

2. Metallic oxides and hydroxides in soils of the warm and humid areas of the world: formation, identification, evolution

P. Segalen
Services Scientifiques Centraux de l'ORSTOM,
93 Bondy (France)

INTRODUCTION

Over large areas of the world, one can see that soils are bright coloured, with red or yellow hues (both colours can exist at different levels in the same profile). They contain appreciable amounts of iron oxides and/or hydroxides, and sometimes aluminium hydroxides, manganese and titanium oxides. Sometimes, but always locally, oxides and hydroxides of cobalt, chromium and nickel.

A glance at a world map (Ganssen and Hädrich, 1965) shows that these coloured soils are located mostly between the tropics, but that some of them can be found north and south of these limits. They all belong to equatorial, tropical, subtropical, mediterranean climatic régimes and are seldom found in cool climates; they are completely lacking in the deserts. They can be found mostly where the climate is wet and warm; they are seldom found (and inherited from past climatic conditions) in the deserts, but can be found isolated in subtropical and mediterranean zones; they become unusual with altitude as well as in the cool temperate zone. On account of past climatic conditions, it does not appear possible to ascertain the limits of their present genesis; all we can do is to give the actual geographic limits.

Thus it is for the equatorial, tropical, subtropical and mediterranean zones that I am going to try to discuss the formation of metallic oxides and hydroxides. This great area, which is split up in the northern part of Africa by the Sahara, presents no interruption in southern Africa or in South-East Asia, for instance, where climatic conditions change gradually from one type to another. The distribution of these zones is given in Figure 1.

One can see that this distribution has been modified by the forms of continents, the relative position of shorelines and winds (trade winds and monsoons) and

cold or warm currents. The height and direction of the main mountain ranges, the relief in general, all have consequential effects on rainfall and temperature which can be greatly modified.

After this quick and unavoidably hasty survey of the climatic conditions, let us see the materials which rainfall and temperature are liable to affect. All parent materials are present and, with some remarkable exceptions, the main igneous volcanic, metamorphic and sedimentary rocks are present but are not spread in any sort of distribution; they are closely related with geomorphology. There are roughly two major types of relief: mountain ridges and islands on the one hand, plains and plateaux on the other. Consequently, these differences have important effects on drainage.

Considered as a whole, Africa, Europe and Asia are crossed by an almost continuous mountain range. In Africa and western Asia, the climate is mediterranean; in eastern Asia and Indonesia, the climate is tropical and equatorial. These make up the northern boundary of the area under study. On the other hand, in America, mountain ridges run from north to south on the western rim of the continents. Generally speaking, they are composed of marine sediments (mostly limestone and marls) on which large masses of volcanic materials have piled up, especially in America, Indonesia and Japan. Ultra basic rocks are known in such places as Cuba, the Philippines, New Caledonia.

The remainder of the continents consists of flat stretches joining plateaux seldom more than 1,000 metres high, and low-level plains. Thus, in South America, plateaux of Brazil and Guyana together with the Amazon and the Parana plains; in Africa, different plateaux from Guinea to Angola and the plains of the Niger, Chad, Congo, Sudd, etc.; in India, the Dekkan and the Ganges plain. All these plateaux are often bevelled through eruptive or metamorphic rocks and



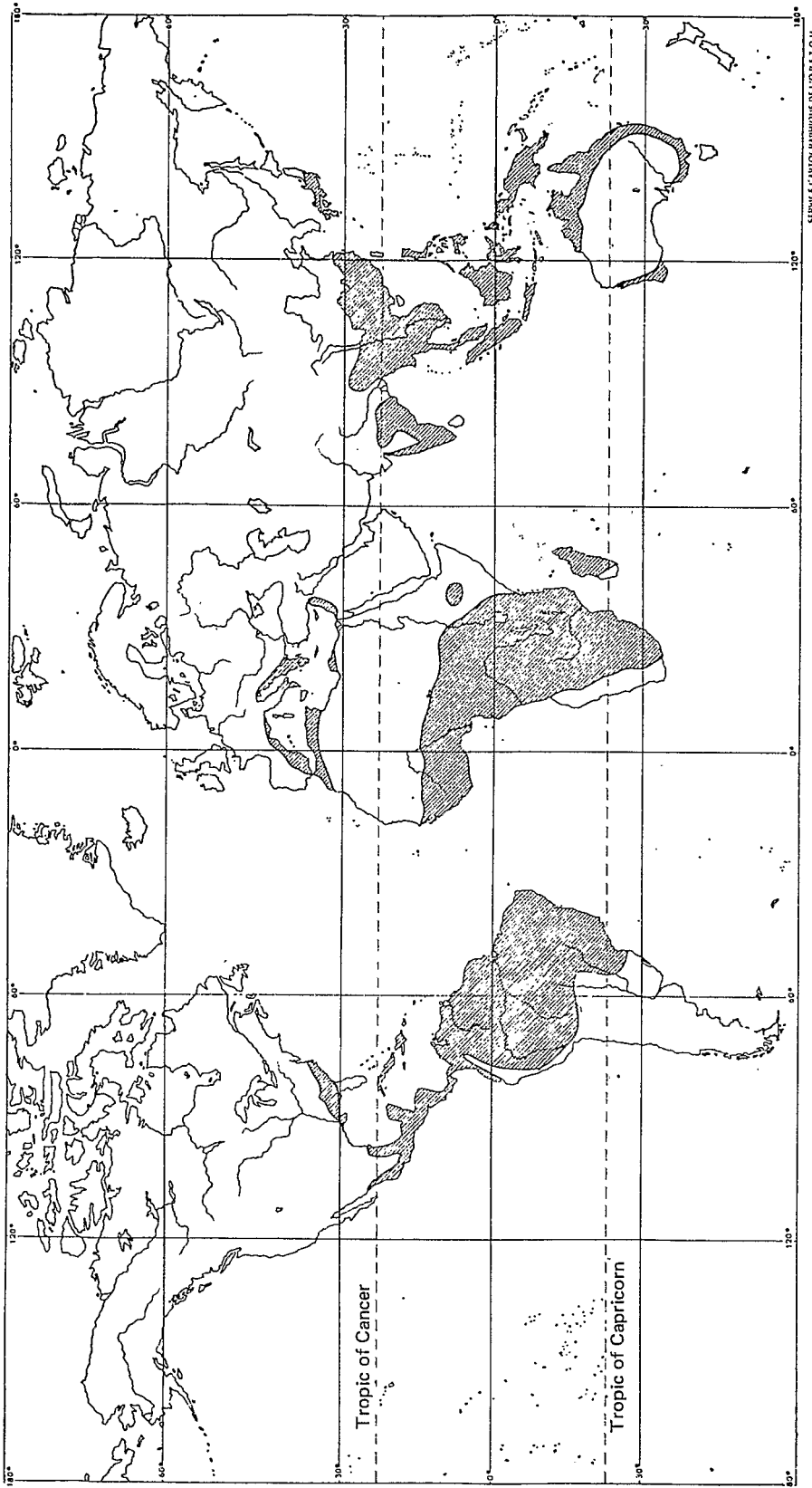


Fig. 1. Areas occupied by soil containing notable amounts of metallic oxides and hydroxides. After maps by Ganssen and Hädrich (1965).

capped with powerful lava flows. Sedimentary rocks are mostly detritic and of continental origin; marine sediments are uncommon except on the outskirts. These plateaux have undergone long erosion cycles and presumably soil-forming factors have been in action for very long periods. This is, to be sure, one of the main features of these plateaux. Moreover, the flexible tectonics which affect the mountain areas are here completely lacking. On the other hand, faults with large-sized grabens are common, as in eastern Africa. While the temperate zones (in the north as well as in the south) are strongly marked with Quaternary glaciations, nothing similar can be seen in this area. No glacial tills or outwash, no loess is encountered. In temperate zones, soils are rather young and develop under mild climatic conditions. In warmer and variously humid areas, weathering carries on for ages on materials submitted to drastic climatic conditions.

