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Chapter 3

PEDOGENESIS, CHEMICAL WEATHERING AND PROCESSES OF FORMATION OF SOME SUPERGENE ORE DEPOSITS

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INTRODUCTION

In metallogeny, the term supergene is applied to ores or ore minerals which have been formed by generally descending meteoric waters, as opposed to hypogene, which corresponds to ascending waters (Routhier, 1963). But this term is also used by surface or subsurface geologists in a more general sense, to designate all processes originating at or near the earth's surface, such as weathering and denudation, and the continental deposits and sediments formed through such processes. In this general sense, the term supergene is nearly synonymous with the term epigene (see "Geochemistry of epigenesis", Perel'man, 1967), but it is more restrictive than the term exogene, in which the processes of marine sedimentation and diagenesis are included.

The main processes corresponding to supergene evolution may be defined as follows:

(1) Pedogenesis: formation of soil profiles, with more or less vertically differentiated horizons, which are derived from the in-situ evolution of preexisting parent rocks, through the action of meteoric and biological agents (waters, carbonic and humic acids, living organisms, etc.).

(2) Weathering: any alterations, either mechanical (e.g., fragmentation) or chemical (e.g., decaying) of materials of the earth's crust under the influence of atmospheric agents (heat, frost, surface and subsurface waters, etc.). The weathering acts not only in soil profiles, but also in deeper cracks, veins, faults and any porous layers, which are connected to the atmosphere. The resulting formations are termed regoliths, saprolites or alterites; they may have been differentiated either strictly in-situ (residual, sedentary alterites) or at a certain distance from their present location (reworked, migratory, or transported alterites). Thus, the concept of weathering is more general but not as well defined and delineated as is the concept of pedogenesis.

(3) Erosion: removal and displacement of materials on the land surface, which are produced either by the mechanical work of meteoric forces (rainfall, running water, stream water, winds, ice, etc.) or by the chemical dissolving action of waters, combined with the force of the earth's gravitational attraction. The mechanical and chemical erosion provokes the lowering of the land surface (denudation) and the flattening of the

landform, as the transported substances (solid or dissolved) tend to be displaced from higher to lower land surfaces.

(4) Continental sedimentation: local accumulation of debris (detrital sedimentation) or reprecipitated matters (chemical sedimentation) which have been moved and transported by erosional forces, into propitious continental sites, low lands, depressions and basins. These accumulations are often transitory deposits, since they are reworked by the continuing erosion and ultimately carried from the continents to the ocean basins. "Burial in the sea is the ultimate fate of most sediments" (Ordway, 1972).

The geochemical differentiations occurring during these supergene processes, are produced by two opposite mechanisms: (a) mechanisms of subtraction which proceed through leaching of the more mobile constituents and result in relative residual accumulation of the less mobile ones; and (b) *mechanisms of addition, which proceed through* migration of the more mobile constituents and result in absolute, lateral accumulation of these constituents. The former are considered to prevail during the weathering processes, whereas the latter are considered to prevail during the sedimentation processes (Millot, 1964). In fact, however, the supergene evolution often shows composite differentiations, proceeding through both mechanisms: for example, the B horizons in illuviated soils result simultaneously from relative and absolute accumulation of clay minerals (formation in-situ of these minerals through leaching of vulnerable primary silicates, translocation of clay minerals coming from the A leached horizon). In some cases, the two mechanisms may act successively, for example, in the genesis of placer deposits, which result firstly from the residual accumulation of heavy, stable minerals during weathering and secondly from their absolute accumulation during sedimentation of alluviums or alluvial fans.

In the present contribution, the role of the chemical weathering processes in metallogeny will be principally considered. This role is indeed very important, being at one and the same time direct and indirect. Weathering processes govern directly the genesis of economically considerable residual ore deposits, such as bauxite, laterites and associated mineral concentrations. They also indirectly govern the formation of continental or even marine mineral concentrations, since the lithologic differentiations encountered in sedimentary basins are really correlative formations of the weathering differentiations which occur in the neighbouring landscapes (Erhart, 1956). In the first section of this contribution, the problem of the geochemical differentiation produced through pedogenetic processes will be developed. The following sections are devoted to the problem of the genesis of strictly residual (or so considered) ore deposits, such as bauxites, laterites, and associated concentrations (Mn, Ni). In the last section, we shall attempt a more general approach to the supergene behaviour of chemical elements, in order to understand other aspects of supergene metallogeny, such as mineral concentrations related to continental, detrital or chemical sedimentation.

Even so delineated, the subject remains large and must be further reduced for the present treatment:

(1) The limits of the weathering zone, beneath the land surface, are not sharply fixed and the weathering processes are limited in deeper zones by cementation and hydrothermal processes. Schematic relationships between the different subsurface hydrodynamic zones and the resulting supergene differentiations, soil profiles, weathered crust and cementation zone, etc., are depicted in Fig. 1. The zone of weathering is assumed to correspond to the zones of percolation and of active circulation of ground waters, which are located above the hydrostatic level. This zone is characterized by the more or less intense renewal of meteoric waters, by the presence of oxygen and the influence of biological factors. The underlying zone of catagenesis is characterized, on the contrary, by the slowness or stagnation of the waters, by the lack or scarcity in oxygen and by the existence of highly mineralized water (Perel'man, 1967). The processes occurring in this latter zone will not be considered here.

(2) Another limitation of the subject consists in excluding the study of paleo-landsurfaces which have been more or less weathered during past geological time, then buried and now covered unconformably or disconformably by sediments. Varied and sometimes complex metallic concentrations are often found along these paleosurfaces. However, it is often difficult to establish to what degree weathering processes or subsequent epigenetical, diagenetical or even hydrothermal processes were responsible for these concentrations. We do not try to resolve this problem.

(3) The last limitation we introduce concerns the peculiar weathering processes which develop in ore-bearing parent rocks or hydrothermal vein ore deposits; these processes give varied superficial oxidized products termed iron caps ("chapeaux de fer", Eisener Hut, gossan). They are greatly complicated by the role played by some unusual constituents, anionic or cationic, which may react together to give quite complex mineral paragenesis. In spite of their interest, these peculiar weathering products are actually very localized and we now consider only the metallogenic aspects of the weathering differentiation of ubiquitous or common parent rocks.

The experimental study of the supergene geochemical processes has progressed far these last years, through alteration and synthesis experiments under laboratory conditions (pressure and temperature), near the land surface conditions. Inasmuch as these processes may be considered as resulting from equilibrium reactions between primary minerals,

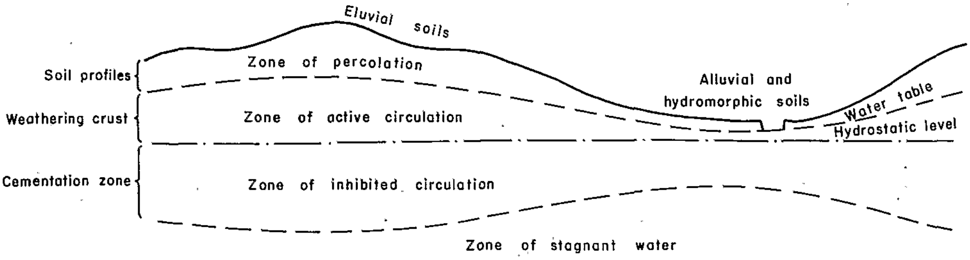

Fig. 1. Schematic relationships between the principal supergene processes, the hydrodynamic zones and the resulting formations: soil profiles, weathered crust and cementation zone.

aqueous solutions and secondary minerals, the thermodynamical method may be successfully applied; this method permits to calculate and to predict the fields of stability and mobility of minerals and mineral products, in relation with a few physico–chemical variables (ionic concentration or activity, pH, Eh, temperature, etc.) Some examples of such calculations will be given incidentally in this chapter (see p. 118 and p. 127), but we do not attempt a general presentation of the thermodynamical approach to the supergene processes, because the available thermodynamical data concerning weathering minerals and chemical trace elements are scarce, absent or still subject to discussion.

GEOCHEMICAL DIFFERENTIATION DURING CHEMICAL WEATHERING AND PEDOGENETIC PROCESSES

The weathering and pedogenetic processes are the subject of a great number of works which deal mainly with: (a) morphological characteristics of soil profiles, from fresh or little weathered parent rock (D or C horizon) to superficial eluvial horizons (A horizons), with occasionally an intermediate weathered or illuvial horizon (B horizon); (b) granulometric, mineralogical and chemical characteristics from bottom to top; (c) origin and evolution of clays and secondary minerals; (d) evolution of the organic matter and its interaction with the mineral matter; (e) weathering balances.

Since all these aspects cannot possibly be listed here, we recommend to the reader some recent comprehensive works, which treat the subjects with an either geological (Millot, 1964; Loughnan, 1969), pedological (Duchaufour, 1968), or geochemical emphasis (Perel'man, 1967).

Soviet authors make a distinction between the weathering products: the soil profiles, the formation of which is directly influenced by the living matter (biogenetic accumulations, action of the roots of vegetables, etc.) and the weathered crusts. The latter designate the different products accumulated residually: fragmented rocks, weathered or not, and the more or less hydrolysed deep layers in the zone of active circulation of water; they generally exhibit the relict structure of the parent rocks, and their thickness, which varies strongly according to the climatic conditions as well as the lithological properties of the rock, is often much greater than the thickness of the soil profiles. Here, the term weathered crust will not be used and the concept of soil profile will be considered with its widest meaning: all the residual products and deep layers of weathering will be included in the more or less weathered bottom C horizon.

Pedogenesis and chemical weathering types

The problem with which we are concerned, considered from a metallogenic point of view, is to state precisely what are the geochemical differentiations due to superficial chemical weathering and pedogenesis. This problem raises two questions: (a) Are the types of differentiations as numerous as the types of pedogenesis? (b) How do the pedogeneses have to be classified with respect to their geochemical effects?

Major zonal pedogenesis. To the first question, it may be answered that geochemical differentiations are actually very numerous when referring to the variations in main factors of soil formation: climate, vegetation, parent rock, topography and time (Jenny, 1941). But for parent rocks of common composition, e.g., granitic rocks, which evolve superficially under normal topographic conditions (good drainage and limited erosion), the type of soil depends mainly on bioclimatic conditions (climate, vegetation). For the sake of simplicity, it may be said that five major pedogeneses related to the five main climatic zones occur (Erhart, 1935; Millar et al., 1958; Ganssen, 1965 and 1968; Pédro, 1968; Kovda et al., 1969):

(1) Humid temperate–cold regions, where the typical vegetation is moorland and conifers, give podzolic soils (spodosols).

(2) Mild temperate regions, where the vegetation is hardwood plants and meadows, give brown soils, leached brown soils and acid brown soils (inceptisols or alfisols).

(3) Either cold or hot continental but always more or less dry regions, where the vegetation is steppe, give isohumic soils (mollisols or aridisols).

(4) Subtropical regions with a more or less xerophytic vegetation of dry savanna, give fersiallitic and tropical ferruginous soils (alfisols or ultisols).

(5) Equatorial or wet regions with a dense forest vegetation, give ferrallitic soils (oxisols).

The soil nomenclature used above, is that of the French classification; the American classification terms are noted in parentheses.

Soils related to these pedogeneses occur in roughly parallel belts extending from the poles to the equator, but the steppe isohumic soils develop not only in temperate or even cold continental zones, but also in arid regions with hot climates. From a climatic point of view, the five zones are characterized by a decreasing mean annual temperature and increasing annual range of temperatures from the equator to the poles, and by a rainfall presenting a maximum in the equatorial zone and a minimum in subtropical continental regions.

Under very extreme climatic conditions (arctic or subarctic zones, or desert regions), there is practically no geochemical differentiation, since very low temperatures or the lack of rain reduce the weathering processes to nearly zero.

"Weathering balance". A good understanding of geochemical differentiations due to each pedogenesis calls for a "weathering balance" giving the mineralogical and chemical absolute variations from bottom to top of the soil profiles and allowing the losses and gains of matter to be defined in the different horizons. Therefore, a reference constituent must be selected.

Up to now, the more commonly selected reference element was Al, Ti or Fe. These elements are generally fairly stable in superficial conditions, if considered on the scale of broad areas, but in certain soil profiles they undergo vertical or lateral migrations, which result in a relatively significant removal from some horizons and accumulations in some other ones. The isovolumic method (Millot, 1964) is a more accurate means for calculating geochemical balances and has been successfully employed by many authors (Tardy, 1969; Novikoff, 1974), but this method can only be used when the structures of the parent rock are conserved, which is not always the case.

For illustrating here the complete geochemical trends, up to the destructured superficial horizon, the isoquartz method has been chosen (Lelong, 1969; Souchier, 1971): in soil profiles, even in intensively weathered ones, the quartz is indeed the only constituent which shows a progressive increase from bottom to top, except in illuvial horizons; this fact confirms its relative stability.

A suitable reference constituent having been selected, the balances still have to meet the following conditions:

(1) They have to deal with sedentary (not reworked) soil profiles derived from homogeneous rocks.

(2) They must be established from numerous samples in order to get mean results and well-defined standard deviations.

(3) Parent rocks of soil profiles have to be of the same nature, since the pedological evolution depends largely on the nature of the parent rock.

(4) Polycyclic soil profiles resulting from several different evolutions must be excluded.

"Weathering balance" of zonal pedogeneses

The balances already published are very few and deal especially with the pedogeneses of temperate regions (Dejou, 1959 and 1967; Tardy, 1969; Lelong and Souchier, 1970) or of equatorial regions (Harrison, 1933; Bonifas, 1959; Leneuf, 1959; Lelong, 1969; Tardy, 1969; Novikoff, 1974). Moreover, the method used (isoalumina method, isoquartz method, isovolume method, etc.) differs from one author to another so that the results cannot be easily compared.

Examples of pedogeneses in equatorial and temperate regions. We will give only two examples of balances which are established in a quite similar way ("bilan isoquartz"), and which correspond respectively to soils under a wet temperate climate and soils under an equatorial climate (Lelong and Souchier, 1972). Their results are summarized in Table I and Fig. 2. In both cases, the conditions of location are: relatively high topographic position, low gradient slope, dense forest cover. Consequently, the soils are well drained and little affected by erosion. They are mature soils of Quaternary (Post-Würm) age for the temperate soils, and older soils evolving perhaps from the final Tertiary or Early Quaternary Period for the equatorial soils.

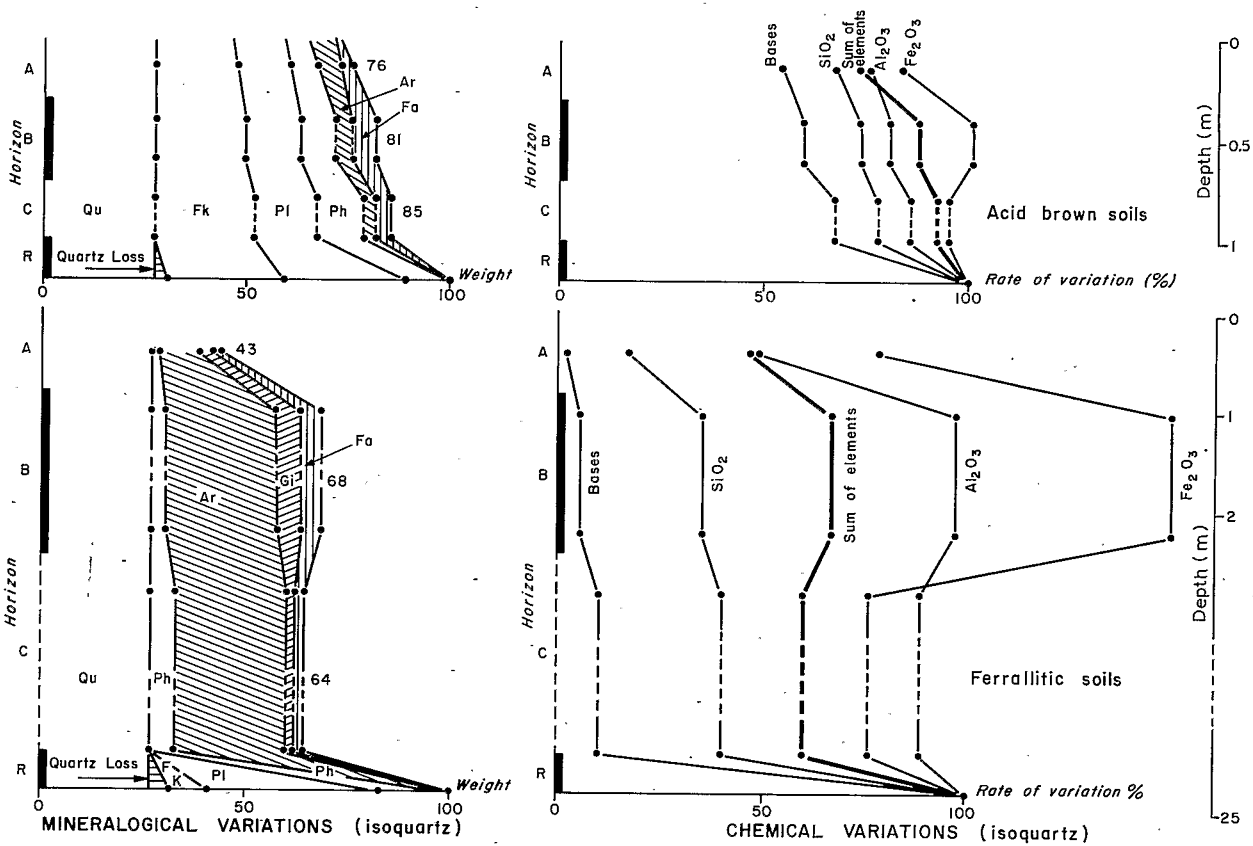

Fig. 2. Mineralogical (left) and chemical (right) balances in soil profiles of temperate and equatorial soils, on granitic rocks, referring to a constant weight of quartz (after Lelong and Souchier, 1972). The mineralogical abbreviations are similar to those of Table I.

TABLE I

Mean weathering balances referring to constant weight of quartz (isoquartz balances) in profiles of "acid brown soils" (temperate climate) and of ferrallitic soils (equatorial climate)[1],[2]

Horizons	Mineralogical balance[3]							
	Primary minerals				Secondary mineral fraction			Total
	Qu	FK	Pl	Ph	Ar	Gi	Fa	
Acid brown soils								
A	27.5	20	12.5	7	6	–	3	76
B	27.5	22	13.5	8	5	–	5	81
C	27.5	24	15	12	2.5	–	4	85
granite	30	29	29	12				100
Ferrallitic soils								
A	27			1	10	3	2	43
B	27			3	27	6	5	68
C	27			6	27	1	3	64
granite	32	9	42	17				100

[1] After Lelong and Souchier (1972).

[2] The quartz losses (7.5% in temperate soils and 15% in equatorial soils) are corrected.

The soils occurring under a wet temperate climate belong to the group of acid brown–podzolic soils, developed on Hercynian granitic rocks in the Massif des Vosges (France) at a relatively high altitude (600–950 m) under a vegetation of fir trees and piceas. Climatic conditions are: annual rainfall of 1200–1800 mm and mean annual temperature of 8°C. The soils found under an equatorial climate are ferrallitic soils, developed in French Guiana on granitic rocks of the Precambrian basement, under large dense forest. The climatic characteristics vary with each particular station: from 2500 to 4000 mm rainfall/year and a mean annual temperature of 26–27°C.

The results for the balances along the soil profiles for each climatic zone (Table I and Fig. 2) are *mean* results, obtained from at least ten samples/horizon in soils of the same type. The distinct study of the "bilans" made from separate profiles reveals notable differences within each climatic zone, which are due to the particularities of each location. Despite this, the respective fields of global variations corresponding to the temperate soils and to the equatorial soils are clearly distinct and this fact justifies a mean balance type for each climatic zone, as represented in Fig. 1.

The mineralogical balances represent the aggregate variations of mineralogical constituents from the bottom to the top of the profiles: the mineral-matter losses produced during the evolutionary process appear in the right-angle of the diagrams. The chemical balances give the variations of each element expressed as a variation rate (% of each element compared with the amount originally present in the parent rock); the four bases

Chemical balance[4]

SiO_2		Al_2O_3	Total iron	Bases	Total mineral matter
(quartz)	(combined)				
92.5	67	74	84	54	76
92.5	74	88	101	60	81
92.5	78	92.5	95	68	85
100	100	100	100	100	100
85	17	49	79	1	43
85	35	97	157	5	68
85	40	89	76	10	64
100	100	100	100	100	100

[3] Results in weights, referring to a constant weight of quartz. The abbreviations used are: *Qu* = quartz; *FK* = potassic feldspars; *Pl* = plagioclases; *Ph* = phyllites; *Ar* = clay minerals; *Fa* = inorganic amorphous matter (mainly oxides and hydroxides of Al and Fe); *Gi* = gibbsite.

[4] Result in variation rates (% of each element compared with the initial quantity in the fresh granite).

Na_2O, K_2O, MgO, CaO, are grouped together for simplification. Losses are figured by variation rates lower than 100% and gains by rates higher than 100%.

The results call for some remarks:

(1) A very marked contrast exists between the moderate and progressive evolution of temperate soils and the much deeper and more intense chemical weathering which affects even the bottom part of the equatorial soils. Thus, in temperate soils, destruction of the primary vulnerable minerals is only partial (40–50%). The chemically weathered fraction, termed "complexe d'altération" (secondary minerals such as clay minerals and inorganic amorphous products), is about 10%; the losses, which are not very high, do not exceed 20–25% of the initial amount present in the parent rock. On the other hand, in the equatorial soils, the destruction of vulnerable minerals is almost total and affects even the bottom part. The chemically weathered fraction is very great (30–40%) and the losses are considerable (40–50% of the initial amount).

(2) The disparities in chemical weathering intensity are accompanied by differences in the nature of the secondary minerals: temperate soils contain 2/1 clay minerals especially (illites, vermiculites and montmorillonites) which are due to the progressive transformation of pre-existing phyllite minerals and to neoformations from elements released by destruction of unstable primary minerals, the plagioclasese. Equatorial soils contain 1/1 clay

minerals predominantly (kaolinite, halloysite) or even Al-hydroxides (gibbsite), which are neoformed from elements released by the destruction of the most primary minerals.

