

VARIATIONS IN CONTENTS AND FORMS  
OF SESQUIOXIDES IN "LATERITIC" SOILS

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Presented at the "Eurolat" meeting,  
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## Variations in contents and forms of sesquioxides in "lateritic" soils

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### 1. PLINTHITE

#### 1.1 Definition

The present definition of plinthite, as in use by soil scientists (Soil Taxonomy, FAO), is as follows:

"Plinthite (Gr. Plinthos, brick) is an iron-rich, humuspoor mixture of clay with quartz and other diluents. It commonly occurs as dark red mottles, which usually are in platy, polygonal, or reticulate patterns. Plinthite changes irreversibly to an ironstone hardpan or to irregular aggregates on exposure to repeated wetting and drying, especially if it is exposed also to heat from the sun. The lower boundary of a zone in which plinthite occurs usually is diffuse or gradual, but it may be abrupt at a lithologic discontinuity.

Generally, plinthite forms in a horizon that is saturated with water at some season. The original segregation of the iron normally is in the form of soft, more or less clayey, ed or dark red mottles. The mottles are not considered plinthite unless there has been enough segregation of iron to permit irreversible hardening on exposure to wetting and drying. Plintyhite in the soil usually is firm or very firm when the soil moisture content is near field capacity and hard when the moisture content is below the wilting point. Plinthite does not harden irreversibly as a result of a single cycle of drying and rewetting. After a single drying, it will remoisten, and then it can be dispersed in large part by shaking in water with a dispersing agent.

In a moist soil, plinthite is soft enough that it can be cut with a spade. After irreversible hardening, it is no longer considered plinthite but is called ironstone. Indurated ironstone materials can be broken or shattered with a spade but cannot be dispersed by shaking in water with a dispersing agent".

The above definition has given rise to quite some confusion, especially as regards the hardening requirement. A new definition is being proposed, as follows:

Humus-poor segregations of oxidized iron oxides, on account of present or past hydromorphism, occurring as reddish bands or mottles in a whitish iron-poor soil matrix of high bulk density and low-activity-clay mineral assemblage; except for their centres the segregations can be cut with a knife or spade and they slake in a watery dispersion agent, they are however likely to harden irreversibly within a few years to slag-like material upon repeated wetting and drying in hot open-air conditions.

The following notes should be made:

- Both definitions imply that the "plinthite" of soil scientists is not equivalent to "Buchanan's laterite", "mottled clay", "horizon bariolé", etc. of the geographers/geologists. These latter are however comparable to:

Plinthic horizon (proposed): A soil layer of at least 20 cm thickness with at least 10 volume percent of plinthite; it may be hydromorphic at present ("plinthaquic"?) or have experienced hydromorphism in the past ("plinthaeric"?)

Plinthic properties (proposed): A pocket of soil or a layer of less than 20 cm thick with more than 10% plinthite, or a layer of more than 20 cm thick with less than 10% plinthite.

- The irreversible hardened material is not anymore plinthite, but is called ironstone (or "petroplinthite"). When of massive appearance, the ironstone of the soil scientists is equivalent to the "laterite" or "carapace" or "Eisenkruste" of geographers/geologists.

When consisting of discrete elements (gravel or stone size) then the ironstone of the soil scientists is equivalent to the "iron concretions", "lateritic gravel", "piçarra", "cui rasse", etc. of the others.

- When ironstone material is re-subjected to hydromorphism then one can have new plinthite in a gravelly or stony matrix, either discrete or around the gravels!

## 1.2 Morphology and Composition

The colours (Munsell notation) are red, dark red, light red or weak red, often with yellow or reddish yellow outer bands. The non-plinthitic soil material is either white (aquic conditions) or light gray (aeric conditions).

The consistence is sticky and plastic when wet, firm to very firm when moist, hard when dry; central parts may be indurated. The plinthite and the surrounding matrix have a dense appearance, with bulk densities of 1.5 or more.

The plinthic horizon or the layer with plinthic properties normally has a moderate angular blocky structure, with some clay coatings (argillans). The structure stability of the horizon, as measured by the ratio total clay/water-dispersable clay, is however high. The layer is normally more clayey than the overlying horizons (although the consistence features may cause to an overestimation of such textural differentiation to a foreign hand).

The shape and size of plinthite is as massive bands, or mottles that are either discrete or linked into polygonal, reticular, or vesicular/prismatic patterns.

The mineralogical composition is quartz and sesquioxides: mainly haematite within a kaolinitic-quartzitic-gibbsitic matrix; a low percentage of the iron is in amorphous form ( $Fe_{ox}/Fe_{cbd}$  ratio less than 0.05).