The vegetation which corresponds with such a variety of situations is itself quite diversified. Rainfall is the main factor of diversification, since, except for the top of the mountains, temperature remains always fairly high. Rain, pouring down heavily or dropping sparingly, is responsible for the main vegetation features. Forest cover is most common and varies with hardly perceptible tinges due to gradual climatic changes up to the deserts where all vegetation comes to an end. The primary woody formations are very often associated with secondary ones such as savannahs, steppes, maquis and so on, which are due to human activities (such as clearing the land to bring it into cultivation, repeated bush fires which steadily eat away the forests).

Except for extremely arid zones, warm and humid areas all have in common soils containing iron oxides or hydroxides; manganese and titanium oxides are always present, but in smaller amounts. In wetter areas, in good drainage conditions, aluminium hydroxides are met; accumulation of other metallic oxides is associated with ultrabasic rocks.

Along with these oxides and hydroxides, clay minerals containing aluminium, iron, magnesium and various alkaline metals, can be formed, transformed or accumulated. The presence of ferruginous products is a feature common to the whole zone. But important divisions are provided by the clay minerals. Hence, three provisional divisions can be set out as follows.

1. Presence of kaolinite together or not with aluminium hydroxides. Small amounts of illite can be encountered but no other three-layered clay mineral. All the ferruginous materials are outside the clay lattices. This is true for ferrallitic soils or oxisols, ferruginous tropical soils and some hydromorphic soils.
2. Kaolinite is associated with different three-layered clay minerals (especially montmorillonite). Ferruginous materials are both inside and outside the clay mineral lattice. Soils are fersiallitric (Mediterranean red and brown soils), semi-arid reddish-brown soils,

subtropical chestnut soils, red-yellow podzolic soils and so on.

3. Three-layered clay minerals are dominant. Iron is mostly inside the clay lattice and seldom outside. This concerns vertisols associated with some of the above-mentioned soils.

PART ONE

After an outline of the general distribution of hydroxides and oxides in soils and the climate, parent-rock, geomorphology, vegetation and time conditions that prevail in their formation, I shall now try to go into further details about the minerals which provide them and their weathering, and next describe the main crystallized and amorphous minerals and the way to determine them.

ORIGIN OF METALLIC OXIDES AND HYDROXIDES, ROCKS AND MINERALS

Oxides and hydroxides which are abundant in many soils of the area under study originate in the weathering of the minerals of which the rocks are composed. These minerals belong to various families, not all of which can be studied here. Only those which have an actual pedogenetic interest and are met all over the world will be taken into account here.

Igneous rocks are made up essentially of iron, aluminium, magnesium, potassium, sodium and calcium silicates in various proportions and in different structures. Some other minerals containing the above-mentioned metals are present but their importance is slight.

When they undergo weathering, these minerals are subject to important or minor transformations. The newly created products can stay where they are, be displaced by winds, waters or glaciers. They can form new materials on continents, in lakes, in seas and form sedimentary rocks. All these materials, coming from the depths as well as from the surface, are liable to weathering and can be considered as starting points for oxides and hydroxides.

It is customary to call 'primary' minerals those which form in the depths of the earth and are the main constituents of rocks and 'secondary' minerals those which derive from the former under weathering processes.

Amongst primary minerals, let us mention: peridot, garnets, pyroxenes, amphiboles, micas and feldspars. Their structure is quite elaborate. The three main components are the tetrahedra, the centre of which is occupied mostly by silicon, sometimes by aluminium; the octahedra, the centre of which is occupied by a metal, such as aluminium, iron, magnesium; the hexagonal prisms with potassium in the centre.

Peridots are magnesium and ferrous iron orthosilicates. Silicon tetrahedra do not join by a summit but are connected through hexacoordinated magnesiums. Weathering of these minerals leads to the elimination of silicon and magnesium, while ferrous iron oxidizes and hydrolizes to ferric hydroxides. It is worth pointing out that, in tropical regions, weathering of peridot mountain masses leads to the accumulation of iron products. This happens near Conakry in Guinea, in New Caledonia, near Surigao in the Philippines.

Pyroxenes and amphiboles are made of silicon tetrahedra joining through one or two apexes, to constitute single or double lines. All the tetrahedra are set out the same way: three apexes are in the same plane and the fourth juts out always on the same side, and the tetrahedra line up opposite one another through this fourth apex. Hexacoordinate metals such as ferrous iron or magnesium or calcium link the lines together. Weathering of these minerals leads to the loss of alkaline metals, magnesium and silica when drainage conditions are good. Residual iron accumulates as oxides or hydroxides. When drainage conditions are not so good, clay minerals may form. Aluminium, unless drainage conditions are good, favours clay minerals. Titaniferous augites release titanium to form anatase.

In micas, silicon tetrahedra join through three apexes to form indefinite planes. Two of these planes (where substitution of silicon by aluminium is important) are kept apart by an octahedral layer; the metals are magnesium and ferrous iron in biotite, magnesium in phlogopite, aluminium in muscovite. The hexagonal pits of the tetrahedral layers enclose potassium ions which hold together two mica layers. The weathering of these minerals leads to clay minerals, such as illite or vermiculite but also to iron oxides and hydroxides.

In feldspars, silicon tetrahedra join through the four apexes and are distributed in the three dimensions of space. One in every four tetrahedra is centred on aluminium instead of silicon. Alkaline or earth-alkaline ions are located between the tetrahedra. Weathering leads to clay minerals and/or to aluminium hydroxides.

Clay minerals as well as primary minerals are liable to lead to oxides or hydroxides as far as iron and aluminium are concerned. This is true for three-layered minerals as well as two-layered minerals like kaolinites.