(3) Despite these disparities, a certain geochemical similarity exists between the two pedogeneses. Elements seem to be released and removed in the same order: bases > combined silicon > Al > Fe. Indeed, both pedogeneses are acid and produce an important removal of mineral matter: the major part of the released bases is leached (mainly Na and Ca which do not enter into any secondary minerals) and only a small part of them is retained by the adsorbing complex (clay and humus). The combined silicon is partly leached and partly recombined in the clay minerals formed in the soil. The Fe and Al metallic elements are mainly fixed in an oxide or hydroxide state, or enter into clay minerals; but they are partially leached or translocated from the A to B horizon (illuviation) or even migrate further away. In both soil types, the Fe accumulates more intensely than the Al. The intensity of these accumulations is maximum in the most weathered soil profiles, which explains the formation of very high supergene concentrations of Al and especially of Fe in equatorial soils.

The other zonal pedogeneses. We have no similar balance for the other major zonal pedogeneses. However, the mineralogical and chemical data available allow us to extrapolate the preceding results, with consideration to the different bioclimatic conditions. These pedogeneses will be classified in accordance with the zonal order from the high-latitude regions where the climate is cold and wet, downward to the low latitudes where the climate is hot, whether dry or not:

(1) Under cold wet climates, the decay of vegetal debris is very slow and an accumulation horizon of raw organic matter occurs at the surface. It is formed of vegetal debris which is slowly degrading and which releases soluble organic compounds, liable to complex the metallic cations[1] and to carry them toward deeper layers. Therefore, the soil profiles (podzolic soils and podzols) are very well differentiated (Ponomareva, 1966; Duchaufour, 1970; Targulian, 1971): underlying the A_0A_1 organic horizon, is an A_2 horizon of leached mineral matter, followed by a B illuvial horizon with accumulations of organic compounds and metallic oxides which are translocated from the surface horizons. The clay fraction is constituted of 2/1 and 2/2 clay minerals which are mixed with amorphous matter in the illuvial horizon and which are more or less degraded in the superficial leached horizons. Because of the low-temperature conditions, the hydrolytic processes are rather limited, but under the influence of very acid organic compounds, all the mineral matter released near the surface is leached downward and eventually accumulated in the B horizons (redistribution).

(2) Under the contrasting continental climatic conditions of the medium latitudes, the organic matter undergoes an intense humification[2]; it is incorporated deep inside the

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[1] See Chapter 5 by Saxby in Vol. 2.

[2] Synthesis of dense and stable complex organic molecules (humic acids, humine), liable to associate intimately with the clay fractions of the soil.

profile and gives a dark and thick grumelous horizon (isohumism). The chemical weathering of parent-rock minerals is low, Fe and Al are not released and the clay minerals formed are generally swelling clays (montmorillonites). The only elements to be released in rather large amounts are the bases which may be redistributed to form a carbonated accumulation horizon generally more or less diffuse (chernozems and chestnut steppe soils). The vertisols and eutrophic brown soils described by Paquet (1969), Bocquier (1971) and Boulet (1974) in large areas of Sahelian Africa, exhibit many similar characteristics, namely the richness in swelling montmorillonites. Most of these characteristics are also met within the steppe soils (brown and reddish brown soils) which are developed in dry and subdesert areas, but the organic matter is much less abundant and the massive and often thick carbonate accumulations form a calcareous crust or caliche (Ganssen, 1965; Duchaufour, 1968; Loughnan, 1969). Thus, in these pedogeneses, the leaching and hydrolysis processes are very limited and only the more mobile elements, such as the bases, undergo a certain migration; the soil-pH remains alkaline. These characteristics are related to the low annual rainfall and the marked water shortage recorded at least during dry seasons.

(3) Under subtropical and semi-humid tropical climates, the soils (fersiallitic soils, mediterranean soils and tropical ferruginous soils) generally show a strong development of 2/1 and 1/1 clay minerals, and a marked release of oxidized iron (Duchaufour, 1968; Paquet, 1969; Lamouroux, 1971; Bocquier, 1971), which gives the typical rubefacient aspect of these soils. The iron oxides are linked with clay minerals (fersiallitic soils) or accumulate in concrete masses and crust layer, forming the B horizon (ferruginous soils). Actually, the hydrolysis process is intensive, owing to the high average temperature, while the leaching process is less marked than in the equatorial soils. The removal of bases is not total, the soil-pH is about neutral and the removal of silica is only partial, especially in the fersiallitic soils, whereas in the ferruginous soils the leaching of silica is more intense and the migration of Fe often very spectacular: on low gradients and poorly drained tropical slopes (glacis landform), the hydromorphic conditions of argillaceous deep horizons favour the mobility of this element which accumulates in thick superficial horizons (ferruginous crust).

In brief, two major groups of pedogeneses may be distinguished: (1) the pedogeneses of rainy regions, giving acid soils where the bases, and to lesser extent silica, released are more or less leached and where the sesquioxides tend to accumulate with or without silica (subtractive pedogeneses, corresponding to the "pedalfers" of Marbut, 1928); (2) the pedogeneses of dry or arid regions, giving neutral alkaline soils, where the bases are retained and may accumulate near the surface and where the sesquioxides do not become individualized (redistributive pedogeneses, corresponding to the "pedocals" of Marbut). The main geochemical characteristics of the five major zonal pedogeneses are summarized in Table II: each pedogenesis is defined by the degree of release of elements from the primary minerals (which indicates the intensity of hydrolysis) and by the importance of their mobility during the pedogenetic process (which measures the leaching intensity). Elements with little mobility remain fixed or undergo limited redistribution, very mobile elements tend to be leached out of the profiles and moderately mobile elements behave intermediately.

From Table II and from data on the relative mobility of trace elements presented below (see p. 164), the behaviour of these elements in the major pedogeneses may be partially predicted, that is to say which elements are likely to accumulate with Fe and Al in acid soil profiles or with bases in alkaline ones. Therefore, the exact behaviour of trace elements during pedogenesis is not perfectly known. Some available data (Ermolenko, 1966; Nalovic, 1969; Nalovic and Pinta, 1971; Aubert and Pinta, 1971; Karpoff et al., 1973) give information about the contents of these elements in soils, in relation with the major pedogenetic factors; but the chemical weathering balances and studies dealing with the mechanisms which govern the mobility of these elements are very scarce.

Major factors of pedological differentiation

Let us now consider the pedological differentiation on the large scale of extensive areas and discuss the main environmental factors which govern the geographical distribution of the soils.

Climatic and biological factors: the zonal soils concept. The climatic and biological factors are the two prevailing variables which explain the disparities in the weathering types observed in the different climatic zones, as presented above.

Climate: the warmer and the wetter the climate, the more intense are the hydrolytic processes and the higher the degree of release of elements. The rainfall and the temperature also govern the subsequent behaviour of chemical elements in soil solutions: the mobility of the elements is conditioned by the pH of the solutions, which depends on the quantities of percolating rainwater; the solubilization rates and the solubility limits are influenced by the temperature which also controls the evapotranspiration and the concentration of solutions. Thus, rainfall and temperature are the two paramount parameters influencing the surface mobility of elements.

Vegetation and biological activity: these factors are closely related to the climate, and are fairly uniform over a given climatic zone, except locally where some very specific topographical or parent-rock conditions exist. They influence the pedogenesis either directly or indirectly (Lovering, 1959; Ponomareva, 1966; Duchaufour, 1968; Erhart, 1973a and b) by: (a) the more or less marked acidity of the humus they produce; (b) the role they play in the formation of the organo–mineral complexes, the nature and abundance of which condition the behaviour (solubilization and insolubilization) of numerous heavy cations and; (c) the specific ability of the vegetation to fix some soil elements and to release them later on (biogeochemical cycle).

In brief, the climate directly or indirectly (through the vegetation and the biological activity) controls the pedogenesis and this explains the *zonal distribution* of the major soil types.

TABLE II

Geochemical characteristics of the major zonal pedogeneses[1]

Climatic zones	Soil types	Behaviour of the elements during weathering processes (increasing stability ⟶)			
		alkaline and alkaline earth elements	combined silicium	iron and alumunium	
Neutral-alkaline pedogeneses, weak to inexistent drainage					
Dry continental zone, temperate–tropical	steppe isohumic soils	weak–moderate releasing, intense redistribution (caliche $CaCO_3$ crust)	very weak releasing, remaining fixed at the place of releasing	very weak releasing, remaining fixed	Increasing weathering rate ↓
Subtropical–semi-humid tropical zone	fersiallitic soils and tropical ferruginous soils	moderate–intense releasing, moderate leaching	moderate–intense releasing, weak leaching	moderate–intense releasing, remaining fixed or redistribution (ferruginous crust)	
Acid pedogeneses, intensive drainage					
Cold humid zone	podzolic soils and podzols	moderate releasing intense leaching	moderate releasing, moderate leaching	moderate releasing, intense redistribution or light leaching	Increasing weathering rate ↓
Temperate humid zone	acid brown soils	moderate releasing moderate leaching	moderate releasing, moderate leaching	moderate releasing, remaining fixed, or light redistribution	
Tropical humid zone	ferrallitic soils	very intense releasing, very intense leaching	intense releasing, intense leaching	intense releasing, intense redistribution and leaching	

[1] The term releasing defines the proportion of the element extracted from the primary mineral network; the term redistribution defines the migration of the released element in the profile (generally from the eluvial A horizon to the illuvial B horizon); the term leaching defines the transportation of the element out of the soil profile

Parent rock and topography: the intrazonal and azonal soils concept. Parent rocks interfere essentially through the susceptibility to alteration of their minerals (see below p. 154: weathering sequence of common minerals). Under given chemical weathering conditions, the release and the removal of matter tend to increase together with this susceptibility. The geochemical balances established by Tardy (1969) in temperate and tropical soil profiles derived from acid and basic parent rocks show sharp differences which are related to the type of the parent rocks. The strong influence of the composition of the parent rock in the weathering differentiation, up to the uppermost horizons of the soil profiles, has been emphasized by Lelong (1969) for equatorial soils and by Souchier (1971) for temperate soils. The nature of the secondary minerals developed during the pedogenesis depends directly on the nature of the parent rock (Souchier, 1971; Dejou et al., 1972).

Some rocks influence the pedogenesis processes so much that the soil types – even the mature ones – derived from them, are radically distinct from the zonal soils occurring under the corresponding climate. In temperate regions, for example, calco–magnesian soils, which are formed on carbonate rocks, present characteristics which are more closely related to base-rich soils of dryer regions, as long as the carbonate minerals are not completely leached. Another example is given in wet tropical regions, where vertisols and tropical brown soils, similar to those which develop on most of the rocks of the dry tropical regions, occur on basic, highly vulnerable rocks. The modification of the normal climate zonality of the weathering facies, in relation with changes in the petrographic conditions, has been pointed out by Paquet (1969), in her concept of geochemical prevalence and deficiency.

Topography is also an important factor, inasmuch as the movement of ground-water solutions depends on topography. On fairly steep slopes and relatively high land areas, drainage is generally good, soils are well aerated and pedological evolution is normal. In depressions and flat-lying areas, on the other hand, drainage is sluggish or inefficient, the soil may be temporarily or permanently waterlogged and the pedological evolution becomes different; hydromorphic soil profiles with characteristic bleached gley horizons or mottled pseudogley horizons are observed. The reducing conditions, which are more or less marked in these horizons, may bring about an increase in the mobility of some elements – such as Fe and Mn – and a decrease in the mobility of some others. Thus, the reduction of sulfates by bacterial activity produces hydrogen sulphide which is liable to precipitate, even in minute amounts, most of the metallic elements. Hydromorphic environments are also characterized by a strong development of clays and colloids, in which many elements are likely to be entrapped (see p. 158).

The chemical composition of groundwaters is related with the topography. The salt concentrations of these waters vary with the lateral flow and with the evapotranspiration conditions from upstream to downstream. This explains a certain "ventilation" (fractional separation) of ions along the slopes. From the combination of this phenomenon with the climatic zonality of the weathering types, Tardy (1969) sketches an outline of "chromatographic separation" of the elements in the landscapes. This outline sums up the great geochemical trends in relation with the climate and topographical position.

Thus, it is obvious that in some cases the influence of the parent rock and topographic factors is so determinative that the pedogeneses diverge to some extent from the normal bioclimatic evolution: the corresponding soils are termed "*intrazonal soils*".

Under extreme topographic conditions (mountainous reliefs and steep slopes) the erosion rate is higher than the chemical weathering rate and the pedological evolution becomes ineffective or even non-existent. The same phenomenon occurs in the accumulation zone of recent deposits (dunes, alluvium). Soils which remain immature because of mechanical erosion or continental sedimentation, whatever the climatic conditions may be, are termed "*azonal soils*".

Time of evolution. This factor also may explain very important geochemical differentiations in the surface of the earth. From simple calculations (Leneuf, 1959; Tardy, 1969), the unit of time required to form one meter of alterite leached of silicon and bases in equatorial zones, has been estimated to range from 50,000 to 200,000 years. In wet-temperate zones, the silicon content of subsurface waters and the intensity of drainage are not much lower (Davis, 1964; Tardy, 1969), which suggests that the unit of weathering time should not be much longer. However, the equatorial alterites are much thicker than those of temperate climates. This difference is probably due to the influence of the time factor: on old basements of equatorial regions such as West Africa, Guyana and Brazil, the chemical weathering process might have been going on over a very long period (hundred of thousands, or even millions of years) without being really impeded by any intense erosion, inasmuch as the alterites and the soils were preserved by a thick vegetal cover. In temperate regions, on the other hand, successive episodes of erosion (brought about by Quaternary glaciations) swept away the major part of the alterites formed during more ancient periods.

This example shows that some disparities between pedogeneses may result rather from differences in the degree of the chemical weathering process (duration of evolution) than from qualitative differences (nature of processes). The importance of the time factor has been recently emphasized by Icole (1973). However, as is shown below (p. 154), the chemical weathering and element-mobility mechanisms are so complex that differences in degree may finally bring about strongly marked geochemical contrasts.

Conclusion

(1) In well-drained areas, in which the conditions of weathering are oxidizing, at least two distinctly different major pedogenetic evolutions must be considered from a geochemical point of view: first, the pedogeneses giving rise to leached soils, which selectively concentrate Al- and Fe-oxides, sometimes silica, and all elements presenting a similar behaviour in superficial layers. They correspond to wet and to very wet climates, and the warmer the temperature is, the more rapid and intense is the differentiation they induce.

Secondly, one must consider the pedogeneses producing neutral or alkaline soils, which selectively concentrate the alkaline and alkaline-earth elements and which correspond to dry and to extremely arid climates.

These two major pedogenetic evolutions may be subdivided. Thus, the leaching processes are not exactly the same in the cold and warm wet regions: Pédro (1968) distinguishes the "acidolysis" corresponding to the podzolic pedogeneses of the high-latitude zone and the intense "hydrolysis" corresponding to the rainy tropical zones. Therefore, the acidity is also frequently very marked in the surface horizons of the tropical soils and both pedogeneses can be termed acid. The particularity of the wet tropical pedogenesis is chiefly the presence of a very thick, argillaceous weathered crust (lithomarge).

The geochemical evolution corresponding to the neutral or alkaline pedogeneses may also be subdivided into several types, according to the chemical composition of the environment and the degree of the ionic concentration of the soil solution. Referring to the general classification of the epigenetic processes (Perel'man, 1967, table 27, p. 157), one may distinguish: (a) the neutral carbonatic type, for which the main aqueous migrants liable to be redistributed and to concentrate are HCO_3^-, Ca^{2+} and Mg^{2+}; (b) the gypsiferous type and the chlor–sulfatic weakly alkaline type, for which they are respectively SO_4^{2-} and Ca^{2+} or Cl^-, SO_4^{2-} and Na^+; (c) the sodic, strongly alkaline type, for which they are CO_3^{2-}, OH^-, Na^+ and SiO_2. The type (a) occurs in steppe soils of contrasting climate conditions (chernozems, brown or reddish-brown soils, and vertisols). The types (b) and (c) occur in intrazonal saline soils developed under peculiar topographical and parent-rock conditions, mainly under arid–sub-arid climates where ionic concentration of the solutions may rise strongly through evapotranspiration processes.

(2) Apart from the oxidizing pedogeneses which are developed in well-drained eluvial soils, quite distinct evolutions are encountered in the hydromorphic environments of swamps, marshes and alluvial low-lands, where special geochemical differentiations are related to reducing conditions. These hydromorphic evolutions may be subdivided into several types, according to the dominant nature (organic or inorganic) of the soil constituent, the pH of the environment and the presence or absence of hydrogen sulphide (Perel'man, 1967; Duchaufour, 1970).

(3) The preceding distinction between the main geochemical trends corresponding to weathering and pedogenetic processes is not exactly similar to the distinction, often made, of different geochemical landscapes. A geochemical landscape is the result of the sum and of the interaction of soils, weathered crusts, surface and subsurface waters, erosional features and continental deposits (Millot, 1964; Perel'man, 1967). Typical geochemical landscapes are, for example, the wet-forest tropical peneplains or the dry steppic pediplains, which present specific geomorphological features, corresponding to more or less distinctive geochemical characteristics. But each geochemical landscape constitutes a rather complex system, in which the geochemical behaviour of the elements often varies from one locality to another, according to the parent rock and topographical conditions. Therefore, the concept of geochemical landscape, though very interesting in general,

seems too large in the perspective of the supergene metallogeny to determine the specific haloes of dispersion of the metallic elements.

ALUMINIUM ORE DEPOSITS: THE PROBLEM OF BAUXITES AND LATERITES

Generalities

Geochemical properties of aluminium. With a content of 8.1%, Al is the third most common element in the lithosphere, after oxygen (47.5%) and Si (28.8%). It is relatively concentrated in eruptive feldspathic rocks and argillaceous or schistose rocks, but relatively scarce in carbonate and sandstone rocks as well as in ultrabasics.

Al displays a marked affinity for oxygen and it is not found in the lithosphere in a native state. Its ionic radius (0.51 Å for sixfold coordination) is small compared to that of the other metallic elements, and is almost as small as the Si radius (0.42 Å). It is present in minerals, either in a tetrahedral form (prevailing in minerals originating from deep layers) or in an octahedral form (prevailing in minerals of surface origin).

Al is soluble in water at low pH ($pH < 4$), where it occurs in the form of Al^{3+} ions, or at high pH ($pH > 10$) where it assumes the form of AlO_2^- ions. Consequently, it proves to be only slightly mobile under common surface weathering conditions, and it tends to accumulate in secondary silico-aluminium minerals (clay minerals) or in purely aluminous ones (gibbsite, boehmite).

Aluminium-ore deposits: the bauxites. The major aluminium deposits are the bauxites, defined by Gordon et al. (1958) as "aggregates of aluminous minerals, more or less impure, in which Al is present as hydrated oxides". The most common impurities are kaolinite or similar clay minerals and the oxides and hydroxides of Fe and Ti. Different types of bauxite have been described, with regard to their depositional and assumed genetic conditions (Harder, 1952; Bracewell, 1962; Patterson, 1967; Valeton, 1972). Harder, for example, classified the bauxites according to the nature of the bed rocks on which they are found. Patterson distinguished "blanket deposits" (layers contained in residual weathered crusts), "interlayered deposits" (lens-like formations included in sedimentary series) and "pocket deposits" (accumulations at the surface of karstic landforms on carbonate rocks). Valeton subdivided the bauxites into autochthonous and allochthonous bauxites, depending on the localization of the source of Al. Here, a classification similar to that of Patterson will be adopted:

(1) Lateritic blanket bauxites. These are residual aluminous or aluminoferruginous layers resulting from the intense weathering of eruptive, metamorphic or sedimentary rocks. Such bauxites are said to be autochthonous, the Al present in the bed rock becoming preferentially concentrated in-situ owing to the removal of the other elements. The more common descriptions of bauxites, from various parts of the world, apply to this type of ore deposit (Fermor, 1911; Lacroix, 1913; Harrison, 1933; Harder, 1952; Wolfenden, 1961).

(2) Sedimentary bauxites. These are stratiform aluminous accumulations which are found intercalated in some sedimentary series. They are generally thought to be detrital deposits, colluvial or alluvial particularly and made up of elements or fragments coming from preexisting lateritic blankets, which have been eroded and then accumulated laterally by sedimentary processes (Gordon et al., 1958; Valeton, 1972). Some authors propose the possibility that aluminous sediment can be of chemical origin, formed by precipitation of Al from solutions formed during leaching under conditions of acid pedogenesis (Caillère and Pobeguin, 1964; Erhart, 1969). Both detrital and chemically precipitated bauxites are called allochthnous, the Al-concentration occurring at a more or less remote distance from its original source. However, the formation of sedimentary bauxites related to argillaceous deposits may involve two steps (De Vletter, 1963; Moses and Michell, 1963): (a) accumulation of clays; and (b) transformation in situ of these clays into bauxites. Consequently, these bauxites may be considered as autochthonous, the sedimentary clays playing the role of parent rock.