The elemental composition:  $SiO_2/Al_2O_3$  (of the whole soil mass) at total analysis lower than 2.2,  $SiO_2/Al_2O_3+Fe_2O_3$  lower than 2.0 for the whole soil mass, but lower than 1.5 (?) for the plinthite itself.

### Significance

The ecological significance at present hydromorphism\* can be summarized as follows: Both the periodic water saturation and the denseness of the plinthic horizon are an impediment to root development. Hence forest growth in a humid overhead climate is limited or gives away to a grass savannah if the plinthic horizon occurs within 125 cm. The overlying horizons, if not hydromorphic too, have a fairly instable structure, inducing sheetwash, poor plant emergence, etc. Also soil fauna such as termites avoid the layer

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\* (to be verified by surficial observations in rainy season; with chemicals; or on standpipes - cf. Bouma/ICOMAQ)

itself, but in subhumid overhead climatic conditions they may be very active in the overlying layer and at the surface (mound building: making use of the stagnating water just above the plinthite).

At past hydromorphism, the denseness of the plinthitic layer is a physical drawback to root development and causes limited moisture storage. Termites do however in places penetrate deeply in such a layer and can "chew-up" both the red and the light gray parts of the plinthic layer, mixing both to the extent that the segregations disappear in a homogeneous reddish or yellowish soil mass.

The engineering/management significance at present hydromorphism is quite large: Machine traffic is difficult (slickspots), but the plinthic material itself is often very useful for road surfacing and building purposes because of its capacity to harden. Artificial drainage implies the risk of erosion of the surface horizons and the gradual hardening of the plinthic horizon itself.

At past hydromorphism there is no impediment to field traffic and soil tillage (unless the plinthic horizon is already capped with an ironstone crust). Good constructional material.

#### Genesis and taxonomy

Hydromorphism, in the presence of some organic matter, on rocks or in sediments with at least a fair amount of Fe and in an environment of advanced weathering (low-activity-clay minerals) is thought to be by far the most common driving force of plinthite formation. The exact cause and mineralogic pathway of the irreversible hardening is (to me) still obscure; drying out in hot conditions would seem to be essential. A good knowledge of the past climatic, vegetational and geomorphologic conditions is required to explain the complex nature and the position in the presentday landscape of many plinthite ironstone occurrences.

From agronomic/ecologic and engineering point of view the "aquic" and "densipan" properties warrant a high-level separation in the plinthaquic situation. If there is no (more) periodic aquic moisture regime while still the plinthite has not hardened (plinthaeric situation) then the denseness of the layer and the chemico-physical inertness of the plinthite parts themselves warrant separation at subgroup level. Some notes:

- the fact that in practical all cases a plinthic horizon shows characteristics of an argillic horizon implies that plinthic Oxisols are rare, unless the horizon occurs well below the control section.
- "Plinthite that forms a continuous phase" in the definition of Oxisols gives rise to confusion. What is "continuous"? Does it mean sheets, inter-linked mottles, or continuousness of the layer with plinthite?

## 2. "LATERITE" AND "LATERITIC SOILS"

The terms laterite and lateritic are no longer used in soil science. Instead one distinguishes soils-with-ironstone, and ferralitic soils.

### 2.1 Soil with ironstone

These are the soils with gravel, stones or sheets of humus-poor, slaglike iron oxide, as the result of irreversible hardening of plinthite mottles or sheets.

If the ironstone forms a massive sheet or layer, impenetrable for roots and moisture, then "petroferric" or "litic/paralithic" phases or family distinctions are added to soils which have either an "oxic", "argillic" or rarely a "cambic" diagnostic horizon: Ferralsols/Oxisols, Acrisols/Ultisols, some Luvisols/Alfisols, some Cambisols/Inceptisols, Nitosols\*.

If the ironstone occurs as discrete gravelly or stony elements, then "concretionary", "petric" or "skeletal" phases or family distinctions are applied.

For the soils where the massive sheet occurs quite shallow, or where the amount of gravelly/stony elements is excessive (80% or more), the Revised soils Legend of FAO/Unesco (1987) proposes to apply petroferric or petric Leptosols - to give due account to the low total amount of active soil material, i.e. the fine earth.

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\* for the sake of simplicity only two major international systems of soil classification are discussed here, viz. the FAO/Unesco Legend terminology and the US Soil Taxonomy system and where discussing Latin America also the Brazilian system. It should be noted that also in the French CPCS system and in the scheme of Fauck/Segalen detailed subdivisions of strongly weathered tropical soils are applied or proposed.

