Transition from red colored ferruginous sandstone to mottled sub-horizon lateritization is progressive and is indicated by a) increase of coloration and indurations; b) preservation of the primary sedimentary structure; and c) complete and/or partial epigenesis of the components of parent rock minerals (quartz and orthoclase feldspar). The ferricrete with mottled sub-horizon is originated directly from the ferruginous sandstone with about 15-20% iron oxides/hydroxides as cement and iron oxides supplied by the percolating solutions during weathering. The major process in the transformation of ferruginous sandstone to mottled sub-horizon is the breakdown of the rock into lithic fragments and chemical breakdown of orthoclase feldspar mineral structures and partial dissolution of quartz. This will produce a network of channels and large tubular voids of large diameters (cm) in which kaolinite produced due to breakdown of feldspar and iron-rich cement material can accumulate.

4.3.2. Mottled to nodular sub-horizon

Continued weathering of mottled sub-horizon has produced indurated nodular sub-horizon. It may be related to two processes. 1) The massive iron crust with strong iron-rich cement (mottled sub-horizon) gradually develops into nodules or concretions by partial dissolution of quartz grains and remobilization of iron-rich cement. This is well indicated in the petrographic study where the voids created by the partial dissolution of quartz and breakdown of feldsparsare partially replaced by kaolinite-ferruginous material (Figs. 3, 4& 6). Thus the nodular and concretionary type sub-horizon is produced with colloform and open space filling textures. 2)

Voids developed by leaching of the quartz serve as secondary "reception" structures for kaolinite. This is because the original ferruginous sandstone is devoid of kaolinite and the latter is the result of the chemical breakdown of orthoclase feldspar present in sandstone (Fig. 6). Kaolinite is later replaced and progressively enriched in iron thus producing fine-grained iron ore mineral characterized by small pore size (<< 0.1 mm). In addition, in this sub-horizon, there is an accumulation of secondary quartz developed by precipitation from the percolating silica-rich solutions from the upper parts of the profiles (Fig. 6).

4.3.3. Nodular to pseudo-pisolitic sub-horizon

The mixed nodular sub-horizon further evolved into pseudo-pisolitic possibly due to the following geochemical changes. Removal of Si in the mixed nodular sub-horizon and the subsequent modifications affected the ferruginous components (iron oxides/hydroxides) and kaolinite in the iron and kaolinite matrix. The re-organization of indurated mixed nodular sub-horizon takes place by insitu centripetal way of accumulation of iron oxide and removal of kaolinite and development of pisolitic structures. Continuous reorganization into pseudo-pisolite is accompanied by the gradual removal of kaolinite and further dissolution of the nodules and mobilization of iron oxide/hydroxides. This leads to the reduction in size of the coarse nodular structure into smaller size pisolites and thus producing the pseudo-pisolitic textures and pseudo-pisolitic sub-horizon. Presence of poor matrix in this horizon compared to other sub-horizons exposed the pisolites to erosion and accumulated in the stream channels.

Behavior of Fe, Al and Si in the vertical sections suggests that residual enrichment of iron is significant. Movement of iron oxides downward from the top sub-horizons facilitates coating and thus accumulation of iron around the nodular fragments. Mobility rate of iron being low compared to silica and aluminum gradually accumulated with time and favorable conditions. During which the iron oxide/hydroxides have modified from hydroxide (limonite, goethite) to hematite (iron oxide). Thus, by the combination of absolute and relative accumulations of iron produced ferricrete from the ferruginous sandstone. But during lateritization, precipitation of the silica-rich solutions derived from dissolution of primary quartz produced secondary quartz, chert periodically, thus reducing the size regularly and finally reaches to smaller sizes in the pseudo-pisolitic sub-profile. Al on the other hand oscillates between kaolinite and iron oxy-hydroxides where it will be a substitute and Fe oscillates between dissolved and crystallized forms only.

4.4. Mineral Paragenetic Sequence

The mineral that are involved in the lateritization of sandstone to iron crust (ferricrete) are hematite, goethite, limonite, ochre, quartz, feldspar, kaolinite, chert and iron oxy-hydroxide cement. On the basis of field observation and petrographic study following paragenetic sequence is proposed for the lateritic iron deposit and shown in table 3.