(3) Karst bauxites. These lie, directly or indirectly, on a carbonate and more or less karstified bed rock. Their origin is still not well understood. The two problems discussed are the source of the Al and the site of the bauxitization. Some authors think that the Al was derived from the carbonate rocks themselves because these rocks always contain some significant quantities of clays or aluminous colloids which are likely to accumulate in-situ during the karstification process, resulting under warm and humid climates in residual bauxites similar to the lateritic blankets (De Lapparent, 1924; Hose, 1963). Therefore, they should be considered as true autochthonous bauxites. Some other authors think that Al comes from silico–aluminous rocks (schists, marls, volcanic deposits, etc.) lying on carbonate rocks and which have been subsequently removed through alteration and erosion, leaving a bauxitic residue (Burns, 1961; Bonte, 1965; Rousset, 1968; Valeton, 1972). In this case, bauxites may still be considered as more or less autochthonous. Other researchers do not agree that the Al was derived from the carbonate host rocks nor from overlying rocks, but rather it was imported by water in a detrital or chemical form, or even by the wind from nearby lateritized areas (Roch, 1956; Zans, 1959; Watterman, 1962; Caillère and Pobeguin, 1964; Nicolas, 1968; Erhart, 1969). The bauxites would then be considered true allochthonous bauxites. The problem related to the site or localization of bauxitization concerns only the allochthonous bauxites. Roch, Zans, and Valeton assume that the bauxitization takes place in-situ, at the site where the ore is now located after the preliminary formation of silica–aluminous deposits over the carbonate rocks. Nicolas, on the other hand, thinks that this bauxite formation has taken place at a more or less remote distance from the site of deposition, on the silico–aluminous basement surrounding the karst; therefore, the bauxite was already formed when deposited on the karst. According to this interpretation, karst-bauxites must be considered as being strictly sedimentary. However, most authors accept that bauxites result from a complex evolution which takes place both before erosion and transportation (lateritization over crystalline ancient basements) and after the accumulation of the materials involved within

the karst depositional site (progressive enrichment of the Al contents).[1]

Distribution of bauxites over the world. The foregoing distinction between lateritic blanket bauxite, sedimentary bauxite and karst bauxite may appear somewhat arbitrary because it probably corresponds more to differences in age and successive steps of evolution than to genetic differences in the conditions of formation of Al minerals. As a matter of fact, when analysing the distribution of bauxites over the world (Fig. 3), one may observe that "lateritic" bauxites are mainly located in the present-day intertropical zone, whereas karst bauxites occur predominantly in present-day temperate or subtropical zones. The former, which are of the Quaternary or the Tertiary Period, seem generally more recent than the latter which are of Tertiary age in the West Indies, of Cretaceous age in the Mediterranean zone, and of Jurassic or even Paleozoic age in the Urals and the Far East (Hose, 1963). Sabot (1954) has suggested that the further the bauxites are from the equator, the more ancient they appear to be. Therefore, one may think that karst-bauxites are also related to vast ancient lateritic blankets whose position moved during geological times, following the polar migration. Owing to their very long history, these lateritic blankets may have been successively and/or cyclicly eroded and redeposited, which would explain their sedimentary characteristics.

Other sources of Al. The other potential sources of Al are either less abundant or if they predominate, they contain only small amounts of Al. The metallurgical treatment of such materials is often difficult.

(1) The alunite, $KAl_3(OH)_6(SO_4)_2$, is fairly rich in Al, but is not abundant: it develops through either superficial or deep chemical weathering of aluminous rocks in contact with sulphuric solution (weathering solutions from sulphide lodes and volcanic fumaroles, for example).

(2) The Al-phosphates contain up to 40% Al. Ores of this type have been found in Florida (U.S.A.) and in Senegal, where they formed through lateritic weathering of Ca-phosphate deposits.

(3) Aluminous clays. These are more commonly clays of the kaolinite group, either well or poorly crystallized (dickite, nacrite, kaolinite, fire-clay, halloysite) or they are more exceptionally aluminous chlorites. They often contain small quantities of crystallized or amorphous Al-hydroxides. Their alumina content can amount to 40%. They are of eluvial (weathering of rocks) or sedimentary origin, and in this last case, they seem to have been inherited from continental soils (Millot, 1964). Important aluminous clay layers are known particularly in Florida, Carolina, Pennsylvania (U.S.A.) and Hungary (Keller, 1964).

(4) The dawsonite (Na-Al-carbonate) which is contained in some bituminous schist

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[1] See Chapter 4 by Zuffardi, for other ore deposits in karstic host rocks.

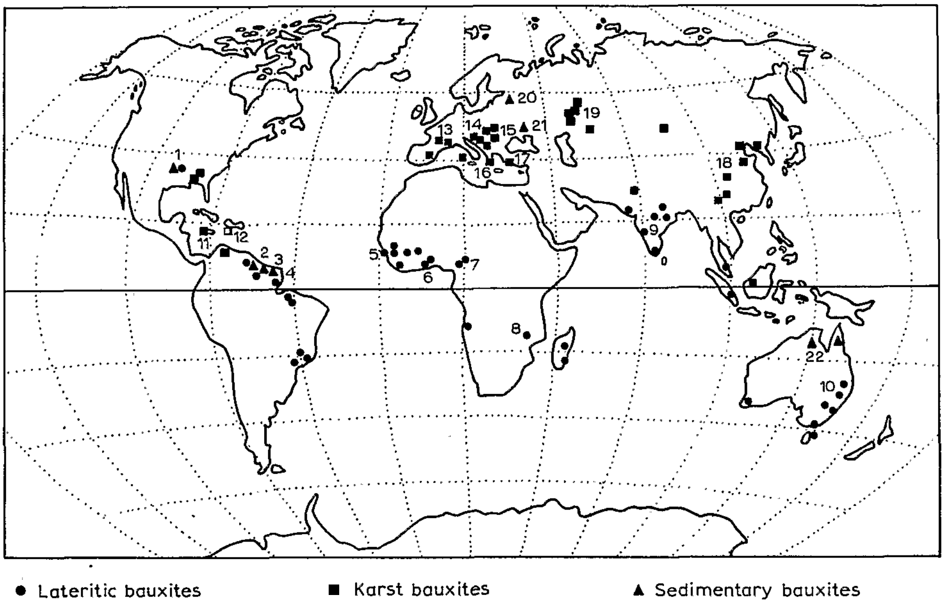

Fig. 3. Principal deposits of bauxite and estimated total reserves in millions of tons (after Patterson, 1967, and Valeton, 1972). *Lateritic bauxites*: *1* = U.S.A. (Arkansas), *2* = British Guyana (80), *3* = Surinam (200), *4* = French Guyana (70), *5* = Guinea (1,200), *6* = Ghana (290), *7* = Cameroon (1,500), *8* = Malawi (60), *9* = India (64) and *10* = Australia (2,000), *Karst bauxites*: *11* = Jamaica (600), *12* = Haiti (85), *13* = France (70), *14* = Yugoslavia (200), *15* = Hungary (150), *16* = Greece (84), *17* = Turkey (30), *18* = China (150) and *19* = Russia (Urals) (300). *Sedimentary bauxites*: *1* = U.S.A. (Arkansas) (44), *2* = British Guyana, *3* = Surinam, *20* = Russia (Tikhvin), *21* = Russia (Ukrain) and *22* = Australia (Northern).

(e.g., in Colorado, U.S.A.) might be a by-product of petroleum. The potential resource of this low-grade ore would be considerable (Guillemin, 1974).

(5) Rocks exclusively or almost exclusively *feldspathic* (anorthosites, nephelinic syenites, for example) form a very abundant potential source, but with low content of Al (20–30%).

Exploitation of aluminium ores. Up to now, bauxites are nearly the only Al-ores being extracted. Their extraction is rapidly increasing: about 30 millions tons in 1961 and 65 millions in 1971. The respective parts of the three genetic types of bauxites in the production are not exactly known, since the genetic characteristics of the bauxites utilized are often not well established. Schellmann (1974) considers only two main types, the karst bauxites and the silicate bauxites (derived from the lateritization of silicate rocks). We may suppose that the latter include the "blanket" and most of the "interlayered" bauxites, even though many karst bauxites are now assumed having a sedimentary origin. The production of karst bauxites, which are chiefly located in or near the industrial countries, was dominant up till 1960–1965; but the minable reserves of silicate bauxites are more considerable and their part of the world production now reaches 55–60% (Schellmann, 1974). The principal producing countries are Jamaica, Australia, and Surinam.

Analytical study of bauxites

Nomenclature: laterites and bauxites. The term "bauxite", defined by Berthier (1821) after the locality of Les Baux (France), was initially applied to aluminous concentrations on limestones. It has then been extended to lateritic blanket bauxites. Indeed, bauxites and laterites are two closely related weathering formations in humid tropical and equatorial regions. But if the term "bauxite" is fairly precise, the term "laterite" covers many aluminous, ferruginous and argillaceous formations, and the concept of lateritization, considered by pedologists to be too indefinite, has been replaced by the concept of ferrallitization (Chatelin, 1972). Nevertheless, we will retain here the old term "laterite", with its wide meaning: weathering formation, indurated or loose, argillaceous or not, and containing Fe- and Al-hydroxides. After Lacroix (1913), we will distinguish: (a) laterites sensu stricto with more than 90% hydrates (Fe–Al); (b) argillaceous laterites with 50–90% hydrates (Fe–Al); (c) lateritic clays with 10–50% hydrates (Fe–Al); and (d) clays with less than 10% hydrates (Fe–Al).

The laterites s.s. are subdivided into aluminous laterites or pure bauxites, alumino–ferruginous laterites or impure bauxites, and ferruginous laterites; the chemical composition of these formations is presented in Table III.

Types of bauxite ore deposits. These types are specified by distinctive morphological characteristics:

(1) Bauxites and laterites of lateritic blankets. Bauxites and laterites s.s. occur most commonly in the upper part of these blankets, as concretionary layers or crusts, more or less indurated, which cap hills and plateaus and which offer protection against erosion. These topographically high levels are fairly widespread in Africa, South America, the East Indies, Indonesia and Australia; they are often considered as remnants of ancient peneplains described in the East Indies as "high-level laterite" and in Africa as "African surface" (Fermor, 1911; King, 1948; Michel, 1970).

The profiles through these blankets present some differences, from one ore deposit to another, and only three fairly typical profiles will be described here, which correspond respectively to pure bauxites, alumino–ferruginous laterites and ferruginous laterites, without making reference to the superficial horizon of loose ground which covers the indurated level in some areas, particularly in forest regions.

(a) Pure bauxite on nepheline syenite. The vertical sequence is from top to bottom (Lacroix, 1913; Bonifas, 1959) in typical deposits of Iles de Los (Guinea): (i) bauxitic crust, massive, indurated, light coloured, with a compact or vesicular structure, and a breccia, pisolitic or homogeneous texture (up to 10 m thickness); (ii) granular bauxite, friable or little indurated, finely porous, with a structure inherited from that of the parent rock (very variable thickness); (iii) fresh bed rock (parent rock).

The vertical section of residual bauxites in Arkansas is about the same (Gordon et al., 1958). The contact between the granular bauxite and the parent rock is very sharp and irregular; in some places argillaceous saprolite formations are developed toward the base of the granular bauxite. All bauxites are generally very rich in Al (see samples 1, 2, 3, in Table III).

(b) Alumino–ferruginous laterites on greenschists, diorites, gabbros or similar rocks. The main levels from top to bottom are as follows: (i) alumino–ferruginous laterite crust, more or less dark-coloured, strongly indurated, massive or scoriaceous, with a homogeneous, breccia or pisolitic texture; the thickness may be up to 10—15 m. The upper part of this crust often appears relatively enriched in Fe, whereas the lower part is relatively enriched in Al (occurrences of secondary crystallization of Al which cement the pore and line up vesicules and fissures); (ii) kaolinic clays (lithomarge), often mottled, with diffuse red spots of Fe-oxides, and in which the structure of the parent rock is sometimes recognizable; the thickness is quite variable and may sometimes reach 50 m or more; (iii) fresh parent rock.

These bauxites are generally impure, more or less rich in Fe (see Table III: sample 7, 8 and 9) and of heterogeneous composition; the Al-content varies from one point to another. Such bauxites are very common; many ore deposits are known in West Africa (Grandin, 1973; Boulangé, 1973), in Guiana (Harrison, 1933) and in Indonesia and Asia

TABLE III

Chemical composition of some bauxites and laterites

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
SiO_2	4.6	2.2	4.1	1.8	1.4	5.4	3.3	0.6	0.8	1.5	0.3
Al_2O_3	62.0	55.8	61.5	60.0	60.5	44.3	46.8	46.2	37.7	9.0	5.3
Fe_2O_3	0.9	5.2	2.0	8.0	9.7	23.1	23.6	24.7	31.8	75.0	72.3
TiO_2	0.4	0.1	2.9	1.1	2.2	1.4	0.7	0.2	4.2	–	–
H_2O	31.6	30.4	30.7	29.4	25.5	24.5	22.9	26.3	24.5	12.0	14.5

(1) Typical bauxite on nepheline syenite (Gordon et al., 1958).
(2) Typical bauxite on nepheline syenite (Lacroix, 1913).
(3) Typical bauxite on schists (Boulangé, 1973).
(4) Typical bauxite on granite (Boulangé, 1973).
(5) Typical bauxite on argillite (Cooper, 1936).
(6) Alumino-ferruginous crust on syenite (Bonifas, 1959).
(7) Alumino-ferruginous primary laterite on dolerite (Harrison, 1933).
(8) Alumino-ferruginous crust on amphibolite (Boulangé, 1973).
(9) Ferrugino-aluminous crust on dolerite (Harrison, 1933).
(10) Ferruginous crust on dunite (Percival, 1965).
(11) Ferruginous crust on peridotite (Trescases, 1973b).

(Harder, 1952; Wolfenden, 1961). They occur on a large variety of rocks, especially basic or intermediary eruptive rocks, on lavas and tuffs, on schists and argillites, less commonly on acid, granitic or gneissic rocks. A thin and irregular level, where the parent rock is more or less totally bauxitized, is often differentiated under the lithomarge.

(c) Ferruginous laterite on ultra-basic rock (Percival, 1965; Trescases, 1973b). The main levels from top to bottom are: (i) ferruginous crust, dark-red–purplish, massive or vesicular but very dense and hard, with a brecciated or scoriated texture; under the crust or replacing it, there may be found a thick gravelly level, essentially formed of ferruginous concretions (from 5 to 10 m thick); (ii) soft layer, of lighter colour, brownish-yellow–red, sandy or silty but non-argillaceous, often preserving the parent-rock structure (variable thickness up to 50 m); (iii) more or less rubefacient, saprolized parent rock, with a coarse texture; and (iv) fresh parent rock.

From the study of these ore deposits, one may distinguish after Harrison (1933) and Erhart (1973b), two types of laterites: first, the "primary" or "typical" laterites in which the structures of the parent rock are preserved and where the Fe- and Al-concentration corresponds to a simple relative accumulation ensuing from the removal of the other constituents. Secondly, the "secondary" or "modified" laterites in which the initial structures vanish through phenomena of both relative and absolute accumulations (D'Hoore, 1954) and probably through some mechanical migratory processes. The absolute accumulation phenomena are confirmed by the presence in laterites of coatings and linings of Fe- or Al-hydrates on the fissure and vesicle surfaces.

Despite their chemical disparities, the first and third types of ore deposit prove to have a real morphological analogy: in both cases a thick level of primary, aluminous or ferruginous laterite lies immediately on the parent rock. On the other hand, the more frequent second type exhibits mostly secondary laterites, separated from the parent rock by a generally thick layer of argillaceous lithomarge.

(2) Karst bauxites. The bauxite ore deposits found on sedimentary limestone rocks in the south of France, generally show a vertical section which, if simplified, is as follows (Nicolas et al., 1967; Nicolas, 1968). (i) top: sandstone, lignitic, argillaceous or carbonate sediments (Upper Cretaceous or Tertiary); (ii) oolitic or pisolitic bauxite becoming richer in clays toward the top; (iii) brecciated bauxite; (iv) red kaolinic clays with fragments of bauxite; (v) bottom: karstified calcareous sediments (Upper Jurassic–Lower Cretaceous).

Nicolas points out the existence of breccias toward the base of the ore deposits, and sometimes the presence of fossils (*Rhynchonella, Terabratula*) in the bauxite itself.

The karst-bauxite deposits occurring along the northern border of the Mediterranean Sea are of the same type. Similar deposits are also found in the Urals and Vietnam, but the calcareous bed rocks are older; those occurring in the West Indies are of Eocene–Oliocene age (Hose, 1963).

(3) Sedimentary bauxites. The diagrammatic section giving the major types of bauxite in Arkansas (Gordon et al., 1958) shows, in addition to residual bauxites, bauxite deposits interbedded in transgressive Tertiary series. These deposits consist of detrital elements

of bauxite, about 1 mm in diameter, rounded–subangular shaped, included in an argillaceous matrix, and occurring in ancient channels or small depressions within the basin which they fill. Intersecting stratifications and grain-sorting sequences may be observed.

Another example is afforded by stratified bauxites, in the recent sedimentary basin of the Guiana littoral zone: several levels of bauxite are reported (Boyé, 1963; De Vletter, 1963; Moses and Michell, 1963), lying either immediately on the weathered basement, or separated from it by sedimentary gravel, sand, clay or lignite layers of the Lower Quaternary or Tertiary Periods.

Mineralogy of bauxites

(1) Lateritic blanket bauxites. Al mostly assumes the form of very fine crystallizations of gibbsite. In primary laterite, this mineral appears as a porous mass, replacing the feldspar minerals (Lacroix, 1913; Harrison, 1933). In the crusts and secondary laterites, the microcrystalline gibbsite is closely mixed with Fe-oxides (goethite, hematite) and with variable quantities of kaolinite. There, it forms compact masses in which more or less abundant, angular or rounded particles (fragments, ooliths, pisoliths) are differentiated inside a homogeneous matrix. Crystals of larger size develop as coatings and linings inside fissures and vesicles. In pisolitic crusts, gibbsite is often replaced by boehmite.

(2) Karst bauxites. Some of these bauxites, and especially the relatively recent ones occurring in Jamaica, are chiefly composed of gibbsite. But most of the bauxites developed on calcareous rocks in Southern Europe predominantly contain boehmite or diaspore (dense dimorphous variety of boehmite). Fe assumes the hematite and sometimes the magnetite form, but it may also be in some proportion included in boehmite and diaspore (Hose, 1963; Caillère and Pobeguin, 1964; Valeton, 1965). Diaspore is the major constituent of bauxites lying on ancient calcareous sediments, as, for example, in some Russian or Asian deposits. In regions where the bauxites have undergone general or contact metamorphism, the recrystallization of boehmite or diaspore in anhydrous minerals (corundum) may occur.

In brief, gibbsite is the most common mineral in recent or little altered bauxite facies (particularly primary laterites). Boehmite and diaspore are, on the other hand, the most common species in more ancient bauxites which have undergone a more or less marked diagenesis. Under metamorphic conditions, corundum develops. Kaolinite which accompanies Al-hydrates seems to be less susceptible than these latter to the transformations affecting the deposits.

Genesis of bauxites and laterites

Since all bauxites, sedimentary and karst bauxites included, seem to involve concentration processes related to weathering under a humid-tropical climate, we will consider here only the problem of the genesis of the lateritic blanket bauxites.

The first point to emphasize is the relative scarcity of bauxite ore deposits, although

Al is quite abundant. This might be explained by the very low mobility of this element under surface conditions. To arrive at significant accumulations, all the other elements must be removed, which implies a very unusual intervention of additional processes.

Bauxites are commonly defined as the ultimate residual product obtained through the weathering of silico–aluminous rocks exposed to extremely intense leaching conditions. These conditions are encountered in warm and humid climates, in relatively high and well-drained locations, and under a dense cover of vegetation allowing the chemical weathering effects to prevail over mechanical erosion. Under such conditions, the pedogenesis gives rise to ferrallitic soils with a profile showing some features resembling the lateritic differentiations:

Ferrallitic soil profile:	*Lateritic bauxite profile:*
leached superficial horizon (A)	residual soil[1]
horizon of Fe- and Al-accumulation (2–3 m thick) (B)	alumino–ferruginous crust (5–15 m)
horizon of mottled clays[1]	argillaceous lithomarge[1]
lower leached horizon[1] (C)	primary laterite
fresh parent-rock	fresh parent rock

The massive and thick accumulation of Fe and Al in bauxites and laterites can, therefore, be considered as the ultimate term of a very prolonged ferrallitic evolution, allowing the accumulations of the B horizons to aggregate progressively as the profile goes deeper and the horizons to migrate downward conjointly with the topographical surface. Induration of these accumulations into laterite crust is often explained by the existence of a climatic change with marked trend toward aridity, involving the destruction of the vegetal cover, the ablation of the superficial A horizon and the induration of the illuvial B horizon.

Primary bauxites and laterites. The concept of primary laterite explains fairly well the formation of very pure bauxites on silico–aluminous rocks free of quartz and poor in Fe, such as the nepheline syenites or even the aluminous clays. As reported below (p. 153), during the leaching process of silico–aluminous minerals and at a pH within the range of the more common pH (4–8), bases are removed first and then combined silica, whereas Fe and Al accumulate residually as crystallized products (gibbsite, boehmite, goethite). These residual minerals have been obtained in leaching experiments, at moderate temperature, from all kinds of crystallized or vitreous rocks and from silico–aluminous minerals, clay minerals included (Pédro, 1964; Trichet, 1969; Pédro et al., 1970). Nevertheless, in bauxites of this type, the bottom part of the profiles sometimes exhibits an argillaceous horizon, with neoformed kaolinite, a mineral which is hardly ever obtained experimental-

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[1] The corresponding horizons do not occur systematically.

ly under normal pressure and temperature conditions (Wollast, 1961; Lerz and Borchert, 1962).

The same concept explains the formation of ferruginous laterites on ultra-basic parent rocks, poor in Al. The origin of these ferruginous laterites and bauxites is strictly residual: they are "*eluvial laterites and bauxites*". Such laterites are essentially primary ones, even if redissolution and re-precipitation processes in the crustal layer progressively obliterate the parent-rock structures, giving facies of "secondary" laterites.

Secondary bauxites and laterites. The development of bauxites is not exclusively limited to some particular rocks: they are also found on acid rocks, containing quartz, such as granites and gneiss, or on intermediary or basic rocks which are more or less rich in Fe, of eruptive, metamorphic or sedimentary origin. The problem of the genesis of these bauxites raises the question of the elimination of the silica and/or of the separation of Fe and Al:

(1) Separation of aluminium and silica. Bauxites derived from feldspathic rocks, either quartzitic or not, generally lie on a kaolinic lithomarge in which the feldspars have been destroyed while the quartz persists. The bauxite formation process seems to proceed in two steps:

step 1 = feldspar → kaolinite;
step 2 = kaolinite → gibbsite.