All rocks are liable, in warm and humid areas, to supply soils with iron, aluminium and titanium material. Ultrabasic rocks are starting points for ferruginous products but also for chromium, cobalt nickel and manganese ones. Basic rocks, like basalt or gabbro, lead to iron hydroxides from ferromagnesian minerals, to titanium oxides from augite, to aluminium hydroxides from feldspars and other aluminous minerals (sometimes through clay minerals). It must be pointed out here that plenty of magnetite is found in these rocks and proceeds unchanged into the soil where it acts as sand. Acid rocks (rhyolites and trachytes, granites and

syenites, gneiss and some other metamorphic rocks) enclose few ferromagnesian minerals, and soils have often small amounts of iron oxides. However, this must not be considered as a rule, as some soils derived from granites in very humid areas can reach 10 to 20 per cent iron oxide. Feldspars are starting points for clay minerals and aluminium hydroxides. Titanium contents are usually low. Rocks containing much quartz (such as sandstones or quartzite) cannot promote aluminium hydroxides very easily, since plenty of silica is present. But iron oxides can form and coat sand grains or grow into concretions. Aluminous and ferruginous products can originate only from non-quartzose grains and these exist in small amounts (few ferromagnesian, feldspars or micas).

As for limestones, the matter is somewhat different. During the pedogenesis, quartz is hardly eliminated, leaving an abundant siliceous residue in the soil; on the other hand, calcium carbonate can be washed away completely or partially. The soil develops, deriving from the impurities of the limestone, clay minerals or primary minerals. This prevails under tropical (Central America, Mexico) or mediterranean conditions (surroundings of the Mediterranean Sea); great amounts of calcium carbonate must be got rid of before the soil develops. This sets the problem of the genesis of bauxites connected with limestones; but it cannot be discussed here at length. Let us recall briefly that quite different opinions have been set forth about the formation of these bauxites. Some authors state that aluminium and iron hydroxides originate through the hydrolysis of all the impurities of limestone rocks after the dissolution of carbonates. But some limestones are very pure, devoid of titanium oxide whereas the bauxite has a high percentage of this oxide. Hence this explanation has been refused by many people. Some think that bauxites derive through weathering from other materials than those they are found upon. They think that some material rich in iron and aluminium (as a volcanic ash) was scattered over the limestone and that the observed bauxite is nothing but the product of the weathering of the ash, and not of the limestone. It can also be considered that bauxite formed elsewhere on another rock from which erosion tore it away (through the action of running waters or wind) and trapped it on limestone. Each case must be examined carefully, as there is probably no unique explanation.

WEATHERING

Except for very few rocks and minerals, all are liable to act as starting points for the oxides or hydroxides found in soils.

The principal process is hydrolysis. Water contains not only HOH molecules but OH⁻ and H⁺ ions,¹ following the dissociation of a small number of mole-

1. Or, better, H₃O⁺.

cules. These ions are enough to ensure the breakdown of primary minerals and modify or destroy the original structures. They are responsible for the carrying away of alkaline or earth-alkaline ions. In even more minerals, these metals are replaced by hydrogens. Where rather large-sized ions are replaced by much smaller ones, structures are weakened and tend to collapse.

The Si-O-Al linking is affected, leading to the separation of aluminium and silicon. If the latter is carried away, aluminium hydroxide precipitates. This happens for feldspars, but white micas are much less concerned as they are resistant to weathering. Clay minerals, and especially three-layered ones, can also break down by weathering.

This hydrolysis leads to the separation of aluminium and one can ponder on the fate of this metal. If pH is lower than 4.2, the ion can subsist and is liable to move but most probably for short distances. If pH is higher than 4.2, a hydroxide will precipitate. The newly formed material is very often amorphous. If it remains surrounded by anions crystallization is slow and some forms, like pseudo-boehmite, may appear. If drainage is good, and if anions are washed away, gibbsite crystallizes directly or through an amorphous phase. In medium drainage conditions, aluminium may combine anew with silica to form clay minerals; two-layered minerals if there is not too much silica and bases; three-layered minerals if silica and bases are abundant.

In many primary minerals, iron is in a ferrous form. When weathering begins, water, which is responsible for the alterations, brings into the soil oxygen in solution. This oxygen is liable to oxidize the ferrous forms into ferric ones. At a pH lower than 2.5, ferric ions may subsist, but such acid soils seldom occur; at a higher pH, a hydroxide precipitates. As in an acid medium, iron offers no affinity for silica, the hydroxide remains as it is, or gradually transforms into goethite or hematite. If the medium is a reducing one, by absence of oxygen or especially by the introduction of organic material, the ferrous ion may subsist up to pH 6.5 or higher in very dilute solutions. This facilitates the movements of iron.

As for manganese, the problem is more complex, since, instead of two valences as for iron, three valences are known in the soil. Divalent manganous ions are stable up to pH 7.5; at higher values, a hydroxide appears which will convert into a tetravalent bioxide. Accordingly, iron and manganese, separated from primary minerals as ions, are easily oxidated and will develop in higher valence forms as oxides or hydroxides. Titanium separated from primary structures cannot exist as an ion above pH 2.2. A hydroxide precipitates which readily converts to an oxide. The redox potentials observed in soils are not low enough to allow reduction of tetravalent titanium (Fig. 2).

Organic materials are also responsible for the tearing off of metals from primary structures. Litter on the top of organic horizons is a source of soluble products

such as acids, aldehydes, phenols, etc., liable to attack minerals and extract metals, especially iron and aluminium. Under poor drainage conditions, these organic substances may be considered as responsible for the movement of iron in many soils. (Alexandrova, 1954; Betremieux, 1951; Bloomfield, 1956; Schatz, 1954.)

THE PRODUCTS OF THE SOIL

Soil sesquioxides may be divided into two main categories: amorphous and crystallized products. Both exist in the soils under study.

Amorphous products

A definition of amorphous products is necessary. They do not have a definite formula. Various names have been proposed such as cliachite or alumogel for aluminium, stilpnosiderite for iron, doelterite for titanium, vernadite for manganese, etc. They are variously hydrated and this water is easily heated away at low temperatures. Their specific area is usually high (300-400 m²/g for amorphous, ten times less for crystallized material). As there is no crystalline system, X-ray diffraction provides only very weak peaks, and no species can be identified. Amorphous products are very seldom alone in soils. Some soils derived from basic rocks contain up to 25 or 40 per cent amorphous material.

Crystallized material

Several types are known such as hydroxides, M(OH)₃ or MOOH and oxides M₂O₃. Very close relationships exist between some aluminium and iron materials. Only one hydroxide with formula M(OH)₃ exists in soils: gibbsite Al(OH)₃; there is no iron equivalent. *Gibbsite* is one of the basic constituents of the soils of warm and humid regions; its colour is white and it is seldom sufficiently crystallized to be seen without the microscope; its solubility is very low. Other hydroxides having the same formula are known. *Bayerite* is obtained in some synthetic preparations and during industrial processes. It develops easily to gibbsite by ageing, and has not been noted in soils. *Norstrandite* was discovered a few years ago; its presence in soils is known but needs confirmation. MOOH hydroxides are *boehmite* and *diaspore*. Both are constituents of bauxites more than of soils. The former alone has been identified in soils but not so frequently as gibbsite. *Boehmite* is a white mineral which can sometimes be recognized under the microscope. The structure of these minerals is now well known. Aluminium occupies the centre of octahedra distributed in planes according to three different models. There are two different iron hydroxides with the same formula of FeOOH: *goethite* and *lepidocrocite*. *Goethite* is a reddish-yellow mineral, often poorly crystallized, a commonplace product in the soils of

the area considered. *Lepidocrocite*, also reddish yellow, is met only in some hydromorphic soils, seldom in others. Goethite and diasporite have the same structure; so have lepidocrocite and boehmite.