## 2.2 Non-stony ferrallitic soils

These are soils of strong weathering in freely draining position, without ironstone, in which the clay mineral assemblage consists of a mixture of kaolinite (or meta-halloysite), quartz and sesquioxides. They have either an open and stable granular or subangular structure throughout without significant textural differentiation in the profile and little or no amorphous sesquioxides: oxic horizon (Ferralsols/Oxisols). Or they have a subsoil horizon that is somewhat dense, less stable and of a blocky structure with some signs of clay transport; the latter expressing itself in clay bridges of films and/or textural differentiation in the profile as a whole: argillic horizon (Acrisols/Ultisols, Luvisols/Alfisols of low-activity-clay, and Nitosols).

### Iron and colour in the soils with oxic horizon

Restricting the discussion in first instance to the soils with an oxic horizon - the most strongly weathered ones, one can say the following as regards the influence of oxihydroxides of Fe (and Al):

The US Soil Taxonomy system (ST) and the FAO/Unesco legend (FAO) give different weight to the composition of the sesquioxides and their total percentage in the whole soil mass and in the clay fraction in particular.

High content of gravel-sized crystalline aluminium oxides (gibbsite) is recognized in ST as "gibbsitic" great groups (the relatively high 3rd categoric level of the system), presumably because of the complete inertness of the material in the colloidal sense (CEC and moisture storage near zero). The proportion and the composition of the crystalline iron oxide (goethite, goethite with Al-substitution, hematite, magnetite, maghemite) is however only recognized, as "oxidic", "ferritic" or "mixed", at the low 5th categoric level. The only implied recognition of high iron or aluminium content in the clay fraction, in well crystallized form, is in the denomination of "acri" at great group level (those soils with extremely low negative or even positive charge). Colour, as indicative for iron oxide in the clay fraction, is not used at all at any level.

The FAO/Unesco legend however adopted a high-level subdivision on colour of the soils concerned, thereby building upon older systems and the

Brazilian system in particular ("xanthic" for yellow strong brown, "orthic" for reddish yellow and yellowish red, "rhodic" for red to dark red, as well as for dusky red - all according to the Munsell notations). The colour is a soil feature that can be easily distinguished in the field, and a degree of correlation was noted with type, strength and stability of the soil structure, with natural plant growth at the same climatic conditions, and with fertilizer needs (especially phosphates) at agricultural production. The precise composition of the sesquioxide fraction of the clay fraction remained however unknown in many instances, because of lack of specialistic laboratory equipment. At best, elemental analysis (with concentrated  $H_2SO_4$ ) was carried out on a routine basis, resulting in the classic ratios  $SiO_2/Al_2O_3$  ( $K_i$ -value) and  $SiO_2/Al_2O_3+Fe_2O_3$  ( $K_r$ -value), with Titanium, Phosphorus and Manganese values as interesting supplementary information.

Research by Schwertmann, Herbillon and others on representative ferralitic soils has however taken place during the last decade in specialistic laboratories in Europe (X-ray diffraction, Mössbauer spectroscopy; measurement of Al- and Ti-isomorphous substitution in Fe oxides, chemical separation on degree of crystallinity, measurement of specific surfaces by EGME or BET- $N_2$ , measurement of saturation magnetisation, thin-section microscopic observations, electron microscopy on crystal structure, etc.). This has resulted in much more insight in form and degree of crystallinity of Fe (and Al) oxihydroxides and their contents in the clay fraction of Ferralsols/Oxisols and related soils of different colour.

As a broad rule one can say that lower colour values are associated with higher total contents of Fe-oxides, higher chroma's with stronger degree of crystallinity, and redder hues with higher ratios hematite/goethite. Dusky red appearance is connected with the presence of magnetite/maghemite (and anatase), also showing up in natural magnetism of the dry and crushed soil material. The soils in the extreme yellow side - for instance the "Latosolo Amarelo" of the eastern Amazon region in northern Brazil (colours of 10-7.5 YR 6/6) - have less than 3% free Fe (of dithionite citrate extraction) in the fine earth and approximately equal percentages of goethite and hematite. The ones of the extremely red side - for instance the "Latosolo Roxo" of the Sao Paulo-Rio Grande do Sul area of southern Brazil (colours of 10-7.5R 5/3-4) - have 12-25% free Fe, with hematite and magnetite predominating. Kämpf and Klamt (1984) proposed a separation of the Brazilian Latosolos into three classes based on Hm/Hm+Gt ratio (ratio less than 0.2