The chemical reaction corresponding to step 2 is:

$$Al_2(OH)_4\,Si_2O_5 + 5H_2O \rightarrow 2\,Al(OH)_3 + 2\,Si(OH)_4$$

The equilibrium is displaced towards the right side through the $Al(OH)_3$ precipitation (gibbsite), but this incongruent dissolution involves a very low concentration in $Si(OH)_4$ (less than 1 ppm SiO_2), and an intermediate range of pH (pH from 4 to 7) in which gibbsite is stable. In very acid or alkaline solutions, the reaction of dissolution of kaolinite becomes congruent and gives ionic Al^{3+} (acid solution) or $Al(OH)_4^-$ (alkaline solution) and the precipitation of gibbsite does not occur.

Thus, the proceeding of the second step of bauxitization normally requires, in the slightly acidic environment of tropical soils, that all the quartz and, a fortiori, the feldspars have been removed (see the diagram of the solubility of kaolinite, gibbsite and quartz, Fig. 4, and the thermodynamics data from Wollast, 1961, 1963; Tardy, 1969; Curtiss, 1970; Gardner, 1970 and Schellmann, 1974). Therefore, a complete bauxitization requires a particularly long evolution which would permit the very slow dissolution of the quartz and also a complete hydrolysis of the kaolinite (a mineral much more resistant than the primary silico–aluminous ones). This two-stage evolution results in bauxitic crusts of the secondary laterite-type. The structure of these bauxites does not generally bear any relationship to the rock structure, for this structure disappears progressively at the level of the lithomarge: they may be termed "*secondary eluvial bauxites*".

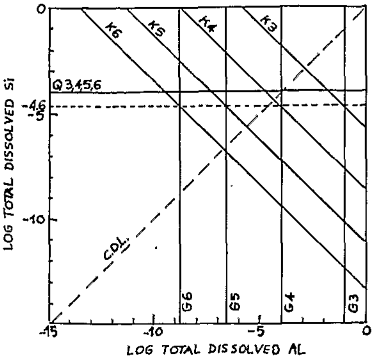

Fig. 4. Solubility of quartz, kaolinite and gibbsite contoured at pH values from 3 to 6. *K* = kaolinite; *Q* = quartz; *G* = gibbsite. Associated numbers indicate pH countours. *C.D.L.* = congruent dissolution line of kaolinite. (After Gardner, 1970.)

However, some aluminous lateritic crusts developed on feldspathic rocks keep the parent-rock structure, although it has disappeared at the level of the subjacent lithomarge (Wolfenden, 1961). Bauxitic crusts on granite, with hardly any lithomarge, but with a preserved granitic structure, are also known (Boulangé, 1973). These ore deposits may be explained by assuming that on feldspathic rocks, either quartzitic or not, the bauxitization may be a direct process, without any argillaceous phase, like on nepheline syenite rocks. This is illustrated by many ferrallitic soil profiles exhibiting a gibbsite horizon lying immediately on a granitic parent rock (Lelong, 1969) and is also confirmed by the results of leaching experiments in the laboratory (Pédro, 1964). The direct process of bauxitization in presence of quartz and feldspar minerals may be explained by the consideration of reaction kinetics. Under intense leaching conditions, the solubility limits of the silicate minerals are not necessarily reached and the evolution may lead directly to the bauxite stage before the feldspars and the quartz are totally destroyed. The temperature may also interfere: the thermodynamic calculations made by Fritz and Tardy (1973) from Helgeson (1969), show that at acid pH a rise in temperature tends to reduce the solubility of gibbsite and to increase that of kaolinite. This favours the direct bauxitization of rocks rich in silica.

Therefore, the aluminium–silicon separation proceeds either indirectly in two stages (rock → lithomarge → bauxite) or directly (rock → bauxite), providing that exceptional drainage and temperature conditions are fulfilled. In the second case, the occasional occurrence of an argillaceous lithomarge underlying the primary bauxite may be due either to subsequent processes of resilicification of the bauxite or the result of incomplete desilicification of the parent rock, related to reduced drainage conditions (e.g., raising of the base level or deepening of the weathering front).

(2) Separation of Al and Fe. Except on parent-rocks very deficient in Fe, the formation of bauxites requires an Al–Fe separation. In profiles of lateritic bauxites of West Africa, Grandin (1973) quoted a more marked enrichment for Fe than for Al in the

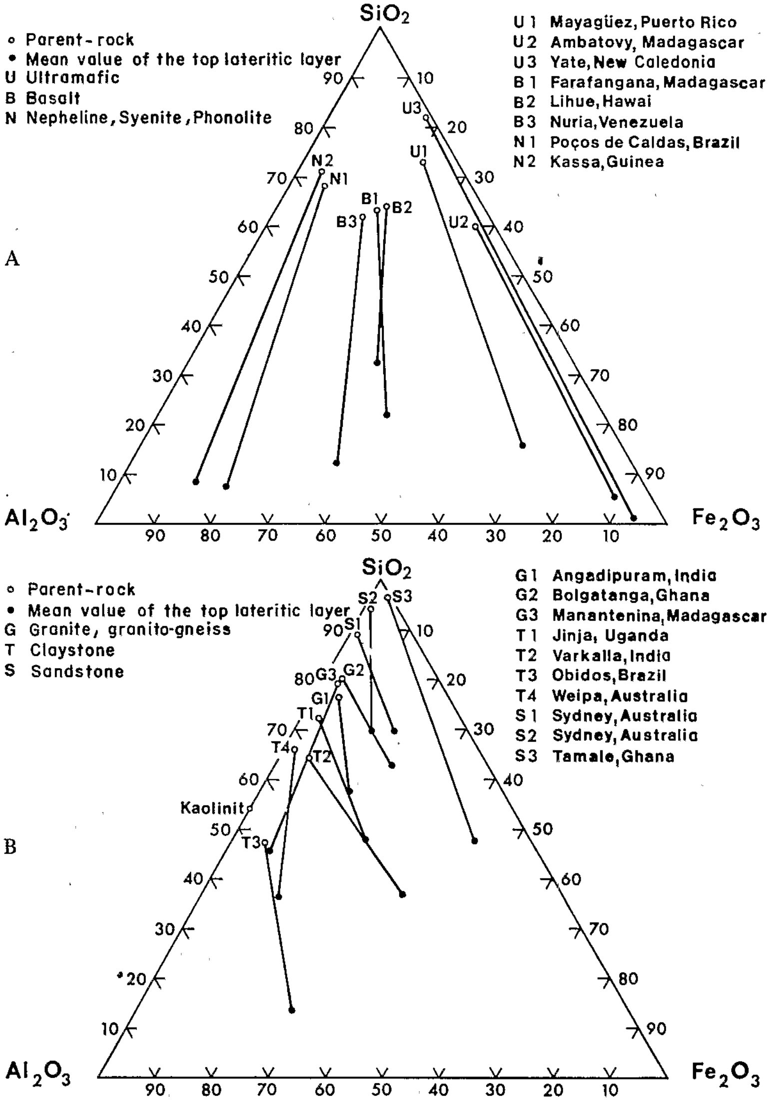

Fig. 5. Variations of Al_2O_3-, Fe_2O_3- and SiO_2-contents during lateritic weathering of: (A) quartz-free parent rocks; and (B) quartz-bearing parent rocks (after Schellmann, 1974).

surface lateritic crust. Schellmann (1974) compared the chemical trends during the lateritization of quartz-free rocks and of quartz-bearing rocks (Fig. 5). On the former rocks, Al_2O_3 and Fe_2O_3 seem to be equally stable; they are enriched in the same proportions in the lateritic crust, whereas on the latter, Fe_2O_3 is more enriched because some quantities of Al_2O_3 are dissolved during desilication processes.

As seen above, in the ferrallitic soil profiles on granitic rocks (see Fig. 1), Fe accumulates more easily than Al at the level of the B horizon, but it is relatively depleted at the level of the hydromorphic lithomarge, as is attested by the frequent bleaching of this formation.

Thus, the removal of Fe, which is required for the bauxite differentiation, may be related to the preferential leaching of this element in the more or less reducing conditions occurring at the lithomarge level. This process of removal, already well marked in the deep layers of relatively high areas, is probably more intense in soil profiles of low, flat or basinal areas, where hydromorphic conditions are more severe. But in the hydromorphic lithomarge, Si is partly retained with Al and the bauxite genesis implies a subsequent stage of desilication, with improved drainage conditions. Therefore, the resulting bauxites correspond to the secondary eluvial type, the formation of which requires two different steps of evolution with changes in the geomorphological conditions. Concerning the formation of the largest bauxite deposits of this type, which occur as perched crusts capping highlands, the supposition is sometimes made that the first stage of differentiation took place in low, flat or basinal areas, where the most propitious conditions for Fe removal exist, and that their preeminent position is due to relief inversion as a result of intensive differential erosion.

However, all the bauxite profiles which are developed on iron-rich parent rocks do not show a thick level of lithomarge, favouring the removal of Fe. Thus, we now have to consider the mechanisms of separation of Fe and Al which are able to operate in the superficial layer of the soil profiles, where these two elements have been accumulated together.

The solubility diagrams of aluminous and ferriferous oxides in relation to pH and Eh (see Norton, 1973) show that for rather low pH ($pH < 4$), Al is more soluble than Fe, when the environment is oxidizing enough ($Eh > 0.4$) (see Fig. 8). Therefore, some dissociation of both elements is plausible, Al being relatively leached in the superficial, acid and well-aerated layers of the profiles, before being redeposited in deeper layers or further away laterally, owing to small increases of pH. The complexing action of acid organic compounds may also lead to the same result. The sesquioxides are then likely to be "cheluviated" (see p. 157) and their mobility is increased in the range of pH existing in the soil profiles, but this action is selective; Al is generally recognized as moving further than Fe^{3+} (Duchaufour, 1968). In this way, one could explain the occurrences of bauxite layers, intercalated between a superficial crust relatively rich in Fe and deeper (argillaceous or not) horizons. This type of bauxite profile on silicate rocks with a high content of Fe, which has been described by Harder (1952), Boulangé (1973) and Schellmann (1974), resembles illuviated soil profiles in which selective leaching and reprecipitation processes may give secondary accumulations originated from the eluvial layer.

In the presence of carbonic acid, the dissociation of Fe and Al is also possible: experimental leaching on various rocks, in a bicarbonic, moderately acid environment, show that the Fe becomes relatively soluble while Al remains immobile (Pédro, 1964; Trichet, 1969). Then the differentiation is the reverse of the preceding one, the Fe being likely to accumulate downward or farther away.

Thus, the mechanisms governing the separation of Fe and Al possibly operate either in the lithomarge layer, where the mobility of Fe is increased, or in the superficial well-aerated layers, where Al or Fe may be selectively leached owing to several factors (Eh, pH, organic complexes, CO_2, etc.). In the first case, the bauxite genesis implies two stages of formation, and the resulting bauxites belong to the secondary eluvial type. In the second case, the bauxites must not be considered as strictly residual, since the Al-accumulations likely result from vertical and lateral redistribution of this element, either related or unrelated to the ferrallitic pedogenesis; for the purpose of simplification, these bauxites would be termed "bauxites of the *illuvial–eluvial* type".

Bauxitization and geomorphology. Except for the primary-type bauxite, developed on particularly propitious rocks, the bauxite genesis is not easily explained. It implies a succession of processes corresponding perhaps to different pedological conditions. For a better understanding of this genesis and of the relationships between the different types of deposits, we will attempt to situate them in the context of space and time, that is to say, to define the corresponding geomorphological evolution.

The forest equatorial pedogenesis normally corresponds to a peneplain landscape, with convex hills cut by a dense network of valleys, where the concretionary and, a fortiori, the superficial crust formations are scarce. Lateritic crusts and bauxites occur instead in the form of more or less indurated residual levels topping some reliefs or lying on vast plateaus. Such occurrences imply a complex history, during which weathering and erosion conditions could have changed several times. Different interpretations are plausible and Fig. 6 schematizes the possible history of some ore deposits in West Africa, by taking into account morphoclimatic changes that have occurred in that area since the Tertiary Period (Grandin and Delvigne, 1969; Boulangé, 1973; Grandin, 1973). The different phases are:

(1) Period of tectonic calm (Cretaceous, Tertiary?), equatorial climate with forest vegetation; a thick lateritic blanket developed, exhibiting a relatively superficial accumulation of Fe and Al (primary alumino–ferruginous laterite) in surface layers and a lithomarge in deeper poorly drained zones.

(2) Deeper penetration of weathering and slow erosion, under steady climatic conditions; Fe and Al may be progressively dissociated, either by a preferential leaching of superficial Al or by the mobilization of Fe in deeper hydromorphic layers. The mobilized elements redeposited more deeply and laterally in illuvial lateritic crusts developed on slopes or above the groundwater table.

(3) Occurrence of erosion due to a drier climatic phase: formation of a crust of primary laterite on the massifs, wearing away of the peneplain, and formation of pediplain with vast plane surface ("glacis") rich in lateritic debris (Pliocene, Lower Quarternary).

(4) Reappearance of a humid-forest pedogenesis, resulting in re-deepening of weather-

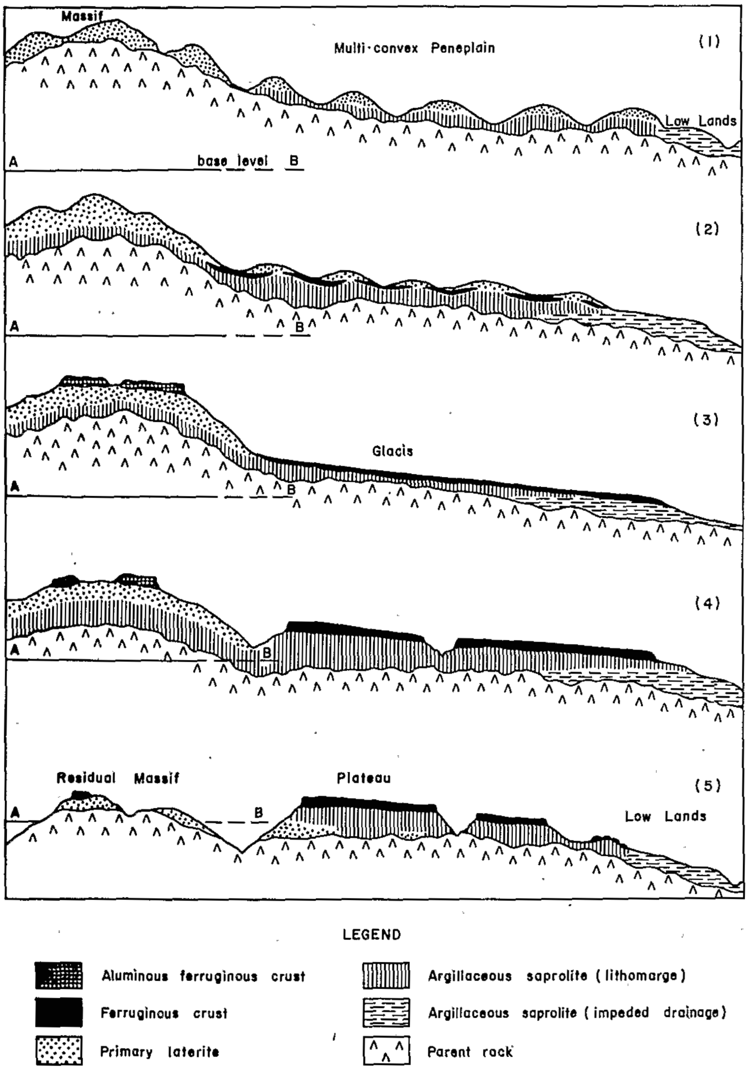

Fig. 6. The possible stages of the formation of West African bauxites and laterites. The stages (1)–(5) are described in the text.

ing profiles and lateritization of the glacis (forming secondary ferrugino–aluminous laterites).

(5) Erosion of tectonic or climatic origin leading to incision, dismantling of residual massifs and breaking up of the lateritized glacis, becoming lateritic crusts of plateaus. The present evolution in West Africa is approximately at this stage.

At the end of the above-mentioned evolution, a complete inversion of the relief may occur; the former massifs together with their primary laterites are eroded, whereas the former peneplain has become a highland covered with secondary lateritic crusts. These are, in turn, likely to be dismantled and destroyed. It is in this way perhaps that bauxite and laterite ore deposits, differently distributed in the landscape and in time, take form, become differentiated, and then are reduced and finally disappear. However long this history may be (in the range of pedological time), it is not endless if considered from a geological viewpoint and all these ore deposits are destined to disappear, unless their residues are recovered through erosion and re-introduced in sedimentary series where they could be entrapped. It is quite normal, therefore, that the stratified bauxites within sedimentary series, generally seem more ancient than lateritic blanket bauxites.

SUPERGENE CONCENTRATION OF MANGANESE[1]

Generalities

Manganese in rocks.

(1) In the decreasing order of element abundance (by wt.%), Mn stands in twelfth place, with a Clarke value of 0.1% or 1000 ppm. It is widely dispersed in the various types of rocks in the earth's crust. The contents in eruptive rocks range between 500 and 2500 ppm (Borchert, 1970). Endogenous concentrations are rare. In sedimentary rocks, where one finds the major accumulations, the contents are more diversified and Green (1953) gives average values of 620 ppm in shales and 300 ppm in limestones, the sandstones containing only some traces. Goldschmidt (1954) indicates contents of 2000–5000 ppm in soils. But the range of variations is greater: some concretionary tropical soils contain up to 5%, while in very acid soils, the Mn is almost totally leached, which may result in deficiencies leading to unfavourable effects on agriculture.

(2) The dispersal of Mn results from the ability of Mn^{2+} to replace other elements. The difference between the ionic radii of Mn^{2+} and Fe^{2+} is only 8%, so substitutions are easy in ferromagnesian minerals (pyroxenes, amphiboles, olivines). Substitutions of six-fold coordinated Al, $3\ Mn^{2+} \leftrightarrow 2\ Al^{3+}$, permit the penetration of manganese in phyllitic minerals (micas, chloritoid, montmorillonite). Substitutions for Mg^{2+} and Ca^{2+} (which have ionic radii differences exceeding 15%) and for Fe^{2+} exist in the garnet and manganesiferous carbonate groups. The trivalent Mn is less common and occurs mainly in the oxisilicates, oxides and hydroxides (braunite, haussmanite, manganite) present in some lodes and in their weathering products. Tetravalent Mn is more commonly found, and occurs mainly in superficial alterites and soils, as oxides and hydroxides (polianite, psilomelane, wad) which are often not well crystallized.

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[1] For additional information on ancient and recent manganese ore deposits, see Chapter 9 by Roy, Vol. 7, and Chapter 8 by Callender and Bowser, Vol. 7, respectively.

Manganiferous ore deposits.

(1) The distribution (age of formations, geological location and size of ore deposits) of Mn-concentrations is very irregular (Varentsov, 1964; Bouladon, 1970). The Precambrian and Paleogene formations contain more than 85% of the reserves actually known, the remaining part being mainly distributed between the Lower Cambrian, the Carboniferous and the Cretaceous. Most of the ore deposits occur in areas of low tectonic activity and especially in littoral zones of continental shelves, or in subsiding troughs exhibiting submarine volcanism and in confined basins within these troughs. Five ore deposits (Nikopol and Tchiatoura, U.S.S.R.; Kuruman–Kalahari, South Africa; Moanda, Gabon; and Amapa, Brazil) provide nearly two thirds of the world production; Nikopol alone supplying about one third (Fig. 7).

(2) This irregular distribution and the large size of some ore deposits differentiate the Mn-concentrations from those of Fe or Al. The ratio of ore-content in mined deposits to the average rock contents is about 10 for Fe and almost 5 for Al, whereas it is 300–500 for Mn. The Mn ore deposits are generally the result of a series of geological histories. For example, the formation of the Moanda ore deposits is explained by "first a volcanic occurrence which raises the geochemical level in Mn, then a sedimentary concentration

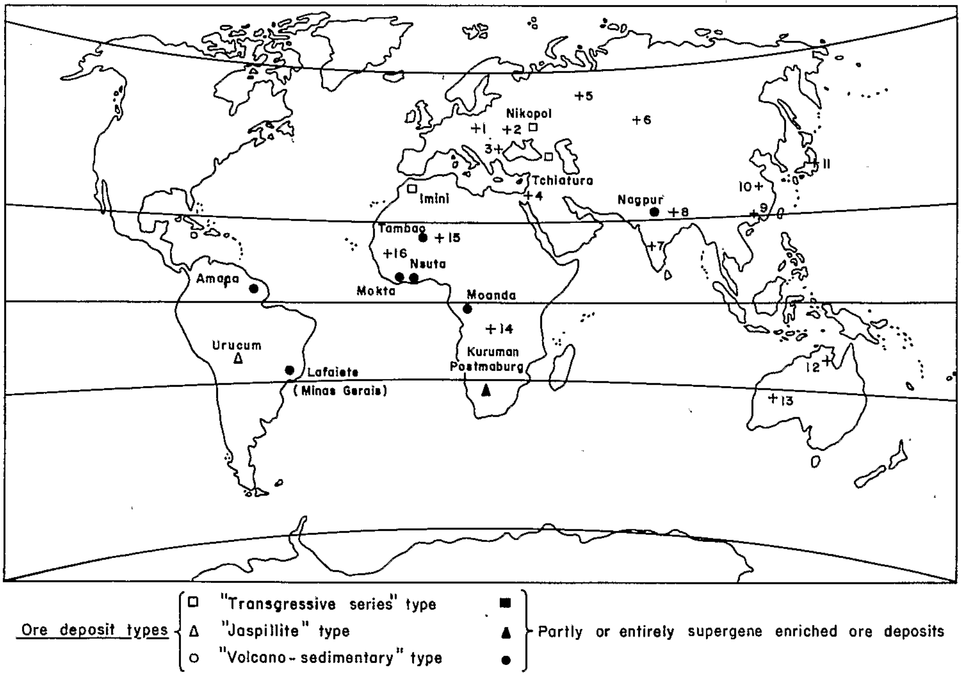

Fig. 7. Mn ore deposits in the world (after Varentsov, 1964, Putzer, 1968, and Bouladon, 1970). Main ore deposits: see the legend. Other ore deposits: *1* = Urkut; *2* = Jacobeni; *3* = Varna; *4* = Timna; *5* = Polunochnoe; *6* = Usink; *7* = Mysore; *8* = Orissa; *9* = Kwangtung; *10* = Kiangsi; *11* = Kotschki; *12* = Groote Eyland; *13* = Peak-Hill; *14* = Kisengue; *15* = Ansongo; *16* = Ziemougoula.

within a carbonate facies and at last, a superficial weathering which enriches and oxidizes the ore" (Weber, 1969). The concentration factors during these three stages are 3, 30–60, and 3–4, respectively.