The M_2O_3 oxides, or sesquioxides, are represented by corundum Al_2O_3 and hematite and maghemite Fe_2O_3 . Corundum exists in soils only when inherited from metamorphic rocks. *Hematite* is commonplace in tropical soils. It is red, non-magnetic and can be found in soils derived from volcanic rocks, in areas where a severe drought prevails during the major part of the year. *Maghemite* is a magnetic oxide. It derives from lepidocrocite by dehydration or from magnetite through oxidation. Maghemite is seldom met in soils and occurs especially in soils derived from volcanic rocks.

Let us bear in mind the *magnetite* Fe_3O_4 , which has a spinel structure, must be considered as inherited from basic parent material, but not as a soil-formed oxide.

Significance of hydroxides in soils

Gibbsite is fairly widespread in equatorial and humid tropical areas; it is sometimes encountered in the Mediterranean area. It is uncommon in very dry places. Its presence appears to be related first of all to a humid climate. Drainage also plays a prominent part in the occurrence of the mineral. Gibbsite is common in soils developed on broken land, even when rainfall is not too heavy, whereas in flat, level central Africa, even under heavy rains (e.g., in the southern Cameroons, in the Gabon, in the Congo) soils contain kaolinite rather than gibbsite. Finally some rocks, like basalt, contain easily weatherable minerals with a low silica content and lead quickly to gibbsite. On the other hand, flat but poorly drained land, containing silica-rich minerals, shows low contents in gibbsite. Boehmite is less common in soils of the area under review. It is sometimes identified in soils derived from limestone and in bauxites related with limestones. Recent laboratory work has led to the conclusion that gibbsite is stable under low pressure and ordinary temperature conditions. Boehmite is stable above $150^\circ C$. It is possible that lateritic crusts, which undergo a rapid increase in temperature, are in favourable conditions for a change of gibbsite into boehmite. Bauxites related to limestones (in western or central Europe) have been concerned with alpine folding and have undergone increasing temperatures and pressures leading to the transformation of gibbsite into boehmite. Bauxites concerned by much older folding (e.g., in the Urals, in the Appalachian mountains, and in Turkey), with still higher temperature and pressure, have diasporite instead of gibbsite.

Goethite is widespread in all the soils. It exists alone in usually wet soils (but not hydromorphic) of equatorial regions. Elsewhere, the yellowish colour indicates, amongst red soils, a wetter area. Hematite is usually present in soils under strongly contrasted climates.

Amorphous materials are present in many soils. Very often red soils depend on them for their bright colour. On the other hand, they lack completely in most yellow soils.

DETERMINATION OF OXIDES AND HYDROXIDES

A number of difficulties must be overcome when one wants to ascertain the nature and amount of sesquioxides in soils. First of all, between amorphous and crystallized material, the main difference, as far as chemical composition is concerned, is due to a higher water content. Usually not just one or two components exist together, but many more and of different nature. Some of them behave the same way when they undergo chemical or thermal treatments. Finally, the products are very small and special techniques are necessary.

Since the beginning of studies on soils, chemical analysis has been relied upon as a means of providing useful information. Alkaline fusion has been and still is in use, but it does not differentiate between minerals. This method was found too drastic and another, using a mixture of three acids, was recommended some time ago and used by Lacroix (1926), Harrison (1933) and many others since. The use of this mixture was generalized, at least for the soils of tropical areas. Unweathered primary minerals, like quartz, may be separated from most soil-formed minerals. This procedure gives a fairly good estimation of the silica/alumina ratio; moreover, it indicates if there is more aluminium than is necessary for kaolinite. For a correct estimation of alumina, it is necessary to know if no clay mineral other than kaolinite is present, but this is not easy using chemical methods only. According to water content, one can differentiate gibbsite and boehmite. With regard to ferruginous products, they can be determined correctly except if three-layered clay minerals, very often iron-rich, are present. The difference between hematite and goethite can be found on a water-content basis. Minerals such as ilmenite or magnetite are more or less attacked by the reagents and most of the iron is liable to be attributed to the soil. Manganese and titanium can be determined easily but it is somewhat difficult to tell which product they belong to. Therefore the method is liable to provide valid information on the centesimal composition but not much as far as identification of constituents is concerned. That is why methods leading to the selective identification of products or groups of products were looked for. Thus, the determination of oxides and hydroxides of alumina and iron were for a long period the aim of soil chemists.

Free alumina has been considered for some time as an unmistakable test of ferrallitization, and efforts were made to determine it quickly. Dissolution of alumina in sodium hydroxide, since the oxide is amphoteric, has been recommended. In addition alumina

reacts with some dyestuffs like sulphonated alizarine. But this dye reacts with other soil products and quantitative determination is not possible.

The determination of *free iron oxides* has given rise to much work in the quest of reagents able to dissolve these products readily. It is worth recalling that free iron oxides stand only for soil oxides and hydroxides, while primary magnetite and iron-holding clay minerals such as nontronite are excluded. The first widespread reagent was that suggested by Tamm (1922), i.e., a mixture of oxalate and oxalic acid. As it dissolves little iron, it was abandoned soon after but has regained some interest in these last years. It is now known that it does dissolve all free iron in soils like podzols, but not in tropical soils. Drosdoff and Truog (1935) recommend hydrogen sulphide, much more efficient than the former reagent. The acid was used in work on red lateric soils and red-yellow podzolic soils of the south-eastern United States and the results were good. But the reagent was not generalized in soil studies, perhaps on account of its nasty smell and toxicity. Dion (1944), Jeffries (1946) have used nascent hydrogen provided by the action of an acid on a metal coil, aluminium or magnesium. But the procedure recommended by Deb (1950) using sodium dithionite rapidly became very popular. The reagent is easy to manipulate and results are obtained quickly. By the addition of buffers and complexing agents, a number of alterations of the original procedure have been proposed. Finally, quite a different technique using ultra-violet irradiation on oxalic solutions was proposed by De Endredy (1963). The value of all these techniques is variable. It is necessary to test them and compare them with others of a quite different nature before good results can be expected.

Thermal analysis is based upon the variations undergone by a sample as it is heated. Two ways are possible: ponderal thermal analysis and differential thermal analysis. The former makes it possible to follow weight losses of a sample while it is heated. These losses may be due to organic matter combustion, decomposition of carbonates, or oxidation of sulphides; in the products we are concerned with, the loss is of water. Two kinds of water can be determined. The first goes off at low temperature (less than 150° C), and is related with the amorphous material; unfortunately at the same temperature, water held between clay layers is driven off. The second goes off at a definite temperature and is related with the constitution of molecules. The amount lost can be measured accurately. Constitution water of goethite or gibbsite can be measured, but both lose this water at about the same temperature. Oxides, of course, cannot be determined this way. Differential thermal analysis is based on the fact that a measurable electric current is produced between thermocouples connected together and heated to different temperatures. In order to study oxides and hydroxides, one of the thermocouples is put in the unknown product. During the

heating, endothermic reactions (absorption of heat necessary to drive away the water) or exothermic reactions (liberation of heat due to internal reactions) take place. The second thermocouple is placed in an inert product. The electric current produced between the couples owing to the different temperatures developed during the reactions, is recorded on a graph which permits the identification of the constituents. Water losses of goethite and gibbsite give rise to endothermic reactions which produce peaks on diagrams. Unfortunately these peaks are often superimposed. The change of maghemite or lepidocrocite in hematite produces an exothermic reaction which is expressed in peaks opposite to the former. This technique gives good qualitative information, but does not yield quantitative data.