with hues yellower than 6YR; ratio 0.2-0.6 with hues between 6YR and 3YR; ratio above 0.6 with hues 2YR or redder). In the sequence yellow - yellowish red - red - dark red - dusky red there is a tendency for the structure to become strong fine granular instead of porous massive weak subangular blocky, associated with an increase in structure stability, in phosphate fixation, in effective moisture storage, in the chemical activity of the soil humus and in the amount of stable humus stored in the deeper layers. Differences in the contents of gibbsite, in the crystallinity of kaolinite, and in the soil climate can however play a blurring role. Really excessive amounts, say more than 25% of iron oxides in the clay fraction, may lead to less stable structures (cf. the Latossolos Ferríferos as recently defined in the Brazilian system; Camargo, Klamt and Kauffman, 1987).

The international committee for improving the classification of Oxisols in the US Soil Taxonomy system (ICOMOX committee, Buol et al.) has come around as to the importance of soil colour, and now proposes to introduce a colour differentiation at the fourth categoric level, more or less along the lines of the Brazilian and FAO/Unesco systems.

During a recent (1986) workshop of the Committee the Sao Paulo-Brasilia area of in Brazil, many research results on a number of carefully selected Brazilian Ferralsols/Oxisols were presented by an array of Brazilian and foreign Universities and Research Institutes (magnetic properties, Mössbauer spectra, Fe-Al chemical extractions, micromorphology, X-ray mineralogy of the deferrified clay fraction, phosphate adsorption-desorption characteristics, specific surfaces, weatherable minerals, geotechnical properties, etc.). At about the same time Klamt studied a range of about 60 Ferralsols/Oxisols and related soils of the world soil reference collection of ISRIC, originating from Africa, Asia and Latin America, including a substantial number of Brazilian profiles (Klamt, 1987).

Thus, there are now many more data becoming available, linked to important soil mapping units, to establish criteria for high level subdivision of the Ferralsols/Oxisols in relation to the sesquioxidic elements of their clay mineralogy and their colour.

#### Iron and colour in soils with an argillic horizon

In the soils with an "argillic horizon" (Acrisols/Ultisols; low-activity-clay Luvisols/Alfisols) a degree of separation on colour is applied in both FAO and ST (rhodic at third or fourth level in ST, "ferric" and "chromic" at

second level in FAO). The ecological significance of iron oxide content and colour is in these cases however often overshadowed by strong variation in the degree of development of the horizon of clay accumulation.

A special case however form the dusky red to dark reddish/yellowish brown soils of blocky to polyhedral ("nutty") structure and shiny ped surfaces. These soils, often developed from basic igneous rocks, extrusive volcanic material or soft limestones, are commonly known as Nitosols or Terra Roxa Estruturada. They are less strongly weathered than the dusky red Ferralsols/Oxisols, but differ from the other argillic horizon soils by their great depth, their gentle textural changes in the profile, the high porosity, good moisture storage per unit of volume, stable structure and rather specific behaviour at fertilizing (cf. Sombroek, 1981).

Since these characteristics are difficult to quantify, there has been a reluctance in most classification systems to separate them at the highest categoric level. It turns out however that they have always an appreciable content of "amorphous" Fe as well as a relatively high ratio between "amorphous" and crystalline free iron oxides. In the draft Revised Legend of FAO (1987) the Nitosols are therefore proposed to have more than 0.2% "amorphous"  $\text{Fe}_2\text{O}_3$  and a  $\text{Fe}_o/\text{Fe}_d$  ratio of more than 0.05. Presumably this "amorphous" iron is mainly the short-range-ordered ferrihydrite, which has about 5 times higher specific surface than the crystalline iron. One can also assume that this ferrihydrite forms a thin film around the crystalline cores. In such a case it is the amorphous iron rather than the crystalline iron which determines the colloidal behaviour of these soils. The specific surface indeed proves to be substantially higher than that of Ferralsols/Oxisols and Acrisols/Ultisols: often twice as high, at comparable clay contents. This would cause the higher net moisture storage of the Nitosols, and also form an explanation of their specific P sorption-desorption behaviour: relatively high available P values of the soils under natural vegetation; high sorption of added fertilizers on the amorphous films around the crystalline iron cores, hence little loss through leaching, but not a real fixation in the crystalline iron oxides because their surface is masked, making the P available through the extractive force of plant roots.

The causal relationship between the specific iron oxide composition and arrangement of the Nitosols and their typical polyhedral structure with shiny ped faces is still to be investigated.