(3) The main processes of concentration are exogenous, either sedimentary or volcano–sedimentary, and result in primary ores with carbonates and/or oxides. These primary ores may be more or less metamorphized, with formation of silicates, such as spessartine, garnet and rhodonite. A disparity in the role played by supergene processes appears between the different types of ore deposits: (a) ore deposits of the "transgressive series"-type, are generally directly minable (Nikopol and Tchiatoura, U.S.S.R.; Imini, Morocco); (b) ore deposits of the "gondite"-type (considered in the broad sense) and of the "associated with black carbon schists" type become generally only minable after weathering concentration (Amapa, Brazil; Nsuta, Ghana; Nagpur, East-Indies; Moanda, Gabon); (c) ore deposits of the "jaspillite"-type are intermediate, some being directly minable (Corumba, Brazil) and some others having been superficially enriched (Kuruman–Kalahari, South Africa). With the exception of the large Paleogene ore deposits in the U.S.S.R., about 3/4 of the ore deposits actually mined proved to have required some supergene enrichment (Thienhaus, 1967).

Another type of concentration of minor importance, which will not be taken further into account, is the mixed iron–manganese-type. This ore deposit occurs when the contents of both elements are high in the bed rock undergoing meteoric action, which does not favour an efficient separation. This is the case for ferruginous and manganiferous itabirites in the Minas Gerais State (Van Door et al., 1956). The supergene leaching gives mixed ores, richer in Fe towards the surface than downwards. Another illustration is given by the ore deposits formed through the filling of karst such as the Dr. Geier Mine (Germany), which originated from the weathering of dolomites containing Fe and Mn in a 2/1 ratio (Bottke, 1969). On the other hand, some bog ores favour the concentration of Mn in addition to that of Fe (Ljunggren, 1953; Shterenberg et al., 1969). But this is the limit between the supergene concentration and the sedimentation phenomena.

Geochemical processes.

(1) Like Fe, Mn is a transition element. The properties of these two elements are very similar and particularly so when occurring in the form of bivalent ions, which is the most common one in the rocks. As a result of supergene processes (oxidation, hydratation, etc.) both elements will undergo chemical changes and will likely be redistributed in alterites and soils. Mn is generally present in much smaller amounts than is Fe and when submitted to the chemical reactions of supergene processes, it often plays a passive role only (Michard, 1969). Reactions, such as dissolution or precipitation of MnO_2 or $MnO(OH)$, do not extensively modify the pH and Eh of the solutions, compared with the effects induced by similar reactions when Fe is involved. Thus, the changes in Mn state, related to pH and Eh variations, seem subordinated to changes in the Fe state. But when Fe is lacking, Mn can play an active role. In supergene processes, therefore, the Mn

behaviour will be governed either by the influence of more abundant elements, particularly Fe, or by its own chemical properties.

(2) When in aqueous solution, however, Fe and Mn show notable differences in behaviour. If the leaching and transport of the two elements proceed similarly, the Eh at a given pH must be higher for the deposition of Mn^{4+} than for Fe^{3+} (see Fig. 8, after Norton, 1973). As soon as the pH goes below the neutrality point, a redox potential exceeding 0.6 V is necessary to permit the precipitation of MnO_2 from a solution containing 1 ppm of Mn (Fig. 9, after Hem, 1963). In fact, in the presence of oxygen, the redox potential always exceeds this value, and Fe and Mn are totally oxidized; but the Mn-oxidation is much slower than that of Fe and, therefore, it is mainly for kinetic reasons that the Mn can migrate further than the Fe in a reduced form (Michard, personal communication, 1974). Thus, in soils and alterites, the Mn may be mobile in the relatively acid upper parts of the profiles, where the environment is nevertheless oxidizing enough to favour the rapid precipitation of Fe. It may be carried downward and accumulated at the lower part of the profiles, or along the slopes, where the pH is higher.

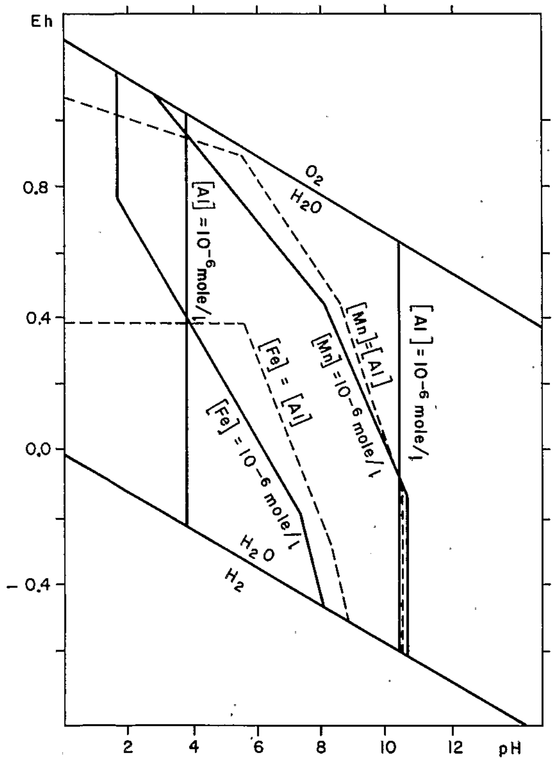

Fig. 8. Eh–pH diagram showing the solubility limits (10^{-6} mole/l) of Al, Fe and Mn, in the systems Al_2O_3–H_2O, Fe_2O_3–H_2O and MnO–H_2O, at 25°C and 1 atm. The lines of equal solubility of Fe–Al and Mn–Al are dashed. (Modified after Norton, 1973.)

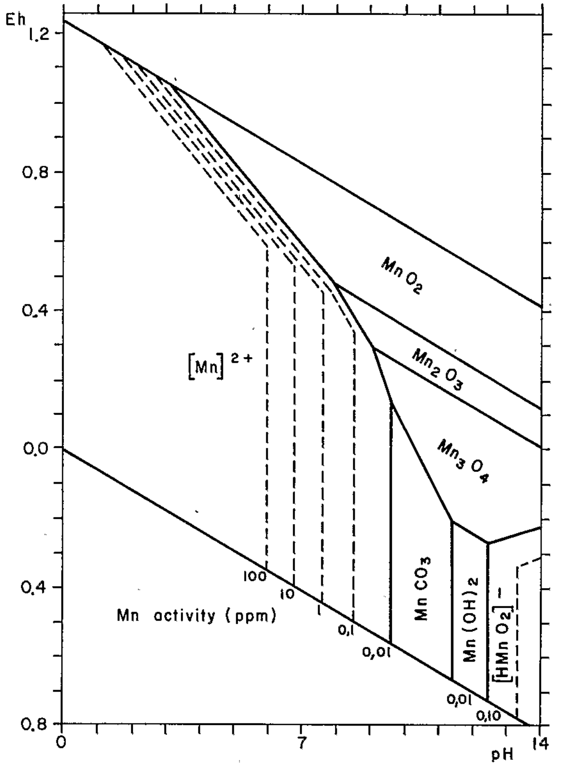

Fig. 9. Stability fields of the Mn-compounds in aqueous solutions with 100 ppm of bicarbonate (after Hem, 1963).

(3) It is also for kinetic reasons that the auto-catalysis phenomena are important in the precipitation of Mn. The oxidation reactions are rendered easier by the presence of propitious solid surfaces: already deposited Mn-oxides constitute such surfaces. When the Mn precipitates alone, it is generally in the form of compact oxide masses (concretionary, stalactitic and massive psilomelanes with a hardness exceeding 6), and redissolution is then very difficult.

Finally, in addition to the chemical processes, the biochemical processes related with the evolution of organic matter in the soil play an important role.[1] Soluble residues of fermentation favour the migration of Mn, in a negative complex-ion form, in environments unfavourable to cation migrations. The oxidation may develop inside the complex so formed; the quantity of protecting matter required being proportional to the valency, the precipitation takes place when complexing matter is present in insufficient quantities after the oxidation process or after its destruction by micro-organisms (Béthremieux, 1951).

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[1] See Chapter 5 by Saxby in Vol. 2 and Chapter 6 by Trudinger in Vol. 2.

Accumulation of manganese in alterites and soils

Types of accumulations.

(1) Before describing the types of secondary Mn-accumulations, three points must be emphasized: first, important superficial Mn-concentrations are only possible in alterites and tropical soils where the hydrolytic conditions are aggressive enough to permit the release of Mn from primary minerals. Second, the Mn-distribution in the alterites of ultra-basic rocks is not the same as in the alterites of other types of rocks: the former become enriched (if compared with the rocks), while the latter are impoverished (Schellmann, 1969). This fact seems to be due to higher pH conditions toward the base of the profiles on ultra-basic rocks, and consequently the Mn rapidly becomes insoluble and then behaves as a residual element (Trescases, 1973b). In alterites derived from more acid rocks, the Mn is more mobile and, therefore, it tends to be carried away and it also may form secondary concentrations elsewhere. Third, there is no manganiferous concentration of economic interest in alterites and soils derived from rocks in which the Mn-content does not exceed the Clarke value. Assuredly, some secondary Mn-accumulations are observed in some types of tropical soils on common rocks, but then this element is mixed with clays and other elements and its content is much lower than 10% Mn. Thus, in vertisols, the Mn accumulates with Ca and Mg in carbonate nodules, and in ferruginous soils it is concentrated with Fe in the concretionary or crustal horizons.

(2) The most common secondary concentrations of Mn observed on rock rich in manganese are: (a) Mn-oxide crusts. These are deep-lying indurated horizons of ferrallitic soils, formed below the primary mineralization levels, on the lower slopes of ridges typical of the relief encountered in humid-tropical climates. The crusts result from an oblique migration of manganiferous and more or less ferruginous solutions through very thick soils, the top part of which is well-drained and forms an oxidizing and acid environment. The Fe and a part of the Mn are fixed in the upper horizons. The remaining Mn migrates downwards and is deposited at the base of the mottled clays in contact with the relict-structured weathered rock (see below Fig. 10C). The crusts are several metres thick and the wt.% of Mn-oxides is about 80–95. These oxides are chiefly psilomelanes and pyrolusite, with a massive, botryoidal or fibrous fabric. There is no transition between the mottled clays and the crust. From the very first stages of concentration, some cutanes formed of quasi-pure oxides appear. These cutanes become thicker and become anastomosed, embodying some clay pockets which persist in the very rich crust with initial white or red colour. (b) Manganiferous pisolites and nodules. These occur in the upper horizon of the ferrallitic soils. Their Mn-content is variable but very rarely reaches the limit of minability. The Mn is in not well-crystallized oxide and hydroxide forms and is associated with Fe-oxides and clays and sometimes with Al-oxi–hydroxide. The induration of pisolites is low–moderate and the horizons containing them remain loose. In this case, the Mn deposition corresponds to phenomena of coprecipitation with the Fe and of

adsorption on clays. Both pisolite horizon and Mn crust may be observed in the same vertical section.

(3) In some ore deposits formed from tilted mineralized strata, one may also observe accumulations of blocks of manganese ores topping these strata. Sometimes these accumulations form an important part of the minable ores. They become concentrated at the top of ridges during long periods of erosion and during the slow lowering of the topographic surface of the mineralized strata which were formerly oxidized and enriched within the weathering layer. Since the enclosing formations are fairly loose and fluidal argillaceous alterites, the strata could have undergone an intense creeping down and fracturation without having actually been outcropping at any time. This explains why they spread in the form of residual block accumulations lying parallel to the topographic surface, predominantly towards the bottom of the slopes (Fig. 10C). Ulterior recurrences of erosion provoked incisions of some of these accumulations and also mechanical and chemical degradation (partial remobilization of Mn).

One example: genesis of the Mokta ore deposit.

(1) The Mn ore deposit of Mokta in the forest zone of the south of the Ivory Coast (Africa) is a small ore deposit, enriched through supergene concentration. The primary ores, containing garnet, braunite and rhodochrosite, have an Mn-content of 10–20%. They form a series of lenticles interstratified within Precambrian tilted sericite schists. These lenticles dot the convex tops of a chain of hills, a few kilometres from which there occur some relicts of plateaus capped with ferruginous crusts, that are remnants of a crust-covered peneplain system formed at the end of the Tertiary Period. The plateau level is about 20–40 m higher than the hill tops, where thick ferrallitic soils contain reworked debris of ferruginous crusts similar to the plateau crusts. At the foot of the ore-hills and of the nearby plateaus, a system of glacis developed under dry climates during the Quaternary Period. Partly occupied by ferruginous and slightly manganiferous crusts, the glacis have been incised during episodes of contrasting tropical climates, prior to the humid-tropical period which favoured the present-day rain forest.

(2) If the protore is of the Precambrian Period, the formation of the ore deposit (considered in its economic meaning) results from much more recent evolution stages. The sequence of the concentration processes may be as follows (Grandin, 1973): oxidized and enriched ores formed first in the interstratified lenticles under the Tertiary plane surface. The migration of Mn was mainly vertical. The top layers became poorer in Mn while accumulations formed in the deeper layers. A ferruginous crust capped the ore deposit which cannot be distinguished from the surrounding material neither by its relief, nor by the superficial indurated matter (Fig. 10A).

A first period of erosion transformed the surface into an elongated plateau. Then, a long evolution (under a humid-tropical climate), dissected this plateau into a series of low convex ridges where the original ferruginous crust became broken up into blocks and gravels. During this evolution, the elevation was lowered by about 30 m (Fig. 10B). A

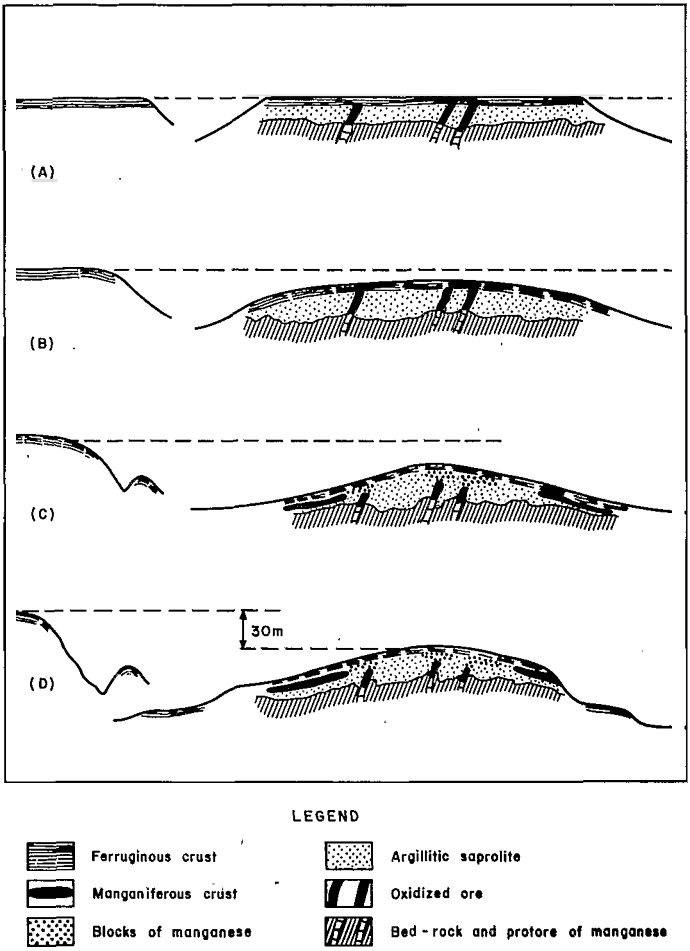

Fig. 10. The possible stages of the formation of the Mokta ore deposits (Ivory Coast). (A) Lateritized plateaus, resulting from Pre-Quaternary planation processes; oxidized protore in the weathering layers. (B) Destruction of ferruginous crust under humid climate; deepening of weathering and oxidation processes. (C) Formation of convex hills, under similar climate; formation of block accumulations and Mn-crusts (Lower and Middle Quaternary). (D) Erosion related with drier climatic phase; incision of some residual ore deposits and formation of piedmont glacis.

redistribution of the oxidized ores occurred concomittantly. The enriched lenticular ores, which existed between the ancient plateau and the newly-formed ridges, were dismantled giving: (a) some masses of blocks at the top of the ridges, which cap the oxidized lenticles and correspond to a relative accumulation of residual products; and (b) Mn-crusts under a barren cover, about 6–7 m thick, on the lower slopes of these ridges (Fig. 10C). These crusts result from the addition of Mn leached from the uppermost parts of the ore deposit, and particularly from the masses of blocks. The migration of Mn through solution was mainly oblique.

During the processes of redistribution, losses of Mn occur through chemical and mechanical erosion (losses restricted by the low relief). But these processes initiated a new type of ore, the crust-ore, which by its very high-grade (50–55%) contributes to increasing the average ore content of the oxidized deposits. At this stage, the balance proves positive. The supergene ores have reached their maximum development. Accumulations of blocks and Mn-crusts constitute about 90% of the minable ore and are located in a superficial stratum 15 m thick.

(3) The period of dissection, which was ended by the formation of the Upper Quaternary glacis, has not been long enough, nor of sufficient intensity, to destroy totally the low hills inherited from the previous evolution. The relative elevation of these hills has even been increased by the dissection, their slopes rendered steeper, and the rims of the Mn-crusts have been broken, creating locally steep cliffs on the slopes (Fig. 10D). In some places, the incisions may have attacked the interstratified mineralizations at the convex summits of the hills and may perhaps have removed some of them. At this stage of the geomorphological evolution, the impoverishment of the ore deposit started. But the resistance of the chain of hills and of the hard ores to the dissection, the low susceptibility of the compact blocks of Mn-oxides to leaching, the slow continuation of the protore oxidation and the dismantling in-situ of the lenticle tops prevented a too rapid degradation during the climatic fluctuations which were typical of the Quaternary.

Application to other ore deposits.

(1) In West Africa (Ivory Coast, Ghana, Haute-Volta), the end of the Tertiary Period appears as a period of particularly intense enrichment for most of the manganese deposits of any importance. The Pliocene peneplain-system and the Quaternary glacis landforms, which are encountered at Mokta, are known in all West Africa. It was during the time separating their respective formation that the major part of the supergene ores was formed. The ratio of superficial reworked or secondary ore to the enriched ore of the interstratified lenticles varies with the nature of the protore and the local morphoclimatic conditions. But most of the existing ore deposits are remnants of the reserves accumulated at the end of the Tertiary Period (Grandin, 1973).

For a given protore, the thickest supergene accumulations are formed where the weathering process has been fairly long and deep, and the subsequent erosion moderate. In the intensively eroded zones, the hills dating from the Pliocene peneplanation period are more deeply dissected, and most of the time contain only poor ore deposits or merely simple ore indications, which are residues of the ancient ore accumulations. In West Africa, the climatic zonality showed several fluctuations since the end of the Tertiary (extension of equatorial conditions toward the north or reversely progression of dry climates toward the south). Ore deposits presently under relatively dry climatic conditions, such as Tambao (Haute-Volta), resulted from the supergene concentration due to the humid phase of the uppermost Tertiary Period. But such ore deposits are rare, because the erosion conditions under subsequent dry climates do not favour their preservation.

There are still some other Mn ore deposits associated with peneplains either of more ancient origin, such as the remnants of the Eocene "African Surface" with its bauxite crust, or more recent in age, such as the Quaternary glacis. But if the ores are of good quality, the tonnage is very low, and, consequently, these occurrences fail to be of economic interest.

(2) Some ore deposits of other tropical regions of Africa, Brazil or the East Indies and especially those of Moanda (Gabon), Amapa and Lafaiete (Brazil), or Nagpur (Ghana) which are enriched by supergene processes, are also associated with ancient peneplains to which the dissection periods gave some relief. These ore deposits contain interstratified ore-levels, secondary formations related to Mn-crusts, pisolitic horizons and sometimes accumulations of blocks (Fermor, 1909; Van Door et al., 1949; Van Door et al., 1956; Putzer, 1968; Weber, 1973).

These ore deposits, like those of West Africa, benefitted from a major enrichment period, following the completion of vast peneplains. But for lack of convincing arguments, the problem of knowing if the enrichment of the large Mn-deposits over the whole tropical zones have been caused in the same uppermost Tertiary Period, has not been solved as yet.

Conclusion

(1) The relative mobility of Mn in a superficial environment places this element between the Fe and the metals of alkaline earths, and explains its possible accumulation: (a) with Fe in ferruginous crusts; and (b) with Ca and Mg in montmorillonite soils of fairly dry climate, where the bases may accumulate. These accumulations occur even on bed rock which is non-enriched in Mn, but they are not of economic interest.

(2) To get the high-grade ore concentrations required by industry, the Mn must accumulate alone, without being associated with Fe or Si. This involves three conditions: (a) a climate sufficiently hydrolysing to favour the release of Mn from primary minerals and particularly from silicates; (b) deep soils, both oxidizing and acid, able to fix the Fe and to permit a Mn-enrichment through vertical or lateral migration; and (c) a protore with a high Mn/Fe ratio and with a Mn content high enough to form oxidized ores resistant to leaching and to prevent the Mn from becoming entirely fixed by co-precipitation with Fe.

Thus, the formation of supergene ores is related to humid-tropical climates and ferrallitic weathering. However, a good enrichment does not imply only an intense weathering but also a relief low enough to reduce to the minimum the subsequent mechanical erosion and removal of the materials. On the other hand, supergene ores are obtained only from primary ores which have an average Mn-content about one hundred times higher than the Clark value. Before the carbonated protores of Nsuta (Ghana) and Moanda (Gabon) were discovered, some attempts were made to explain the formation of such ore deposits through a simple "lateritic" alteration of rocks with a 0.01–1% Mn-content (Varentsov, 1964; Thienhaus, 1967). In fact, the concentration factor of supergene processes due to tropical weathering rarely exceeds 5–6.