X-ray diffraction is the safest method to identify soil oxides or hydroxides. The diffraction of a beam of X-rays by a powder containing the materials produces a diagram in which a number of distinctive peaks can be recognized. However, where several minerals are present, peaks may overlap and identification is not so easy. Peaks of low intensity are used, in this case, rather than strong ones. As for identification of gibbsite or goethite, no particular difficulty arises. But hematite and maghemite are not so easy to recognize and need a sensitive X-ray set. If large amounts of clay minerals are present, small amounts of oxides or hydroxides are not easily identified.

Infra-red absorption photometry. Few data on the absorption of infra-red radiations are yet available. But, this technique is certainly likely to provide very interesting information.

The identification of constituents by means of *microscopic methods* is unequally successful. The cutting of thin sections, and the small size of the crystals have long been a difficulty. However, the present setting techniques using plastics have allowed a rapid development of *micromorphology* investigations. Furthermore, *electron-microscopy* gives access to the study of shape and arrangement of small particles, tenths of a micron in size.

Determination of amorphous material. This material has long been difficult to identify and study owing to the lack of definite structure and formula. Thermic diagrams exhibit very strong endothermic peaks at low temperatures due to important losses of water. But this happens also for montmorillonitic clay minerals. X-ray diagrams display no characteristic peak. However, if amorphous material is cleared away, peaks of crystallized products which had been obliterated can appear (Tardy and Gac, 1968). A suitable process can be followed to dissolve and determine amorphous material. Tamm's oxalic reagent may prove satisfactory; but a technique using in turn an acid (8N hydrochloric acid) and an alkaline (0.5 N sodium hydroxide) can exhaust a soil of its alumina, ferric and silicic amorphous products (Segalen, 1968). X-ray controls show that

crystallized products are not disturbed by this procedure.

INFLUENCE OF OXIDES AND HYDROXIDES ON SOME SOIL PROPERTIES

This part concerns the properties used to characterize a soil, such as colour, structure or surface, that can be recognized by sight or by touch.

The colours of the soils of warm and humid areas that are due to oxides or hydroxides, can be reduced to two, namely yellow and red (brown colours are usually due to organic matter). These two colours are due to ferruginous, amorphous or crystallized material. The removal of amorphous material enables the basic colour to show up: reddish yellow when goethite is the main crystallized mineral, red when it is hematite, grey when important amounts of magnetite, greyish when clay minerals alone are present. Yellow soils do not change in colour when one tries to dissolve away amorphous material. This leads to the idea that they do not contain any; and in such a case, goethite alone prevails. Dark colours may be due to abundant magnetite. Black colours, that must not always be assigned to organic matter, may be due to manganese bioxide; greenish or bluish colours are usually due to ferrous iron. Heating brings about red colours through oxidation. Aluminous and titanous material only induce light colours. Iron-poor bauxites are pink or greyish.

Structures. Many discussions have concerned the importance of oxides and hydroxides on structures (MacIntyre, 1956; Meriaux, 1958). It seems that clay minerals, organic matter, and associated metal ions are responsible for structure. Little is known of the influence of aluminous, titanous and manganese material. On the other hand, definite influence is assigned to iron compounds in structural features. It seems that the main volumes (prisms, cubes, columns) are not much changed; but that coarse polyhedral forms are somewhat affected. However, the formation of pseudo-sands, made up of crystallized minerals (such as quartz, magnetite, kaolinite) stuck together by amorphous material is greatly influenced by iron. These very small particles are not easily dispersed by the usual procedures of mechanical analysis, and it is necessary to use ultrasonic vibrations to break them down. These pseudo-particles are not specific to any soil type. They can be noticed in different climatic areas and in soils derived from various parent materials such as sands or basalt.

Surfaces. Amorphous material is generally responsible for great specific areas. When amorphous products are dissolved, as well as free iron oxides, specific areas are greatly reduced.

PART TWO

In this part, the dynamic aspects of the metals in soils are examined: first of all, the features which enable us

to explain how they move; next, how they accumulate; and last, what is expected of the accumulated forms. In other words, we will consider here what happens to these metals during pedogenesis.

CONDITIONS OF STABILITY AND MOBILITY OF METALLIC COMPOUNDS

A short review of a few properties of ions and hydroxides is necessary to understand the conditions under which they can exist in soils. Conditions prevailing when they appear will also be considered.

Ions and hydroxides

The concentration/pH curve separates zones where ions and corresponding hydroxides are stable. Figure 2 provides these curves for each element.

Ionic features

The ions corresponding to the metals under investigation are all medium-sized: 0.51 Å for Al³⁺, 0.63 Å for Fe³⁺, 0.75 Å for Fe²⁺, 0.68 Å for Ti⁴⁺, 0.6 Å for Mn⁴⁺. Alkaline and earth-alkaline ions are much larger: 0.9 to 1.3 Å; and metalloids such as C, Si, N, are much smaller: 0.2 to 0.4 Å. The oxides of these metals depend on the ratio:

$$\rho = \frac{\text{cation radius}}{\text{oxygen radius}}$$

This ratio enables us to predict the co-ordination number of the metal, and the sort of structure it will fit into. The elements we are concerned with fit in octahedra Mn²⁺, Fe²⁺, Fe³⁺, Ti⁴⁺; Al³⁺ fits in octahedra and in tetrahedra (Table 1).

TABLE 1. Size of ions of principal elements and co-ordination number¹

Ion	R (in Å)	$\rho = \frac{Rc}{RO}$	Co-ordination number	
			Predicted	Found
K ⁺	1.33	0.95	12	8-12
Ca ²⁺	0.99	0.71	8	6-8
Na ⁺	0.97	0.69	8	6-8
Mn ²⁺	0.80	0.57	6	6
Fe ²⁺	0.74	0.53	6	6
Ti ⁴⁺	0.68	0.49	6	6
Fe ³⁺	0.64	0.046	6	6
Al ³⁺	0.51	0.36	6	4-6
Si ⁴⁺	0.42	0.30	4	4

1. Hexagonal prism is stable when $\rho \approx 1.0$
 Cube prism is stable when $\rho \approx 0.78$
 Octahedral prism is stable when $\rho \approx 0.41$
 Tetrahedral prism is stable when $\rho \approx 0.22$.