Table 3. Paragenetic sequences of the minerals in ferricrete formation (**Note***:* thickness of the line indicates concentration of the mineral).

Minerals	**Stage 1 (Mottled sub-horizon)**	**Stage 2 (Nodular sub-horizon)**	**Stage 3 (pseudo-pisolitic sub-horizon)**
Quartz	▬▬▬	━━━	───
Orthoclase feldspar	▬▬▬		
Iron-rich cement	▬▬▬	━━━	───
Limonite	───	████	▬▬▬
Kaolinite		▬▬▬	───
Secondary quartz		▬▬▬	┈┈┈
Goethite		▬▬▬	▬▬▬
Hematite		┈┈┈	━━━
Ochre			━━━

4.5. Comment on genesis

Hematite, goethite, limonite and ochre are common minerals in the ferricrete. Goethite is seen converted to hematite instead of hematite to goethite as hematite does not show any alteration to goethite as expected in an oxidizing weathering condition. Paragenetic sequence of iron minerals seems to have developed in the following manner. The ferruginous sandstone originally may be devoid of hydroxides of iron (like goethite) because of the transformation of metastable goethite formed in water into hematite during long burial digenesis of sediments of Tertiary to Paleozoic in age (Tardy and Nahod, 1985) and this is noticed by not well developed goethite in the polished sections; b) Goethite does not replace hematite because the temperature is relatively high and do not favor hydration of hematite to goethite in the iron crust particularly that occurs at the top of the profile; and c) The relative stability of goethite and hematite depends on many factors such as grain size effect. If the crystal of hematite is grater or equal to the grain size of the crystal of goethite, hematite is stable than goethite in water but in the reverse situation goethite is stable but in the case concretion and nodules in iron crust (ferricrete) formation both minerals do not from large crystals and appear as a very tiny particle size (Tardy and Nahod, 1985). So, the governing condition for stability of these minerals mainly is dehydration and water activity compared to the particle size.

If iron is released from silicates and from other primary source in water then it will form goethite; if the solubility product of goethite is excess than that of ferri-hydrite. Ferri-hydrite is formed and transformed to hematite through dehydration or to goethite through dissolution; the factor that favors ferri-hydrite formation will also favor the formation of hematite by high temperature by dehydration. The factors controlling the formation of ferri-hydrite in solution are: a) rapid release of Fe; b) low concentration of organic compound which complexes iron (allowing concentration of inorganic Fe^{3+}); c) iron release in ferruginous sandstone being high because the large pore size (with iron hydroxide matrix) favor increasing activity of water; d)presence of negligible amounts of organic matter (or organic compounds) in thesource ferruginous sandstone could be one of the reasons for the stability of hematite over goethite during ferricrete formation; and e) equilibrium condition involving water activity, pore size and nodule formation(Tardy and Nahod, 1985; Nahod et al., 1977; Tardy et al., 1991).

5. CONCLUSION

Ferricrete developed on ferruginous sandstone (Adigrat? of Mesozoic) is composed of a succession of different sub-horizons, namely mottled, mixed nodular and pseudo-pisolitic. Fe_2O_3 content in ferricrete varies from 30-50 wt%, Al_2O_3 upto 25% and SiO_2 upto 30%. On the basis of the field and petrographic data, the successive sub-horizons in the ferricrete are noted as: massive structure (iron pan) and dismantled pisolites →upper mixed horizon (medium nodular)→lower mixed horizon (coarse nodular) → mottled horizon (saprolitic) →the ferruginous sandstone. Ferricrete horizon shows gradational contact with the source ferruginous sandstone. Gradual removal of kaolinite and silica facilitated enrichment of iron oxide/hydroxides in the form of coating around lithic fragments, nodular, pisolitic etc. Iron hydroxides, limonite and goethite with time are changing to hematite due to dehydration. Hematite is fine grained and shows textures like colloform banding, fracture filling, dissemination etc. Geochemical behavior of major elements clearly indicates the role of climate, Eh, pH, ionic activity etc factors in the development of laterite development. According to an approximate estimate the tonnage of the reserve is above 100mt with an average grade of about 35-40wt% iron and among trace elements, V, Zr and Co shows relative enrichment upto 0.3wt% (Ebrahim, 2011).

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