(3) Among these processes, three must be distinguished: (a) oxidation of the primary ore lenticles or strata, with leaching of the superficial layers and enrichment of the deep layers; (b) residual accumulations of oxidized ore blocks, during a progressive evolution of the topography, without abrupt mechanical erosion; and (c) absolute chemical accumulation, giving high ore contents in the deep horizons of soils, after oblique migration.

The enrichment processes, however, prove also to have a negative aspect. As a matter of fact, they are accompanied by: (a) a washing away of a part of the Mn in solution through the surface drainage network; (b) a reprecipitation of Mn with Fe, in the form of low-grade pisolites; (c) a dispersal of ore debris during dissection periods (these debris are particularly common among the spreading materials of glacis).

The supergene manganiferous ores, which are located near the surface, are easily destroyed by erosion. They are only transitory accumulations, and the continuation of the supergene processes leads inevitably to the dispersal of Mn and to its introduction into the cycle of sedimentation.

(4) Consequently, the exploration of such deposits must take into account the geomorphological criteria as much as the geological criteria. In the same manner that exploration is restricted to certain rocks, so must it also be to certain forms of relief, resulting from the evolution of ancient peneplains. In dry tropical or sahelian regions, only the biggest protores, forming hills with a solid structure of mineralized strata, resisted recent dissection. The main criteria of exploration are the nature and the size of the primary mineralizations. In humid-tropical regions, and especially in forest regions, the moderate dissection and the durable action of the supergene processes favour the enrichment of protores containing relatively small mineralized lenticles.

In extending exploration from one region to another, the main objective will vary; sometimes it will be the location of structures and rocks which seem the most propitious for a large primary accumulation, and sometimes the location of sites and landforms which are the most likely to have benefitted from an intense supergene enrichment.

When an ore deposit is discovered, a good knowledge of the regional geomorphology (evolution of the relief and genesis of the related weathering formations) is also of very great help to estimate the ore reserves before undertaking expensive systematic drillings. According to the geomorphologic evolution, one must look not only for the oxidized protores, but also for the accumulations of mineralized blocks which cap these protores and are concealed under superficial ferruginous laterites, as well as for the manganiferous crusts lying below thick layers of loose and barren soils.

SUPERGENE CONCENTRATION OF NICKEL

Generalities on the geochemistry of nickel

Abundance in the different rocks. The average concentration of Ni in igneous rocks is 80

TABLE IV

Nickel content in the lithosphere and in the hydrosphere

Endogene zone (a and b)	Ni (ppm)	Exogene zone (a and b)	Ni (ppm)	Supergene zone	Ni (ppm)
Granite	0.5– 2	sandstones	2– 8	laterites (c)	180
Gabbro-basalt	50 –100	shales	24–95	laterites on peridotites (d)	10,000
Peridotite	3,000	limestones	0	river waters from peridotite massifs (d)	0.06
				sea waters (a)	0.001–0.005

After: (a) Green, 1953; (b) Krauskopf, 1967; (c) Rambaud, 1969; (d) Trescases, 1973b.

ppm. This element is very irregularly distributed in the lithosphere and hydrosphere. As shown by Table IV, Ni is well represented only in ultrabasic rocks. The weathering processes concentrate this element, which becomes a major element in tropical soils derived from peridotites, for example.

Mineralogical forms. The Ni may occur in rocks as microcrystals of Ni-sulfides (pentlandite, millerite, etc.) which generally form inclusions in ferromagnesian silicates or ferrous sulfides (pyrrhotite). It can also be found in the form of alloys of native metals (awaruite; Fe, Ni_2). But the Ni is also camouflaged through substitution for ferrous Fe and Mg in silicates (particularly peridote) or oxide lattices (magnetite).

In the supergene residual formations (saprolites and soils), the Ni is more or less substituted for Mg occurring in nickeliferous silicates, namely the garnierites which are a mixture of serpentine (Ni, Mg) and hydrated talc (Ni, Mg), often interstratified with saponites or stevensites (Ni, Mg) (Brindley et al., 1972; Trescases, 1973b). Nickeliferous sepiolite and chlorite are also known. Ni may be fixed between the structural layers or even in the octahedral layer of ferriferous smectites (nontronite). Ni is also entrapped, probably as cryptocrystalline $Ni(OH)_2$ through adsorption, either in the cavities and cleavage planes of hypogene silicates before they become totally destroyed (orthopyroxenes, chlorites and particularly serpentine), or in secondary products (silico–ferric gels, opal and chalcedony, goethite, asbolane).

Chemical behaviour of Ni. Hypogene conditions favour the Fe^{2+}–Mg^{2+}–Ni^{2+}–CO^{2+} association resulting from their similarity in ionic radius. The ionization potentials of these elements are quite different and their association is partially destroyed under supergene conditions. The solubility of the elements is governed, under given temperature and pressure conditions, by the pH and Eh. In the weathering zones with sufficient drainage, the oxidation of Fe^{2+} is very easy, but the oxidation of Ni^{2+}–Ni^{3+} and Co^{2+}–Co^{3+} is not common since it requires high Eh (Garrels and Christ, 1965; Norton, 1973). Mg is only bivalent. The sequence of the successive hydroxide precipitations is: Fe^{3+} (pH 2–3), Fe^{2+} (pH 7), Ni^{2+}–Co^{2+} (pH 8–9), Mg^{2+} (pH 10–11). Thus, under normal conditions (pH 4–9), Ni and Co are a little more mobile than Fe, but appreciably less so than Mg. The standard values of free energies of formation (ΔG_f°) for ferric and Mg-silicates show that under normal temperature and for normal concentrations in natural environment, the silication of Fe^{3+} is easier than that of Mg (Tardy et al., 1974). Similarly, the silication of Ni seems easier than that of Co and of Mg.

Nickel concentration – importance of secondary concentrations

Different types of ore deposits. Two types of minable accumulations may be distinguished (Lombard, 1956; Boldt, 1967), according to their genesis, namely the hypogene type and the supergene type.

(1) The *hypogene ore deposits* are essentially sulphureted masses and are associated with basic rocks (norites); they nearly always formed conjointly with the Precambrian orogens (Routhier, 1963). The ore deposit of Sudbury (Canada) is the biggest representative deposit of this type. Some others occur also in South Africa (Bushveld), Rhodesia (Great Dyke), Australia (Kambalta), the U.S.S.R. (Petsamo, Norilsk), Finland (Kotalahti), etc. The hypogene mechanisms (late crystallization of the sulphureted phase) locally concentrate the Ni disseminated in the noritic magma, by 300–600 times, the Ni-content increasing from 50 to 30,000 ppm. The mineralization often takes place at the contact of norites with a more acid enclosing formation. Ni occurs in association with Cu, Pt and Pd. Some ore deposits, containing sulphides, arsenides, antimonides and related to granitic pluton, are also known; they contain associations of Ni–Co and Ag, Bi, U (Erzgebirge group). The hypogene ores fall beyond the subject matter of the present chapter.

(2) The *supergene ore deposits* are associated with the thick lateritic blankets covering peridotites in intertropical areas. The most important ore deposit is found in New Caledonia. There are some others in South Africa, Australia (Queensland), Borneo, Brazil, Celebes, Guinea, the Philippines, Porto Rico and Venezuela. Ancient nickeliferous laterites also occur in Western U.S.A. (California, Oregon), in the U.S.S.R. (Urals, Ukraine), Greece and Yugoslavia. The weathering processes form economic concentrations of Ni in residual alterites, because, first, the Clarke value of the parent rock is high (2000–3000 ppm of Ni) and, second, the solubility of Si and Mg is high in tropical climates while Fe and Ni are only slightly mobile. Since the total Si and Mg represent 80% of peridotites, the concentration ratio of the Ni due to supergene processes ranges generally from 5 to 10.

Descriptions of alteration deposits.

(1) Deposits of New Caledonia: these deposits (Lacroix, 1942; De Chetelat, 1947; Ammou Chokroum, 1972; Trescases, 1973b) are representative of weathering blanket

deposits. The area covered by peridotites is about 5000 km^2, with almost 4000 km^2 extending continuously in the southern part of the island. These rocks which are supposed to be of the Oligocene Period (Routhier, 1953; Guillon, 1973) are mainly harzburgites (peridote, orthopyroxene and accessorily chromiferous spinel) partially serpentinized during a phase of retromorphism.

The weathering of the peridotites has been going on since at least the Pliocene Period, under a humid and warm climate. The low percentage of slightly mobile elements (Fe, Ni, Al, see Table V) in the parent rock explains the quasi-solubility of peridotites. This property favours the development of a karstic relief (Wirthmann, 1970; Trescases, 1973b) including dolines and poljes, which look like marshy depressions. A tectonic uplift has been affecting New Caledonia since the Pliocene (Dubois et al., 1973) and the remnants of several "erosion surfaces" which are levelled and covered by a thick alterite blanket lie at different levels on the landscape. These flat areas are separated by steep slopes bearing thin soils. It is generally the lowest surface that offers the largest number of marshy poljes.

The weathering profiles of low-gradient slope surfaces (Fig. 11) are often 20–30 m thick. Below the average level of the weathering front, and sometimes in more than 10 m thickness, diaclases, faults and crushed zones are occupied by some secondary quartz and chalcedony, with garnierities at some places. Pseudo-lodes and even real quartzo–nickeliferous box-works, which constitute the richest ores (up to 35% NiO), are formed. At the

TABLE V

Mean physical and chemical characteristics of weathering formations on peridotite in New Caledonia[1,2]

	Plateau soil profiles				Glacis soil profiles		
	rock	coarse saprolite	fine saprolite	gravelly horizon	coarse saprolite	fine saprolite	gravelly horizon
Thickness (m)	–	0.2–6	10–40	2–10	0.1–2	5–20	1–5
Mean density	2.8	1.6	0.9	–	1.6	0.9	–
Fire losses	10.5	13.0	13.7	13.5	13	13	13
SiO_2 (%)	38	33	1.2	0.5	33	3.5	2
FeO (%)	5	2	1	0.3	2	1	0.3
Fe_2O_3 (%)	3.5	17	72	74	18	71	73
Al_2O_3 (%)	0.4	2	4.5	5	1	4	6
CaO (%)	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
MgO (%)	41	29	0.9	0.5	29	1	0.7
Cr_2O_3 (%)	0.4	0.8	4.0	5.5	0.8	3.8	3.8
MnO_2 (%)	0.14	0.29	1.0	0.5	0.5	1.0	0.4
NiO (%)	0.40	2.5	1.0	0.4	2.5	1.0	0.3
CoO (%)	0.02	0.08	0.2	0.07	–	–	–

[1] After Trescases, 1973b.

[2] Localization of the weathering profiles: Kouaoua (plateau profiles) and Prony (glacis profiles).

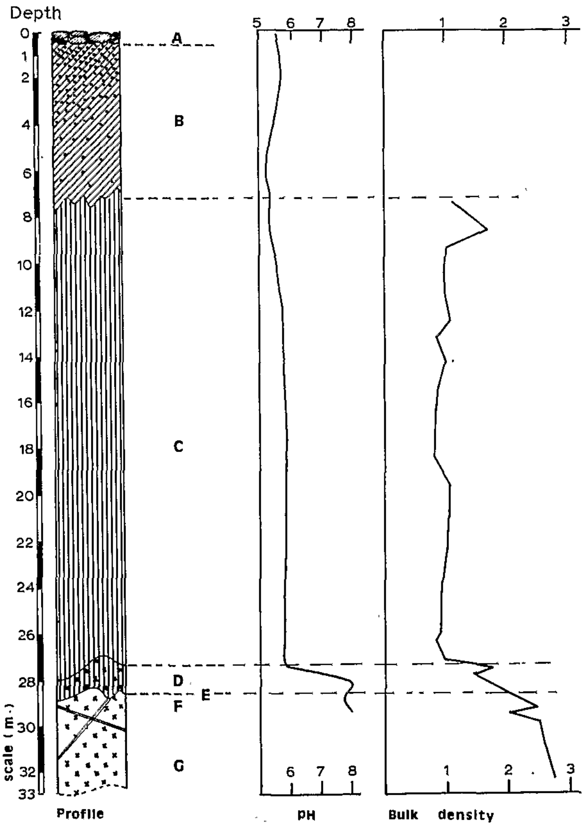

Fig. 11. Weathering profile on ultramafic rock (Kouaoua Plateau, New Caledonia), after Trescases, 1973b. *A* = ferruginous crust; *B* = gravelly ferruginous horizon; *C* = fine saprolite; *D* = coarse saprolite; *E* = weathering front; *F* = quartz and garnierite in diaclases; *G* = parent rock.

bottom of the weathered blanket the rock is transformed into a plastic mass where numerous rock fragments, ranging in size from some centimeters to some decimeters, still persist and the initial structure is preserved (horizon of coarse saprolite facies). The contact with the fresh rock is extremely irregular (lapiez aspect). In this horizon, some centimeters to some meters thick, the retromorphic serpentine is inherited, and entraps Ni through a physical adsorption; olivine alters into silico–ferric gels (zone of well-drained plateaus) or into nontronite (piedmont zone) and the orthopyroxene is replaced by talc and secondary quartz. The horizon of the coarse saprolite constitutes the *silicated Ni-ore* mined at present.

Over this horizon, a very thick formation occurs (from some meters to some tens of meters), in which the serpentinous framework of the bedrock is replaced by goethite and where the granulometric fractions $<50\ \mu$ represent 80–90% (fine saprolite facies). Si and Mg, which are only partially leached from the coarse saprolite horizon, have almost completely disappeared in the fine saprolite. This increase in intensity of leaching of soluble elements is accompanied by moderate settling. Some silicates neo-formed in the subjacent horizon (quartz, talc) persist in it, and accumulations of asbolane (cryptocrystalline hydroxides of Mn, Co, Ni) may be observed. The horizon of fine saprolite constitutes a lateritic *oxidized Ni-ore,* which is not exploited at present because of its too-low metal content. The profiles are capped by a reworked gravelly ferruginous horizon and sometimes by a ferruginous crust. These last two horizons are considered unproductive. The weathering of chromiferous spinel is very slow, and proceeds along the whole profiles. The average characteristics of these horizons are given in Table V, for a plateau profile and a piedmont profile. The quantitative mineralogical evolution of 100 cm^3 of harzburgite (Kouaoua profile) is given in Fig. 12.

On steep slopes, the profile is not thick and resembles the coarse saprolite horizon occurring at the bottom of the profiles developed in low-gradient zones.

The silicifications and the pseudo-veins of garnierite are much more frequent in sectors of plateaus than in low zones. Also, the Ni-content in the coarse saprolites varies considerably according to the location of the plateau profiles: it is high (up to 4 or 5% NiO) on

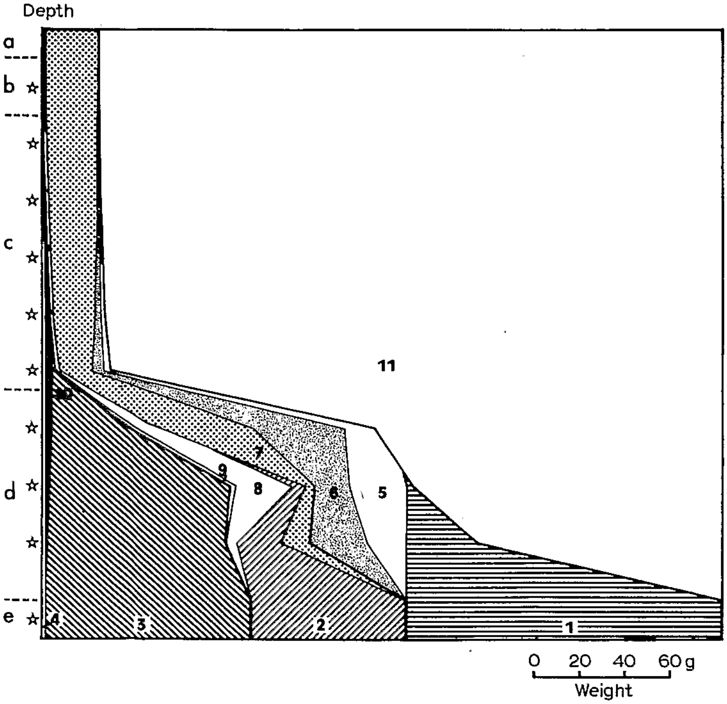

Fig. 12. Quantitative mineralogical evolution of 100 cm^3 (about 300 g) of harzburgite (Kouaoua Plateau, New Caledonia), after Trescases 1973b. *Horizons: a* = ferruginous crust; *b* = gravelly ferruginous horizon; *c* = fine saprolite; *d* = coarse saprolite; *e* = fresh rock. The stars show the emplacements of the samples. The scale is disturbed in depth. *Minerals: 1* = olivine; *2* = orthopyroxene (enstatite); *3* = serpentine; *4* = chromiferous spinel; *5* = silicic gel; *6* = ferric gel; *7* = goethite; *8* = talc; *9* = quartz; *10* = asbolane; *11* = soluble phase (Mg^{2+}, H_4SiO_4).

the plateau edges, in the breccia zones occurring along the large faults or in the cavities of the rock substratum and low (2–2.5% NiO) in the high parts of the plateaus. In low areas, in contrast, the Ni-content of the coarse saprolite horizons does not differ much from the mean value given in Table V.

(2) Comparison with other weathering ore deposits. The extent of the New Caledonian peridotites is quite exceptional and the other supergene ore deposits known in the world are much smaller. They are generally associated with uplands (remnants of "peneplains") and they can be compared to the New Caledonian ore deposits on plateaus.

The ore deposits of the Western U.S.A., especially that of Nickel Mountain, Oregon (Hotz, 1964), closely resemble those of New Caledonia. Like them, they contain a silicate horizon of coarse saprolite where the Ni is concentrated and quartzo–nickeliferous pseudo-veins embedded in the bedrock. In South Africa (De Waal, 1971), Australia (Zeissink, 1969), and Brazil (Farina, 1969), the parent rock is strongly serpentinized. The silicate horizon of coarse saprolite is thick, but the garnierites are not well represented. All these deposits occur in fairly dry climatic zones. They are called "silicate ore deposits".

In other deposits, in contrast, the silicate horizon of coarse saprolite at the bottom of the profiles is very thin or even absent. This is the case in Cuba (De Vletter, 1955), Guinea (Bonifas, 1959; Percival, 1965), the Philippines (Santos Ynigo, 1964), and Venezuela (Jurkovic, 1963). All these ore deposits occur in very humid regions. The weathering profiles show only ferruginous horizons, similar to those of fine saprolites and to superficial gravelly layers reported in New Caledonian deposits. Sometimes the Ni-contents of 1–2% Ni remain constant in almost the entire profile, but it is more common to find the Ni concentrated in the bottom part, where the content reaches or exceeds 2% Ni. All these ore deposits are named "oxidized ore deposits".

(3) Sedimentary ore deposits. In all supergene ore deposits, formed through weathering processes, the horizons with the highest Ni-content are those altered in-situ where the rock structure is preserved or little modified. In the superficial, pedologically more or less reworked levels, the Ni-content is not really higher than that of the parent rock. Thus, the reworking processes do not seem to favour the concentration of Ni.

The problem of sedimentary processes is still to be discussed. A deposit of oolitic Fe, containing 0.5–3% Ni, occurs at Lokris in Greece; this formation, which is probably of marine origin, lies on Triassic limestones and is covered by Cretaceous limestones (Petraschek, 1953). Nickeliferous laterites developed in neighbouring ultrabasic rocks are likely to have supplied the sedimentation. The Ni-concentration does not seem to have been favoured by this translocation, since the metal contents are generally lower than in weathering ore deposits.

In New Caledonia (Trescases, 1973b), mechanical erosion affects the weathering profiles of the different surfaces, and results in the transportation of these materials toward the low areas, e.g., "intermontane", marshy, depressions (poljes) or littoral mangroves. The Fe, which is transported in the goethite form, combines with the Si dissolved in aquifers to give nontronite. Lenticular levels, very rich in organic matter, are intercalated between the neoformed nontronite. The nontronite deposits contain 2–3% Ni and up to

5% in levels rich in organic matter. In these environments, Ni is essentially supplied in a detrital form, with the goethite. During the transformation process of hydroxide into nontronite, Ni becomes incorporated either into the lattice or between the sheets of the silicate. In addition, the nontronite can fix the small quantities of Ni mobilized by the complexing action of the organic matter. Thus, there is no possibility of concentration during the sedimentation processes except locally through organic matter and the Ni seems generally stabilized in the sedimentary environment. Actually, the silication occurring during the formation of these deposits induces an evolution which is opposed to that produced by weathering and the Ni-content turns out to be lowered.

Conditions of formation of weathering ore deposits

Mineralogical evolution. The secondary minerals derived from the three essential minerals contained in peridotites (namely, peridote, orthopyroxene and serpentine) during weathering in tropical zones, are schematized as follows:

Rock	Coarse saprolite	Fine saprolite
orthopyroxene →	talc + quartz + goethite →	goethite
peridote →	opal + ferric gel (humic climate, rapid drainage) nontronite (dry climate, slow drainage)	goethite
serpentine →	inherited serpentine →	goethite

Moreover, the drier the climate, the slower will be the weathering of the different minerals. Desilication even may fail to reach completion at the surface. On the other hand, on steep slopes, erosion inhibits the completion of the chemical weathering.

Geochemical separations. The weathering of peridotite is characterized by the high ratio of products removed in solution, particularly under humid climates. The Mg leached out is almost totally transported in solution, except for the small amounts entering into talc and garnierite neoformations. Si is also leached, but not so quickly and its removal is not total. The Fe, occurring in a ferrous state in the rock, becomes oxidized into insoluble Fe^{3+}, as soon as the chemical weathering starts. Therefore, the Fe-accumulations in profiles are relative ones. The Si and Fe separation is effective in well-drained zones and under very humid climate, but becomes very poor in low zones or when the climate turns drier.