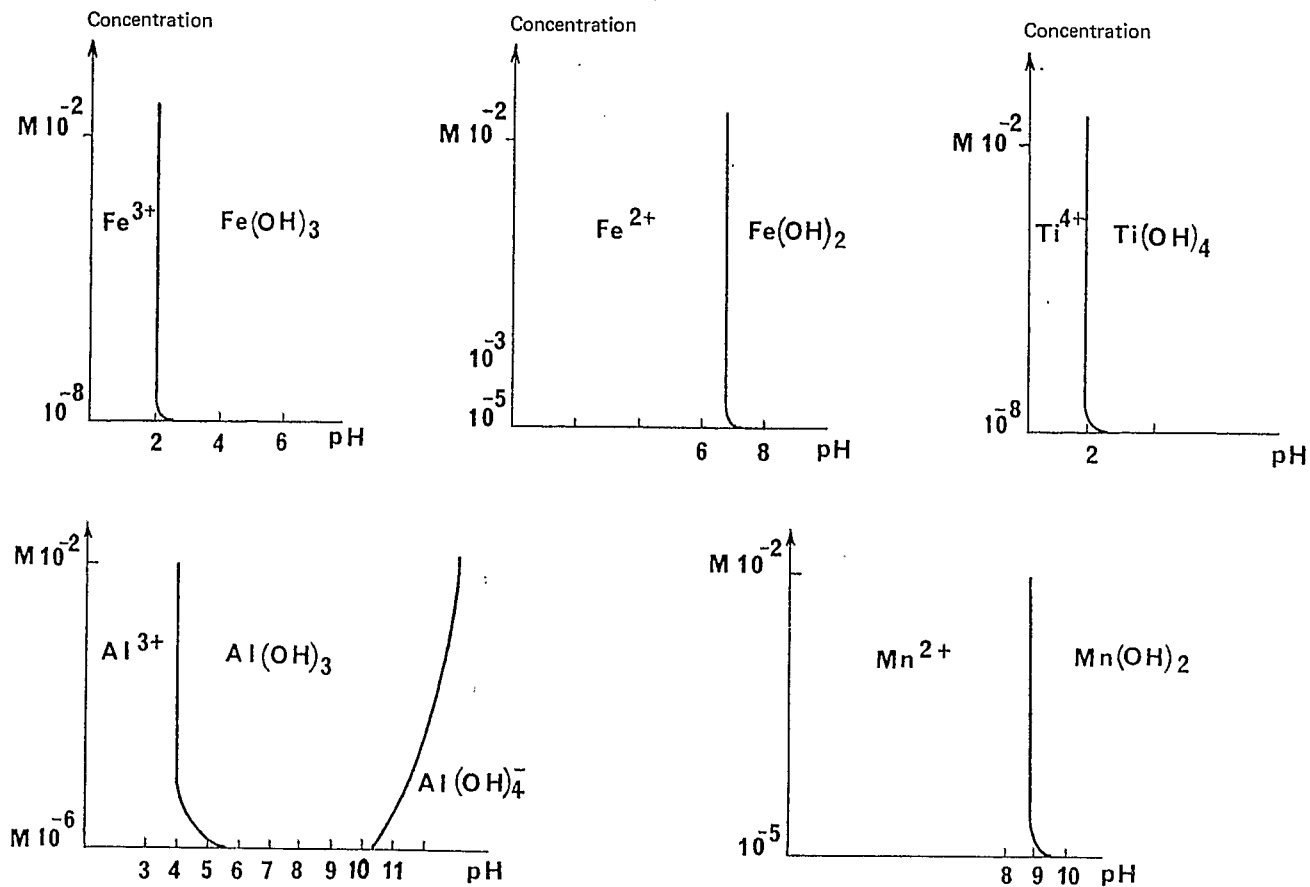


FIG. 2. Stability areas of ions and hydroxides (after Charlot).

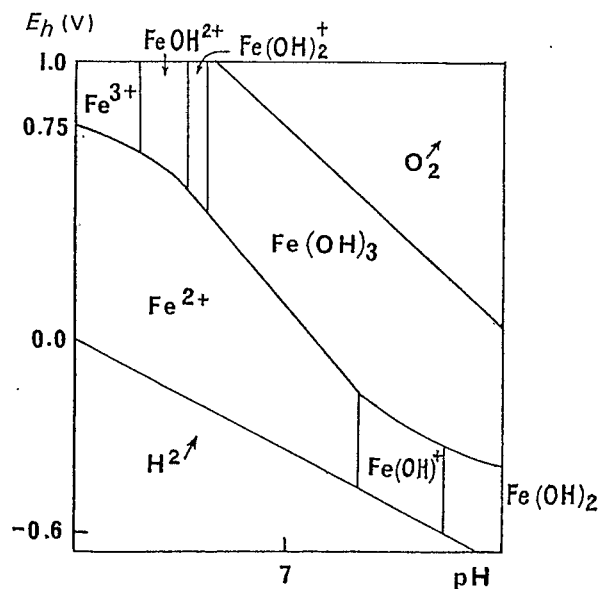


FIG. 3. Ferrous-ferric chemical equilibria as function of pH and redox potentials (after Hem and Cropper).

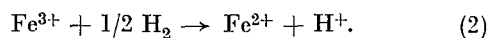
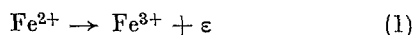
Solubility of hydroxides

Another interesting characteristic is the ionic potential, defined as the ratio of the charge Z on the ionic radius.

All the elements considered here have an ionic potential allowing us to situate them among the elements of low solubility (2 to 7); whereas soluble cations have a very low potential (< 2.0) and complex anions have a much higher one (9-40). All the hydroxides we are dealing with have a very low solubility product (10^{-15} to 10^{-39}). Consequently, except for very acid or very alkaline conditions, it appears highly improbable that any mobility of the above-mentioned products can be suggested when they are in the hydroxide form. Once they are precipitated it seems very difficult for water alone to be responsible for any solution and movement. Recent work by Herbillon and Gastuche (1962), shows that when iron or aluminum hydroxides precipitate, interesting developments take place, if at the same time, one proceeds to an effective dialysis. An amorphous product precipitates first, followed soon by a depolymerization which looks very much like a solution; little by little a crystalline phase (trihydroxide) appears. This can be related with what happens in some soils of humid tropical areas where water is so abundant that few ions are present in solution. So far, the hydroxides behave roughly in the same way, but some differences appear when redox potentials are concerned.

Redox potentials

Variations of redox potentials are due, in soils, to the presence of reducing organic material, and to the absence of oxygen in soils and waters, related to permanent or temporary high water tables. The variations of redox potentials concern some elements (like iron or manganese but not aluminium). But their effect depends on the reaction of the medium. At low pH, reduction is very easy; at high pH, stronger redox potentials must operate for the same result (Fig. 3). Iron and manganese behave in very much the same way. Iron proceeds from the ferric to the ferrous form very easily in moderately acid conditions but not so in neutral or alkaline ones. Therefore, in tropical acid soils, under poor drainage conditions, ferrous iron is easily obtained and this is liable to explain the mobility of this element every time even slightly reducing conditions occur. The oxidation or reduction reactions are the following:



Complexation and chelation

Some elements can belong to bulky molecules where they no longer have the same properties as they had when they were ions (Martell and Calvin, 1959). These

elements are called 'electron acceptors' and are liable to fix on their outer layer a number of electrons provided by other molecules called 'electron donors'. Acceptors are metals, such as iron or aluminum, donors are oxygen or nitrogen. Bulky molecules are constituted in which the metal is surrounded by a number of oxygens and belongs then to an anion liable to be solubilized in conditions very different to those of the central atom. If the elements of the donor are not bound together, a *complex* is formed (such as potassium ferrocyanid or cryolite). If the elements are bound together a *chelate* is formed. Whenever there is a bulky organic molecule with several functions where oxygens, oxhydrils, amins, amids... are close to one another (e.g., oxalic, citric acids, phenols, EDTA, etc.), chelates can form. Metals are then considered to be held in a claw (chela). The newly formed anion is liable to move in pH conditions when hydroxides usually precipitate. The synthesis of chelating substances in the upper part of soils is now generally admitted but their actual presence is not always demonstrated, as it is in podzols. In the laboratory, it has been shown that iron could be displaced easily with the help of complexing agents. In soils of the warm and humid area, where mineralization of organic matter is rather fast, chelating agents are not liable to exist very long. So their influence must be taken into account only when one can show they exist.

Lastly, one must consider the possibility of *displacement* of very minute particles, by a simple mechanical washing away. The size of particles of oxides and hydroxides is very small (less than one micron), much smaller than the smallest pore space of soils. But they are very often bound to the clay minerals and move along with them. Migrations can take place inside or outside the profile.

IMMOBILIZATION OF OXIDES AND HYDROXIDES IN SOILS

I shall try in this section to explain how, after having been solubilized as ions, metals assume one of the various aspects known in soils.

First of all, what happens to aluminum, iron, titanium, manganese, when the primary minerals which contain them are broken down by weathering?

A crystallized mineral may be formed right away, in the place of a mineral, the other constituents of which have been entirely eliminated. Goethite or anatase may crystallize in place of a plagioclase (Millot, 1964). These crystals may be observed with the help of a polarizing microscope or an electron microscope. Sometimes the crystals are large enough to be seen without a microscope (Lacroix, 1926, Madagascar). But crystals may not develop largely enough to be identified and amorphous material is present. X-rays are unable to show any geometric pattern. These amorphous

materials are very largely distributed in some of the soils considered in this study.

The metals take their part in the synthesis of new products: clay minerals such as kaolinite or halloysite (aluminium), montmorillonite (aluminum and iron), depending on the characteristics of the surroundings.

How are the oxides and hydroxides distributed in soils? A relative accumulation, by exportation of soluble material (alkaline, earth-alkaline bases, silica), may occur. This concerns mainly aluminum and titanium which are not easily mobilized, and also iron in many situations. An absolute accumulation may also occur, due to migrations inside the profile or by introduction in the profile of compounds coming from elsewhere. This concerns iron and manganese which are very sensitive to variations of redox potential (D'Hoore, 1954). Oxides and hydroxides concentrate in different ways:

First, they deposit on clay minerals. This was shown long ago by Barbier (1936) and confirmed by Fripiat *et al.* (1952) and recently by Follett (1965). Products are distributed in very minute particles along the flat planes of kaolinite and can be seen on electron microscope photographs.

Local concentrations of ferruginous or aluminous material occur with or without concentric structures. One can then have a series of forms differing by their external or internal appearance or by their contents in one or several components. These elements seldom exist alone and embody grains of quartz or magnetite, clay minerals like kaolinite, and unweathered rock material. These concentrations are usually from one to a few centimetres wide. Their origin has given rise to much discussion and probably varies from one sample to another. They exist as nodules, concretions, accumulations and so on. Small concentrations of sand (quartz or magnetite), of well-crystallized clay minerals (kaolinite) exist, bound together with amorphous products; they are named 'pseudo-sands'. The usual mechanical analysis techniques are unable to disperse these small aggregates, so the sand fraction is unusually high. The use of ultrasonic vibrations is necessary to break them down.

These accumulations can have a much larger extent. The oxide or hydroxide-enriched zones interest a whole horizon and concern soils occupying large areas (Aubert, 1963). Cuirasse¹ then forms with variable composition or morphology. They may be platy, vesicular, massive, etc., and result in binding of coarse sand grains, quartz pebbles, rock or cuirasse residues, by oxides and hydroxides. Sometimes their aspect is conglomeratic. Their composition is either dominantly aluminous (bauxitic) or ferruginous. Sometimes, the content in manganese is high, as well as in titanium. The mineralogical composition is the same as in the non-indurated horizons: goethite and hematite for iron, gibbsite and sometimes boehmite for aluminum. Hardening of these materials does not seem to be

directly related to the nature or to the amount of oxides or hydroxides; they seem rather to be related to alternate seasons and a topography dominated by subhorizontal planes, where drainage is often poor. This is the case for Africa and other continents where laterite is abundant on flat surfaces, but not in mountainous areas or even on very rough land. There seems to be a close connexion with the general pattern of relief. But most laterites formed in past geological times—and some of those formed nowadays—are at present high above the valley floors as a result of reversing of relief. Relations with past and present climatic conditions are not always easy to determine but one can consider as a reasonable thesis that the equatorial climate, as observed in central Africa and parts of some countries of west Africa for instance, as well as the subtropical and mediterranean climates do not favour formation of laterite. On the other hand, a tropical climate with alternate seasons, related to a rather flat topography, is most propitious to the formation of laterite. Those that can be seen in other climatic areas are to be considered rather as relicts of past conditions.

SUMMARY OF THE EVOLUTION OF SOILS

Having reached this stage, one could think that oxides and hydroxides have found definite form and place of accumulation. In some bright-coloured soils, oxides are firmly fixed on clay minerals, and binding of particles in pseudo-sands is effective; what then about concretions and laterite? The latter occupies large areas, is sometimes millions of years old and does not seem affected by time.

Are the materials thus stored in the landscape brought to a definite standstill or are they concerned with a new pedogenesis? The answer to this latter question is undoubtedly positive. But the introduction of the oxides in a new pedological cycle can happen in two different ways. The products are either solubilized, or remain in a solid state but are broken down. Both cases will be examined.

Solubilization of sesquioxides

This process concerns only iron and can hardly be retained for alumina. Reduction and chelation are possible and usually occur together. A first example is provided by the bleaching of bauxites, which has been considered by many authors (de Lapparent, 1930; Choubert, Henin, Betremieux, 1952). Organic matter is the agent (lignites for bauxites in southern France; march in Guyana) responsible for the reduction of iron, which is then easily leached away. Another example is provided by Maignien (1958, 1966) in his studies of

1. In his paper the French term 'cuirasse' is considered as equivalent to 'laterite'.

laterite, in Guinea and in all Sudanese Africa. The top of the laterite-capped plateaux is the source of iron; it is mobilized there and moves down to the surrounding gentle slopes where it contributes to the formation of new laterite. But it is necessary to locate an ill-drained area where local hydromorphy can allow the accumulation of organic matter liable to reduce an complex the iron. But this does not always exist. So one is led to the conclusion that the hardening of the new laterite is a result of a redistribution of iron on the slope itself, due to poor local drainage conditions. Iron proceeds from the fragments of the upper laterite carried down by gravity and not by solution.