In addition to Ni, several accessory elements are present in the parent rock: Al, possibly in clinopyroxenes and particularly in chromiferous spinels, which is associated with Mn and Va, and Co which is associated with Ni. All these accessory elements exhibit a residual behaviour during weathering.

The Al, and much more rarely the Cr, contribute to the formation of nontronite, when this process takes place within the profiles. On Al- and Cr-rich parent rocks, minerals of the kaolinite group generally form after the nontronite phase: such minerals may also be chromiferous (Maksimovič and Crnkovic, 1968). If the desilication goes on (humid climates, well-drained high lands) these elements become adsorbed to the goethite. As for Fe, the maximal concentration of Cr and Al takes place in the upper part of the profiles where the contents may exceed 5% for Cr_2O_3 and also 5% for Al_2O_3.

Mn, oxidized into Mn^{3+} and then into Mn^{4+}, and Co partly oxidized into Co^{3+}, are poorly soluble and never undergo silication. They segregate into asbolane concretions. However, these oxides are destroyed near the topographic surface: the most important accumulation (residual) of Mn and Co generally takes place in the middle part of profiles. The contents may be up to 1% CoO and 3% MnO_2.

The Ni is retained, either by the silicates (inherited or neoformed) in the horizon of coarse saprolite (silicate ore deposits), or by Fe- or Mn-hydroxides in the horizon of fine saprolite (oxidized ore deposits), or even by both silicates and hydroxides (New Caledonia, Western U.S.A.).

Thus, the distribution of chemical elements in profiles and landscapes is related to the stability of their host minerals and their own solubility. The Fe–Cr–Al separation is always negligible and that of Fe–Ni generally remains incomplete. Despite the high Fe-content (80% Fe_2O_3), the products resulting from peridotite weathering do not generally constitute a good Fe-ore. The ore deposit of Conakry (Guinea) is an exception: its parent rock is poor in Ni and Cr and the absence of a coarse saprolite horizon at the bottom has probably restricted the retention of Ni within the profile.

Mechanisms of nickeliferous accumulation. The presence of garnieritic pseudo-veins partly embedded in the bedrock once favoured some hydrothermal hypotheses (New Caledonia, Western U.S.A.). But for more than 30 years now, all authors have been in agreement on the point that the genesis of ore deposits associated with the lateritic blankets of peridotites is only governed by the weathering processes.

Most authors who have proposed an explanatory scheme for the concentration mechanism have emphasized the low solubility feature of Ni. Through elimination of Si and Mg, the Ni and Fe become relatively concentrated in the goethitic levels. After this first concentration phase, the Ni is thought to undergo a slow leaching downwards through the profiles, leaching being either vertical (De Vletter, 1955; Schellmann, 1971) or lateral (De Chetelat, 1947; Avias, 1969). This metal would then reprecipitate with Si and Mg, near the bedrock, where the pH is higher. The ore deposits which have a nickeliferous silicate layer at the bottom of the profile would, therefore, be the oldest, and the older they are, the richer they should be (Hotz, 1964).

Nevertheless, Trescases (1973a) notes that in New Caledonia, the Ni-content remains almost constant through the whole thickness of the fine saprolite ferruginous formations.

The leaching of this metal occurs only at the top of the profiles, together with the superficial pedological effects. In addition, the presence of a silicate horizon downward and its Ni-content depend mainly on the morphoclimatic environment. Consequently, Trescases (1973b) put forward another explanation, involving three mechanisms:

(1) If a silicate horizon exists at the bottom of the profile, the first type of trap for the Ni released from peridotes, is constituted by the neoformed or inherited and relatively little weathered silicates. In the first stage, the accumulation is relative. As the weathering front penetrates deeper, these minerals generally become weathered. The released Ni is then subjected to physico–chemical conditions quite different from those which provoked its immobilization; Mg has been leached, the pH becomes more acid and some organic acids may be present. Thus, the Ni tends to migrate down toward the bottom of the profile where it meets again the initial immobilization conditions (primary or secondary silicates still non-weathered). If the weathering goes on long enough, the quantity of Ni accumulated at the bottom of the profile becomes quite considerable. This accumulation follows the descending motion of the weathering front: it is a "compacted" relative accumulation.

(2) The total amount of Ni released by the weathering of the silicates does not migrate downward because one fraction (about 1/3 in New Caledonia) is entrapped in more or less crystallized asbolane and goethite hydroxides. This trap is very effective and immobilizes the Ni in the major part of the oxidized soil profile; only the near-surface horizon becomes impoverished in Ni. It is a true relative accumulation. When a silicate horizon is missing at the base, this mechanism occurs as soon as the weathering starts (oxidized ore deposits).

(3) The third type of accumulation is subsequent to the first two. The weathering balances established through isovolumetric or isochromium considerations with many samples of various soil profiles of New Caledonia (Trescases, 1973b) indicate that some zones of the lateritic blanket have lost Ni, while some others became enriched. The enriched zones are localized wherever groundwater circulations concentrate, e.g., in tectonic zones, at low sites, and along the edges of plateaus. The accumulation is absolute and implies lateral migrations; it can form in inherited silicates (serpentine, chlorite), in the products resulting from the weathering of peridotes (silico–ferric gels, nontronite), in the nontronite neoformed in swamps, and even in true nickeliferous silicates (garnierite) filling the diaclases of bedrock.

The result of these three processes of accumulation is a complex distribution of Ni between the minerals. Table VI and Table VII give the Ni-distribution of a plateau profile and a piedmont profile, in New Caledonia.

Factors controlling the mineralization.

(1) Parent rock. The weathering processes are likely to develop economic concentrations of Ni only on rocks with very high Ni-contents, i.e., on ultrabasic rocks. Among these, the Ni-richest rocks should normally be the most favourable for the formation of

TABLE VI

Nickel distribution in a plateau profile of New Caledonia (Kouaoua)[1]

Horizons	Olivine	Enstatite	Serpentine	Si–Fe gels	Asbolane	Goethite	Σ	(a)
Gravelly ferruginous horizon	0	0	0	0	0.9	95	–	A
	–	–	–	–	3	0.5	–	B
	–	–	–	–	0.03	0.47	0.50	C
	–	–	–	–	6	94	100	D
Fine saprolite (top)	0	0	0	0	1.2	94	–	A
	–	–	–	–	6	0.8	–	B
	–	–	–	–	0.07	0.73	0.80	C
	–	–	–	–	9	91	100	D
Fine saprolite (bottom)	0	0	0	14.3	5.2	71	–	A
	–	–	–	0.7	9.2	0.8	–	B
	–	–	–	0.09	0.48	0.57	1.14	C
	–	–	–	8	42	50	100	D
Coarse saprolite (top)	0	0	24	36	1.6	27	–	A
	–	–	2.1	0.6	8	0.7	–	B
	–	–	0.51	0.22	0.13	0.19	1.05	C
	–	–	49	21	12	18	100	D
Coarse saprolite (middle)	0	0	49	26	0.6	2	–	A
	–	–	1.5	0.7	8	0.6	–	B
	–	–	0.76	0.18	0.05	0.01	1.0	C
	–	–	76	18	5	1	100	D
Coarse saprolite (bottom)	16	10	40	24	0.4	6.5	–	A
	0.50	0.10	1.9	0.7	8	0.7	–	B
	0.08	0.01	0.77	0.17	0.03	0.05	1.11	C
	7	1	69	15	3	5	100	D
Rock	47	22	29	0	0	0	–	A
	0.50	0.10	0.40	–	–	–	–	B
	0.25	0.02	0.13	–	–	–	0.04	C
	63	5	32	–	–	–	100	D

[1] After Trescases, 1973b.

(a) Results in: A = g mineral for 100 g of sample; B = NiO % in each mineral; C = NiO % of the sample; D = Ni % of the total Ni of the sample.

supergene ore deposits, but such a relationship is only valid for strictly residual and oxidized-type ore deposits.

The role of the parent-rock mineralogy is important, and more especially its degree of hypogene serpentinization. As a matter of fact, the complete weathering of the serpentinites and the total release of the Ni they contain are only possible under the most

TABLE VII

Nickel distribution in a piedmont profile of New Caledonia (Prony)[1]

Horizons	Olivine	Serpentine	Enstatite	Nontronite	Asbolane	Goethite	Σ	(a)
Fine saprolite	0	0	0	0	2	94	–	A
	–	–	–	–	5	1.1	–	B
	–	–	–	–	0.10	1.03	1.13	C
	–	–	–	–	9	91	100	D
Coarse saprolite (bottom)	20	48	9	15	2.5	3	–	A
	0.40	4.0	0.10	6.8	12	0.7	–	B
	0.08	1.92	0.01	1.02	0.27	0.02	3.32	C
	2.4	58	0.3	30.7	8	0.6	100	D
Rock	37	58	4.4	0	0	0	–	A
	0.40	0.35	0.10	–	–	–	–	B
	0.15	0.18	–	–	–	–	0.33	C
	45	55	–	–	–	–	100	D

[1] After Trescases (1973b).

(a) Results in: A = g mineral for 100 g of sample; B = NiO % in each mineral; C = NiO % of the sample; D = Ni % of the total Ni of the sample.

humid-tropical climates. The probability of nickeliferous supergene ore deposits occurring is, therefore, lower for serpentinites than for peridotites which are little or only moderately serpentinized. In contrast, a strongly serpentinized zone in a peridotite massif constitutes an impervious obstacle inhibiting water circulations and favouring a nickeliferous accumulation just above it. Finally, the most favourable conditions correspond to moderately serpentinized environments where the hydrolytic process is relatively slow, and where the presence of a silicate horizon at the bottom of the profiles constitute an effective Ni-trap.

The structural features of peridotites take a fundamental part in the genesis of nickeliferous ore deposits. Weathering proceeds more rapidly in fractured zones. In addition, the tectonic trends constitute preferential drainage-axes and are the seat of the most important absolute accumulations, such as garnierites. Finally, tectonism controls the formation of relief and so indirectly governs the distribution of the Ni (see below).

(2) Climate. Disparities in the behaviour of minerals become more strongly marked when the climate becomes drier and less hydrolyzing. They tend to disappear under equatorial climates. Thus, under the most aggressive climates, all the primary silicates are weathered almost at the same time, and the fringe of fresh serpentine occurring at the bottom of the profiles is very reduced, while the removal of Si is too rapid to permit the neoformation of silicates. The Ni-accumulation can only be residual and oxidized, and the ore deposits are only of low content, inferior to 2% (Guinea, Cuba, etc.).

In a subtropical climate (New Caledonia and California, for example), in contrast, the silicate fringe above the weathering front retains a large part of released – or in transit – Ni and favours its precipitation, and consequently the ore deposits prove to be richer. If the climate is temperate or too dry, the weathering becomes very slow and the amount of Ni leached is too small to permit the development of rich supergene concentrations.

(3) Time. The effect of the time factor is a function of the climate. Under very humid climates, the weathering is rapid and the nickeliferous laterites are thick, except when the landscape is dissected into steep slopes through intense tectonic uplift, as in New Guinea (Davies, 1969). Owing to the intensity of the leaching, however, the Ni-contents tend to become poorer with time, and so the most important supergene concentrations are not related to the oldest alterites.

Under drier climates, the mobility of Ni is lowered and the weathering is less rapid: the formation of large concentrations implies long durations of time. The lack of dense vegetation favours an intense erosion which is likely to destroy the potential ore deposits before they have the opportunity to become of economic value.

(4) Landform and tectonic activity. The accumulation of Ni occurs differently according to the morphological conditions; this is particularly the case in New Caledonia where a very differentiated landform developed owing to the large extent of the peridotite massifs and to the effects of the tectonic activity (Routhier, 1963; Avias, 1969; Trescases, 1973b). This landform is related to an ancient peneplain, with features of the karstic type, which has been uplifted and faulted during the Pliocene and Quaternary. It exhibits the following distinctive units, from the top which is formed by remnants of the peneplain, downwards: steep slopes, glacis and marshy depressions.

On the steep slopes, the mechanical erosion removes the alterites before the Ni is released. The thicknesses of profiles, as well as the Ni-contents, remain very small. However, Ni translocated from the plateaus may contribute to the enrichment of the upper parts of these slopes. In glacis zones the ore deposits are large and the Ni-content is medium (2–3%). In the marshy depressions the Ni-content falls to 1–2% except in peat horizons where it can reach 5%. In faulted zones and along the edges of plateaus (old glacis) incised by erosion, the groundwater circulations are more intense, the oblique leaching of nickeliferous alterites already formed is more effective, and high-grade ores may be formed.

The formation of important supergene Ni-accumulations seems favoured by a tectonic activity, which must be neither too low nor too intense; when the uplift is not intense enough, the leaching and succeeding remobilization of Ni are reduced and the content remains low; when the tectonic activity is too intense, the relief undergoes a strong dissection and the nickeliferous concentrations are rapidly eroded. The most favourable conditions correspond to a moderate tectonic activity, permitting the progressive formation of a peneplain, as in New Caledonia where the uplift seems to be due to the sliding of the Australo–Tasmanian plate under the oceanic plate (Dubois et al., 1973). Thus, the peridotite massifs related to an orogenic arc are normally more propitious to the formation of nickeliferous ore deposits than the peridotites embedded in old basements.

Conclusion

In spite of its rather low Clarke value, nickel may reach important economic concentrations:

(1) Through hypogene mechanisms. Due to its chalcophile property, this element concentrates in the sulphide phase of basic magmas. The local concentration ratios are extremely high, but the ores are restricted to the edges of massifs. These deposits have not been discussed in this contribution.

(2) Through supergene mechanisms. Ni then behaves as a lithophile element. The concentration ratio remains small, and the formation of ore deposits by this process implies a previous hypogene preconcentration; only the rocks derived from the upper mantle (peridotites), which are much richer in nickel than the other igneous rocks, are likely to form supergene ore deposits. On the other hand, such deposits may be very large, since they extend over the whole surface of massifs.

The world production of Ni was about 600,000 metric tons (m.t.) of metal in 1970. About 2/3 of this production came from hypogene ore deposits. The supergene ore deposits of New Caledonia supplied 100,000 m.t. and those of Cuba 35,000 m.t.

The supergene ore deposits seem to be promising reserves for the future. The ore resources in New Caledonia alone would ensure a supply for hundreds or even thousands of years, provided that a metallurgical process appropriate to ferruginous levels ("poor" lateritic ore) could sufficiently reduce the cost price of the metal.

BEHAVIOUR OF CHEMICAL ELEMENTS IN SUPERGENE CONDITIONS

In the previous sections, the geochemical differentiations corresponding to the present-day soil profiles (major elements) and to some residual ore deposits (Al, Fe, Mn and Ni) have been described. The formation of these deposits, which are considered strictly residual, actually implies a rather long and complex history, including pedogenesis, reworking, erosion and eventually continental sedimentation processes.

Consequently, the metallogenic role of the pedogenetic and chemical weathering processes should not be studied without referring to the other supergene (s.l.) processes. In this review, we attempt now to approach the general problem of the behaviour of chemical elements in supergene conditions, during the surface evolution of the landscapes, with special emphasis on the behaviour of trace elements. The knowledge of the supergene mobility of these elements is particularly useful from a theoretical and practical point of view: i.e., understanding of the genesis of supergene ore deposits and determination of the haloes of dispersion of the elements.

The plan will be as follows:

(1) Study of the distribution of chemical elements in minerals and rocks. This feature conditions their geological distribution and their susceptibility to be released into the weathering products and soils.

(2) Empirical determination of element behaviour by field investigations or laboratory tests.

(3) Theoretical study of the successive mechanisms controlling the element mobility: vulnerability of rock- and soil-minerals to chemical weathering, solubility of elements in aqueous solution, ability of the elements to enter into secondary-mineral composition, adsorption of elements on clay and humus surfaces, and fixation by plants and living organisms.

Distribution of elements in minerals

The localization of trace elements in rocks may vary greatly (Goldschmidt, 1954; Goni, 1966; Pédro and Delmas, 1970):

(1) They are often incorporated in the network of the essential minerals, especially silicates; they replace major elements presenting either a similar or different charge, provided that the radii of the ions are not appreciably different. Such elements are termed *camouflaged.* In feldspars, for example, Rb^+, Cs^+, Ba^{2+}, Sr^{2+} and Pb^{2+} may replace K^+, while in ferromagnesian silicates Mn^{2+}, Co^{2+}, Zn^{2+}, Li^+, Cr^{3+} and V^{3+} may replace Fe^{2+}, Fe^{3+}, Mg^{2+}, or Al^{3+}.

(2) They may also be located outside the structures of the essential minerals, and enter into the composition of accessory minerals. Such elements are termed *autonomous.* Thus, S, Cu and chalcophile elements are found in sulphide minerals, B is found in tourmalines, Zr in zircons, Cr in chromites, rare earths in apatites and monazites. These accessory minerals may be well established individually in rocks between the essential minerals, but they also may form inclusions inside them.

(3) The trace elements may be linked to the network surface and retained in an adsorbed form, on the intercrystalline surfaces, inside the physical discontinuities of the crystals or inside the fissures. Such elements are said to be *fissural:* Ni, Co and Mn, for example, may concentrate inside the microfissures in antigorite and Cu, Cr, W and V inside the micro-faults in biotite (Goni, 1966).

This qualitative distribution of elements conditions their behaviour during the chemical weathering processes; the release rate of camouflaged elements depends on the degree of destruction of the containing minerals as opposed to fissural elements which are generally very rapidly released.

From a quantitative viewpoint, some sources of data give the average contents of trace elements in the earth's crust (Ahrens, 1968), but the true contents depend greatly on the nature and the mineralogical composition of the rocks. For example, the sulphur and the sulphur-like elements are particularly concentrated in basic rocks, while Zr, B and rare earths are mainly found in acid crystalline rocks. Concerning the camouflaged elements,

TABLE VIII

Chemical composition of essential minerals[1]

Mineral	X (%)	0.X (%)	0.0X (%)	0.00X (%)	0.000X (%)
Plagioclase	K	Sr	Ba, Rb, Ti, Mn	P, Ga, V, Zn, Ni	Pb, Cu, Li, Cr, Co, B
K-feldspar	Na	Ca, Ba, Sr	Rb, Ti	P, Pb, Li, Ga, Mn	B, Zn, V, Cr, Ni, Co
Quartz				Al, Ti, Fe, Mg, Ca	Na, Ga, Li, Ni, B, Zn, Ge, Mn
Amphibole		Ti, F, K, Mn, Cl, Rb	Zn, Cr, V, Sr, Ni	Ba, Cu, P, Co, Ga, Pb	Li, B
Pyroxene	Al	Ti, Na, Mn, K	Cr, V, Ni, Cl, Sr	P, Cu, Co, Zn, Li, Rb	Ba, Pb, Ga, B
Biotite	Ti, F	Ca, Na, Ba, Mn, Rb	Cl, Zn, V, Cr, Li, Ni	Cu, Sr, Co, P, Pb, Ga	B
Olivine		Ni, Mn	Ca, Al, Cr, Ti, P, Co	Zn, V, Cu, Sc	Rb, B, Ge, Sr, As, Ga, Pb

[1] After Wedepohl (1967).

Table VIII shows that feldspars are enriched in Na, Ca, K, Sr, Ba, Rb, Ga, and Pb, while the amphiboles, pyroxenes and biotites are enriched in Ti, Mn, Fe, Mg, Cr, V, Ni, Cu, Co and Zn. Olivine prefers the concentration of Fe, Mg, Ni, Mn, Cr and Co.

Empirical determination of supergene behaviour of elements

Field investigations. The concept of element mobility during weathering processes was introduced by Smyth (1913) and then by Polynov (1937). These authors proposed a mobility classification, based upon a comparison between the element contents of river waters and of igneous rocks. The classification obtained by Polynov is shown in Table IX.

This concept has been the subject of many studies (Anderson and Hawkes, 1958; Miller, 1961; Udodov and Parilov, 1961; Feth et al., 1964; Tardy, 1969; Cernajev, A.M. and Cernajev, L.E., 1970; and Trescases, 1973b). Except for a few variants, the relative mobility sequences obtained by these authors generally agree with the Polynov sequence.

There is another method, based on the comparison between the element contents in weathering products and in fresh rocks. Results are also very numerous and deal with incipient weathering processes (Dennen and Anderson, 1962; Isnard and De la Roche, 1966; De la Roche et al., 1966) or with well-differentiated alterites (saprolites) and soils under temperate-climate conditions (Butler, 1953, 1954; Dejou, 1959, 1967; Dejou et al., 1972; Harris and Adams, 1966; Lelong and Souchier, 1970) and humid-tropical conditions (Harrison, 1933; Leneuf, 1959, Delvigne, 1965 and Lelong, 1969) or with alterites

TABLE IX

Relative mobility of common elements during weathering processes[1]

Group	Element	Relative mobility
Sesquioxides	Al_2O_3	0.02
	Fe_2O_3	0.04
Silica	SiO_2	0.20
Basic cations	K_2O	1.25
	MgO	1.30
	Na_2O	1.40
	CaO	3.00
Anions	CO_3	57
	Cl	100

[1] After Polynov (1937).

related to different climates (McLaughlin, 1957; Tardy, 1969). Again, the results are similar. The sequence commonly found for incipient weathering and temperate climate weathering is: Ca > Na > Mg > K > Si > Al and Fe; in tropical regions the release rates are appreciably increased, and it is not always possible to classify the most mobile elements such as Ca, Na and Mg.

Investigations giving a classification of the mobilities of trace elements are less numerous, however. Two examples only will be presented here. The first example groups data which have been recently obtained by Tardy (1969) and Trescases (1973b), with a hydrogeochemical method for sharply defined rocks and climates (Fig. 13). The reference elements used for granite and ultra-basic rocks are Na (base 1,000) and Mg (base 100) respectively. Ba and Sr, as well as Na and Ca, obviously appear as the most highly leached elements, whereas Ti, as well as Al and Fe, are the most retained. The other elements range generally in intermediate positions.