Breaking down of laterite

Iron crusts are often limited by ledges which overhang the surrounding slope by several metres. Erosion is active on the soil immediately below the crust, which gradually breaks to pieces and is scattered on the slope. At the foot of the slope the fragments cannot go any farther and are, little by little, covered by the fine soil under the crust. In tropical areas, vegetation seems able to bring to a standstill all the fine earth, which thickens down the slope. The fragments of laterite are joined by pieces of quartz deriving from veins and form a regular sheet beneath the surface of the soil. Differences in texture and structure on very long smooth slopes, hardly ever cut by talwegs, favours, during the rainy season, a provisional hydromorphy, which is responsible for the formation of ferrous iron and for local movements of iron. A new sheet of laterite, made of pieces of the former and bound together by iron oxides, is obtained. The first, due to erosional processes, may disappear completely. The second, when a new water table settles may, in turn, appear above the surrounding plains. One can be surprised to find, at some height, laterite formed from debris of a sheet which has been completely destroyed by erosion. The ferruginous material may serve for several laterite caps and seems to step down a true flight of stairs. As a matter of fact, iron probably moves a comparatively small distance, either as solid fragments or in solution.

Bauxitic deposits, observed in Guyana (Bleackley, 1964), probably have a similar origin. Flat bauxitic plateaux located inland have been broken down by erosion and the debris were redistributed near the sea, where they are reworked now.

The course followed by ferrous iron when it reaches an underground water-level is probably more important. A water normally loaded with carbonic acid and dissolved organic substances can easily keep its iron in the ferrous form. But as soon as it reaches the surface, the redox potential rises, and a ferric hydroxide precipitates. The influence of micro-organisms during the precipitation of hydroxides of iron and manganese has often been pointed out. Various bacteria and fungi are

considered to be responsible for concretions and hard-pans containing these products.

Finally, if some of the iron escapes to continental precipitation, it will reach the ocean waters, where pH is usually high, as well as the salt content. Precipitation of the remainder of the iron happens then, except for the part which was consumed by some living organisms.

CONCLUSION

The studies accomplished in the laboratory, where more and more accurate techniques are used to identify amorphous and crystallized products, to determine the amounts present and their location in a sample, have made substantial progress. Associated with field work, they have led to a knowledge of the distribution of the elements in a profile, or in a landscape. Recently, studies have even been carried out on the distribution of some elements throughout the world (Pedro, 1968). Such a synthesis is now possible in many fields of research as more accurate methods develop and more samples are analysed.

We are now in a position to review briefly our knowledge of the oxides and hydroxides of the warm and humid areas of the world.

1. Near the Equator, goethite is the dominant iron mineral. Gibbsite is often encountered. Oxides of titanium as well as manganese are locally abundant. Amorphous products are seldom found in yellow soils. Iron is always outside the clay minerals lattice essentially kaolinitic. Concentrations of any of the above-mentioned minerals can be encountered in all tabular areas of the equatorial area. In Recent mountains, or in volcanoes, hardened types of concentration are hardly ever seen.

2. In the tropical zone, goethite and hematite are common. Gibbsite is seldom found. Amorphous materials are ferruginous or manganic. The former are very often responsible for the red colours of the soils.

In smooth slopes, where oxidation-reduction process can interfere, important migrations of iron occur. In acid soils it gathers to form laterite sheets or concretions, nodules, dots, etc. In neutral or alkaline soils, iron is often trapped by 2:1 clay minerals such as montmorillonites (Paquet, 1969).

In moderate or steep slopes where these processes do not interfere, soils are red coloured (seldom yellow), by amorphous material associated or not to goethite or hematite.

3. In the subtropical zone, goethite, associated with amorphous products, appears to be the dominant iron mineral. Gibbsite seldom occurs. Soils are usually well drained down the profile; however, mottled zones rich in concretions are known, as in Australia or the United

States. The iron content is high. Clay minerals are mostly kaolinitic, but 2/1 minerals such as vermiculite or montmorillonite, containing iron in the lattice, or presenting aluminum interlayering often occur (Rich, 1968).

4. In the Mediterranean zone, soils are dominantly red or brown. The brownish colour is due to goethite; the red colour is due to goethite and amorphous material, seldom to hematite; gibbsite is uncommon. Soils belonging to well-drained areas are red, those to poorly drained ones are brown (Lamouroux and Segalen, 1968). Clay minerals are varied (kaolinite, illite or montmorillonite). Concretions are small and scarce. No laterite is known.

What can be said about amounts? First of all there is no definite relation between the colour and the amount. An aluminous accumulation can be recognized by its colour, if little iron is present, but a red sample can be rich in alumina or not. A red or yellow sample contains much or very little iron. It is difficult to decide without personal experience of the studied area and without the help of analysis.

Soils containing the highest amounts of iron are those deriving from ultrabasic rocks. Weathering gets rid of silica and magnesia and iron accumulates by difference. This happens near Conakry in Guinea, at Surigao in the Philippines, in central New Caledonia (the amounts of iron oxide reach 75 per cent). Elsewhere, the figures are quite variable according to the parent rocks; soils deriving from basalts contain 20 per cent, and from granites or gneiss 12 to 18 per cent.

In the tropical zone, total amounts are low in the fine earth (usually less than 5 per cent), with accumula-

tion taking place in concretions or laterite. In the subtropical zone, amounts go up to 15 per cent and depend on the parent rocks. In the Mediterranean, soils deriving from limestone range from 8 to 12 per cent.

The contents of titanium are generally low as far as acid rocks are concerned. On the other hand, soils deriving from volcanic rocks contain much more (5 to 10 per cent) with exceptionally high values in Hawaii (Tamura *et al.*, 1953). The manganese contents are generally quite low; concentrations in soils are not uncommon. Concentrations in chromium, cobalt and nickel are closely related with ultrabasic rocks.

However, we still have much to learn about oxides and hydroxides in many a field. Even if we have better knowledge of the geographic area where these materials appear in soils, we must learn more about the conditions of climate, drainage, and parent material which prevail when they are formed. The knowledge of these conditions in the past must be studied thoroughly, as we are sometimes liable to assign to the present what is actually inherited from the past. Much progress must be made in observing the structure of the materials and their association: microscopic observation for microstructure, electron microscopy to see the individual particles and their shape. These two levels of observation, associated with the two extremes—eye and magnifying glass on one hand, X-ray diffraction on the other—will complete the previous work.

In the field, much remains to be done to spot, describe, and understand how these products appeared in soils and landscape. It seems that immobilization and migration of oxides are still questionable. But it is felt that progress can come only from careful examination of basic laws and relationships in physics and chemistry.

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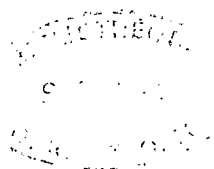
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