The second example is a more general scheme of the migrational ability of elements from siliceous rocks under temperate climate, given in Perel'man (1967), after Polynov (1937), (Table X). The coefficient Kx of migrational ability is:

$$Kx = \frac{mx\ 100}{a\ nx}$$

where mx is the x element's content in water (in mg/l), nx is its content in the rock (in %) and a is the mineral residue contained in the water (in %). The comparison of the oxidizing and reducing environments is very interesting and shows the migrational contrast of some elements, such as U and Zn. Other elements, such as Fe, Mn, Co and Ni also

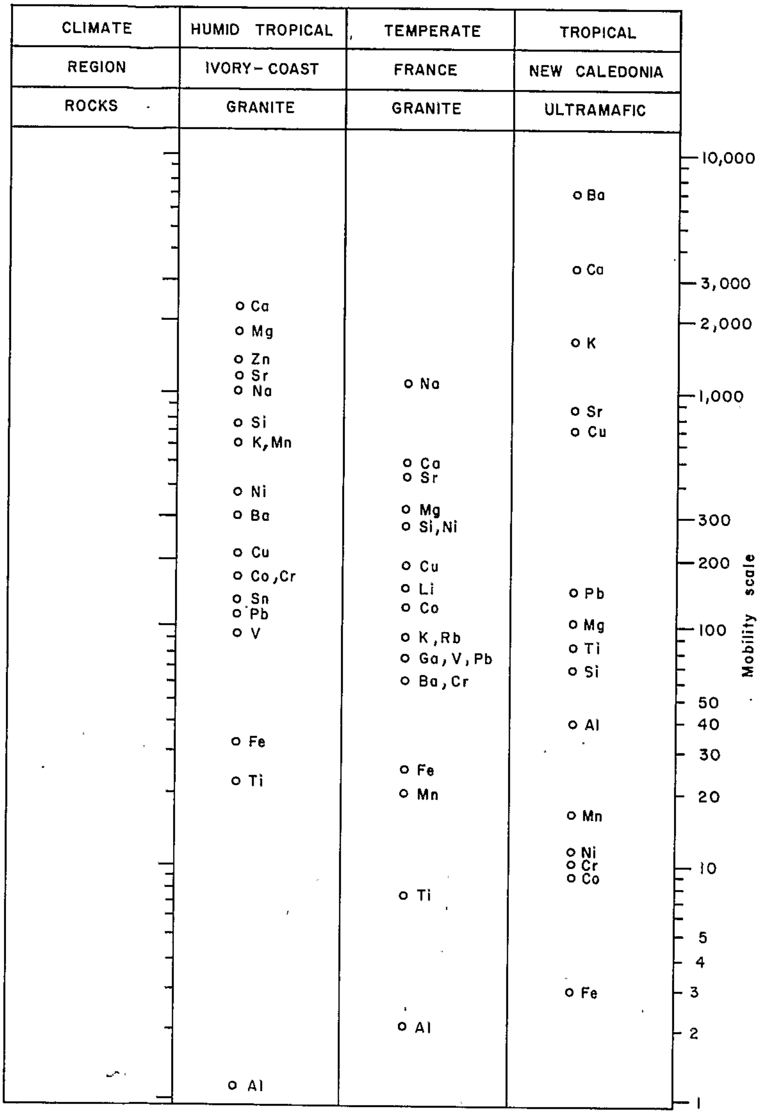

Fig. 13. Mobility scale of the elements on granitic and ultramafic rocks, under temperate and tropical climates (after Tardy, 1969; and Trescases, 1973b).

behave differently according to the values of the redox potential, but their strongest mobility corresponds generally to the more reducing environments.

Experimental studies. It appears from the above results that at least three important factors influence the mobility of elements, namely, the climate, the nature of the parent rock and the characteristics, either oxidizing or reducing, of the environment. But these variables are complex and involve additional parameters: temperature, drainage intensity,

TABLE X

Migrational series during the weathering of siliceous rocks in temperate climates[1]

Migrational intensity	Oxidizing environment K_x							Contrast of migration		Strongly reducing environments K_x						
	1000	100	10	1	0.1	0.01	0.001	↔ weak	← strong →	1000	100	10	1	0.1	0.01	0.001
Very strong	Cl, I Br, S							← Cl, Br, I →		Cl, I Br						
Strong			Co, Mg Na, F Sr, Zn U					← Ca, Mg, Na, F, Sr →	← Zn, U →			Ca, Mg Na, F Sr				
Medium				Ca, Si, P, Cu Ni, Mn K				← Si, P, K →	← Cu, Ni, Co →				Si, P, K			
Weak and very weak						Fe, Al, Ti, Y, Th, Zr, Hf, Nb, Ta, Ru, Rh, Pd, Os, Pt, Sn		← Al, Ti, Zr, Hf, Nb, Ta, Pt, Th, Sn →							Al, Ti, Sc, V, Cu, Ni, Co, Mo, Th, Zr, Hf, Nb, Ta, Ru, Rh, Pd, Os, Zn, U, Pt	

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[1] In Perel'man, 1967, following Polynov.

acidity, chemico–mineralogical composition and rock texture, for example.

Only experimental studies of chemical weathering performed in a laboratory allow the mechanism of each parameter to be analysed separately. Such studies are numerous, and only the most important ones, carried out under pressure and temperature conditions simulating natural surface conditions, will be mentioned here (Pickering, 1962; Correns, 1963; Wollast, 1961, 1963; Pédro, 1964; Trichet, 1969).

(1) Correns (1963) studied the role played by the pH in the chemical weathering of K-feldspars through successive water-filtration experiments. When the pH is lowered from 6 to 3, the Al becomes relatively more abundant than the Si in the solution, and its mobility is increased. This result is in agreement with the curves representing the water solubility of these two elements as a function of the pH. These curves are well known today and are available in many works (see, e.g., Loughnan, 1969, p. 32, fig. 15 and Perel'man, 1967, p. 40, fig. 11). Most of the metallic elements behave like Al in acid solution, and their mobility must increase rapidly when the pH decreases. However, Correns quotes earlier experiments dealing with some other minerals, which do not always provide similar results.

(2) Pickering (1962) presented leaching tests carried out on silicate rocks free of quartz (latite, andesite and peridotite) either by an immersion or by a filtration method at several pH values falling within the common range of pH and at different temperatures (from 0 to 35°C). The ratio of Si in solution is much higher for glassy rocks than for crystalline rocks. This ratio increases considerably when the pH passes from 7 to 4.8 (hence, the acidity is less marked than in the experiment carried out by Correns) and also when the temperature rises. On the other hand, no significant variation was observed in the ratio of Al and Fe in solution, under these conditions. From this, the author concludes that laterite formation can develop under fairly acid pH conditions.

(3) Pédro (1964) studied some rock fragments with the help of a Soxhlet apparatus designed for continuous leaching, and proceeded to separate investigations of the roles played by the parent rock (granite, basalt and acid lava), by the drainage and temperature conditions, as well as by the pH in relation to the nature of the major weathering agent (pure water pH = 6; sulphuric water pH = 4.5; carbonic water pH = 4; acetic acid pH = 2.5). These investigations produced the following results: (a) Bedrock. The weathering and leaching rates increase in the following order: granite, acid lava, basalt. Hence, they increase together with the basicity and the glassy characteristics of the tested rock. But the composition of the leachate does not change appreciably; in the presence of pure water, bases and silica are preferentially leached, the Fe after being oxidized remains stable, and the Al behaves in an intermediate way. (b) Drainage and temperature. The reduction of drainage limits the leaching intensity of all elements, but the effect is more marked on Al than on Si and bases. Any drop in temperature has the same effect, and below a certain temperature limit, the Fe does not form any more distinctive oxide or hydroxide products, but instead tends to become incorporated into residual argillaceous minerals of the smectite type. (c) pH. A decrease in pH and an increase of the partial

pressure of CO_2 favour the dissolution rate of minerals and increase the solubility limits of most metallic elements (bases, Fe, Al, etc.). Consequently, the relative content of Si in the leachates decreases (the pH is lower than in the experiments carried out by Pickering, which may explain the discrepancy). (d) Chemical weathering agent. The role played by CO_2 has just been noted. In a hydrogen-sulphide solution, the Eh (oxidation–reduction potential) decreases together with the pH and this favours the relative leaching of the Fe and elements such as Mn, Ni and Co, if they are not precipitated in the form of sulphides.

Mechanisms controlling the mobility

The successive stages which influence the element mobility are: weathering of primary minerals, the rate of which is a function of their alterability; dissolution of the elements; formation of secondary-mineral products; adsorption on colloids of soils; and fixation by the vegetation and living organisms.

Susceptibility of the minerals to chemical weathering. Goldich (1938) was the first author to have defined a full stability sequence of the silicate minerals formed in crystalline rocks, in accordance to their susceptibility to superficial weathering. This sequence,

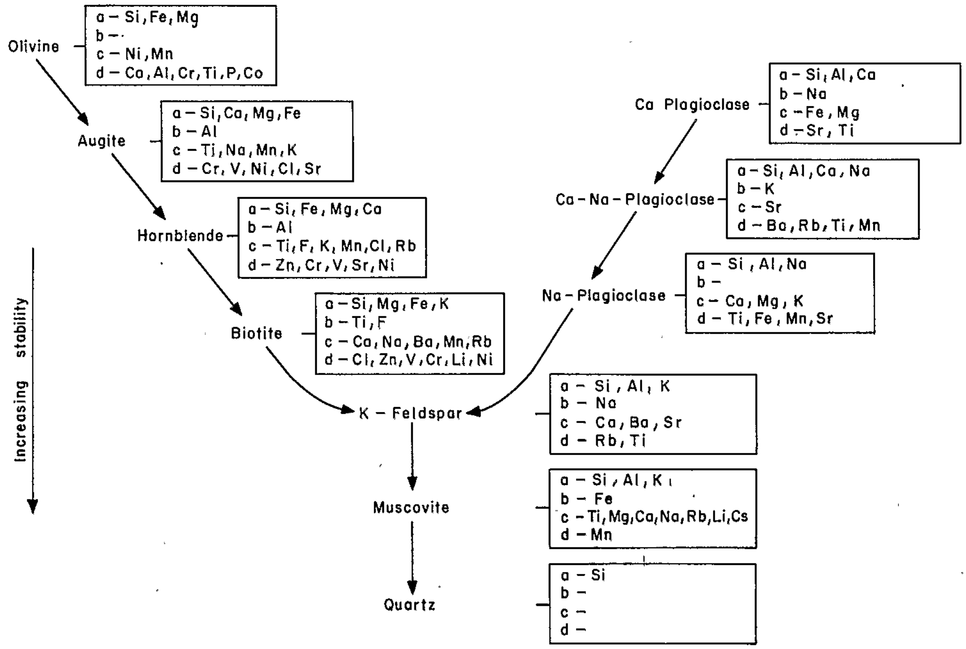

Fig. 14. Sequence of stability of common minerals during weathering processes (after Goldich, 1938). The element content in each mineral is given in order of relative abundance (*a* = 10x%; *b* = x%; *c* = 0.x%; *d* = 0.0x%). (After data from Wedepohl, 1967 and Deer et al., 1963.)

which has often been confirmed by more recent studies, is presented in Fig. 14, with complementary data about the element contents camouflaged in the minerals.

This sequence may be completed with the results obtained by Pettijohn (1941) by comparing the degree of persistence of minerals in sediments. The anatase, rutile, zircon and tourmaline are placed close to the muscovite. Consequently these minerals are preserved in soils and weathering crusts and they may be accumulated, through erosional processes, in alluvial fans, to form placer deposits. The monazite, garnet, apatite and ilmenite are close to the biotite; the epidote and the sphene are close to the hornblende. Jackson (1968) has also classified the fine minerals found in soils, in relation to their susceptibility to the leaching of bases and silica. The weathering stability is higher for most clay minerals – especially for aluminous chlorites and kaolinite – than for quartz. On the other hand, calcite and, particularly, gypsum are much less resistant than the least-resistant silicates.

In very wet-tropical climates, most of the minerals are rapidly hydrolyzed; only those most resistant persist (quartz, kaolinite, gibbsite, goethite and anatase). In dry climates, almost all minerals persist and in intermediate climates, temperate climates, for example, the weathering stability differences of moderately resistant minerals appear. Several attempts have been made to interpret this differential stability; the causes commonly put forward (Loughnan, 1969) are: (1) disparities in compactness of structure and packing of crystalline networks; the most stable structures are those of tectosilicates, such as quartz, and the least stable are those of neosilicates, such as peridotes; (2) discrepancies in the formation energies of the tetrahedral bondings Si–O and Al–O or of the octahedral bondings M–O and M–OH, which are more or less hydrolysis resistant, depending mainly on the electro-negativity of the M elements and on the more or less ionic characteristics of the bondings; highly ionic bondings seem to be less resistant to hydrolysis than the covalent ones.

To these factors, the differences in stabilization degree of ions in the electronic field of crystalline polyhedra (Burns, 1970) may also be added. All these factors explain, at least partly, the variations observed in the dissolving rates of elements according to the structures in which they are present. Hence, Si is less rapidly dissolved from quartz than from feldspar and a fortiori from peridote; the rate reaches the maximum with amorphous Si-gel. Also, in a particular crystalline polyhedron, an element such as Mg with a fairly strong electro-positivity and a predominantly ionic bonding, will be of comparatively lower stability than Fe or Al.

Solubility of elements in aqueous solution. The element mobility depends, in the second place, on their solubility limits which are a function of the pH and, for some elements, of the Eh. The solubility also depends on the presence of other ions or organic complexes (Charlot, 1963; Krauskopf, 1967; Pédro and Delmas, 1970):

(1) In pure aqueous solutions, the solubility limits are determined by the value of solubility products (*SP*) of the hydroxide compounds of the $M(OH)n$ type:

$SP = -\log Kc$

where $Kc = [M^{n+}]\,[\mathrm{OH}^{-}]^{n}$

The elements may be classified in several categories (Table XI) according to their ionic potentials ϕ (ratio of the charge to the ionic radius) as defined by Goldschmidt (1954). The following divisions may be proposed: (a) elements forming soluble hydrated or simple cations in the full range of pH; these are alkaline and alkaline-earth elements (ionic potential below 2); (b) elements forming insoluble hydroxides in a certain range of pH; these are the metallic cations Fe^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+}, Cu^{2+}, Cr^{2+}, Cr^{3+}, Al^{3+},

TABLE XI

Solubility products (*S.P.*) of the hydroxides and of some compounds[1]

Category	Elements	*S.P.* hydroxides	*S.P.* carbonates	*S.P.* sulphurs	*S.P.* varied compounds	Category	Elements	*S.P.* hydroxides
A	Na^+	− 2.9				C	Be^{2+}	20.8
($\phi < 2$)	Cs^+	− 2.8				($3 < \phi < 7$)	Ce^{3+}	22.3
	K^+	− 2.6					Hg^{2+}	25.5 (HgO)
	Li^+	− 1.4					Sc^{3+}	26.3
	Tl^+	0.2		20.3			Cr^{3+}	30
	Ba^{2+}	2.3	8.8	–	10.0		Bi^{3+}	30.4
	Sr^{2+}	3.5	9.6	–	($BaSO_4$)		Al^{3+}	32.5
	Ca^{2+}	5.3	8.4	–	4.5		In^{3+}	33.2
					($CaSO_4$)		V^{3+}	34.4
							Ga^{3+}	35
							Fe^{3+}	38
							Ti^{4+}	40
							Th^{4+}	44.7
							Tl^{3+}	45
B	Ag^+	7.6	–	49.2	9.8		U^{4+}	45
($2 < \phi < 3$)		(Ag_2O)			(AgCl)		Mn^{4+}	56
	Mg^{2+}	11.0	5.1	–			Sn^{4+}	56
	Mn^{2+}	12.7	10.2	12.6				
	Cd^{2+}	13.7	11.3	27.8				
	Ni^{2+}	14.7	6.9	25.4				
	Co^{2+}	14.8	12.8	20.4				
	Fe^{2+}	15.1	10.5	17.2		D	V^{5+}	14.7 (V_2O_5)
	Pb^{2+}	15.3	13.1	27.5	8.0	($7 < \phi < 11$)	Si^{4+}	8.0 (SiO_2)
	Zn^{2+}	17.0	10.8	22	($PbSO_4$)		Ge^{4+}	2.3 (GeO_2)
	La^+	19.0		12.7				
	Cu^{2+}	19.7	9.3	36.1				
						E	B^{3+}	
						($\phi > 11$)	As^{5+}	< 0
							P^{5+}	

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[1] In Pédro and Delmas, 1970 (after data from Charlot, 1963; Krauskopf, 1967; and Perel'man, 1967).

V^{3+}, Fe^{3+}, Ti^{4+}, Th^{4+}, etc., which have an ionic potential between 2 and 7. Most of them are only soluble at acid or very acid pH; some, like Al, are emphoteric and are soluble at both very acid and alkaline pH; (c) elements forming simple or complex anions (hydroxi- or oxi-anions) more or less soluble within a large range of pH; this are Cl^-, Br^-, $(CO_3H)^-$, $(SO_4)^{2-}$, $(NO_3)^-$, $(PO_4)^{3-}$, $(SiO_3)^{2-}$, etc., which have an ionic potential above 7.

(2) In the presence of anions, such as HCO_3^-, HSO_4^-, SO_4^{2-}, HS^-, etc., the preceding values of solubilities are no longer valid. Table XI, established by Pédro and Delmas (1970), shows in each category of elements, different ranges of solubility product, which correspond to different compounds. The solubility products of the sulphides, for example, are very high and this fact explains that, as soon as the solutions contain some traces of HS^-, the immobilization of most metallic elements is almost total. Similarly, in the presence of important quantities of SO_4^{2-} and CO_3^{2-}, such as in strongly mineralized waters of arid areas, the precipitation of the very mobile elements may occur in the form of carbonates and sulphates.

(3) In the presence of complexing agents, such as organic acids, an increase of mobility is noted for slightly soluble or insoluble elements, such as metallic elements belonging to the Fe- or Al-group. This phenomenon of mobilisation by organic compounds, termed chelation or cheluviation (Swindale and Jackson, 1956; Lehman, 1963), favoured the congruent dissolution of primary and secondary silicate minerals[1] (Huang and Keller, 1970, 1971).

From these data, it is clear that the pH has a determinant influence on the limits of solubility of the metallic elements and, consequently, on their mobility, once they have been released by hydrolysis. For elements with variable valencies, the limits of solubility also depend on the oxidation–reduction potential: for Fe and Mn, and also, to a lesser degree, for Ni and Co, the solubility increases when Eh decreases. On the other hand, some other elements, such as V, Cr and U, are more soluble in an oxidizing environment than in a reducing one (Garrels and Christ, 1965; Perel'man, 1967; Norton, 1973).

Under natural conditions, the solutions contain the elements as different soluble species. In addition to the free ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, etc.), major elements are found in complex forms ($Mg(OH)^+$, $Ca(OH)^+$, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$ etc.) and that is also frequently the case for the trace elements (e.g., uranyl cations $(UO_2)^{2+}$, $(UO_2)OH^+$, etc.). As the anions are very numerous (OH^-, SO_4^{2-}, SH^-, CO_3^{2-}, CO_3H^-, Cl^- and many complex anions of Si, P, V, As, etc.), the order of precipitation is not easily determined since the exact nature of all possible compounds is not always known, particularly for trace elements. The less mobile elements are those for which the solubility products are reached first, the most mobile elements are those for which the solubility products are reached last.

Mechanical migrations. The problem of the mechanical transport and redeposition of

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[1] See also Chapter 5 by Saxby, Vol. 2.

heavy or coarse particles by erosional forces is beyond the scope of this study, but the possibility of migration of some substances in a colloidal state must be considered. Perel'man (1967) reports that elements, such as V, Cr, Ni, Be, Ga and Zn, are transported mainly in suspensions or adsorbed on colloidal matter. The common elements of the soils, Al, Fe, Mn and P, which are concentrated in the fine, organic and inorganic fractions (humus, colloids, and clay minerals), are selectively displaced by erosion in the form of suspended matter in the runoff waters. This "selective erosion" is very efficient, even in the soils protected by a dense forest cover, and this explains the presence of "impoverished horizons" (horizon depleted in colloids, Fe, Al, etc.) at the top of the soil profiles (Roose, 1973). Thus, the possibility of distant migrations also exists for the less chemically mobile elements, in landscapes well protected against the erosional forces and a fortiori in arid countries, without plant-cover.

Entrapping within secondary mineral products. The mobility of the elements released and being made soluble by the hydrolysis of primary minerals, also depends on the formation of secondary-crystalline or amorphous mineral products, into which the elements can enter.

The secondary minerals likely to be formed are quite numerous: sulphates, carbonates, phosphates, silicates (clays), oxides and hydroxides. A very large mineralogical variety of salts of metallic – even rare – elements occurs in the superficial chemical weathering zones, where the subsurface solutions are exceptionally rich in various kinds of ions, as in the gossan capping ore bodies. But, apart from this particular and very localized case, the only common minerals produced by chemical weathering, which are characteristic of alterites and soils, are clay minerals, oxides, hydroxides, carbonates and, locally, sulphates.

These common minerals may be formed in two ways (Millot, 1964; Millot et al., 1965):

(1) By "transformation" of pre-existing minerals: clay minerals are frequently formed in this way. They may be produced from primary phyllites which evolved during the hydrolysis process through leaching and exchange of some elements with soil solutions, without destruction of the mineral structure. It is in this way that vermiculite, Al-chlorite, or montmorillonite of certain acid soils, are formed from micas or chlorites derived from crystalline rocks; the process is termed degradation or aggradation, according to whether the subtraction or the addition of elements prevails in the transformed minerals. This evolution is typical of cold–temperate climate soils, where the chemical weathering processes, which are slow and moderate, are nevertheless accompanied by a fairly marked mobility of Fe- and Al-oxides favoured by organic compounds.

(2) By "neoformation" of new mineral species, which crystallize directly from elements in solution or after aging of amorphous precipitates. To each chemical weathering-type there corresponds a certain number of more or less typical neoformed minerals which have, as previously mentioned, a development process predominantly conditioned by climatic conditions:

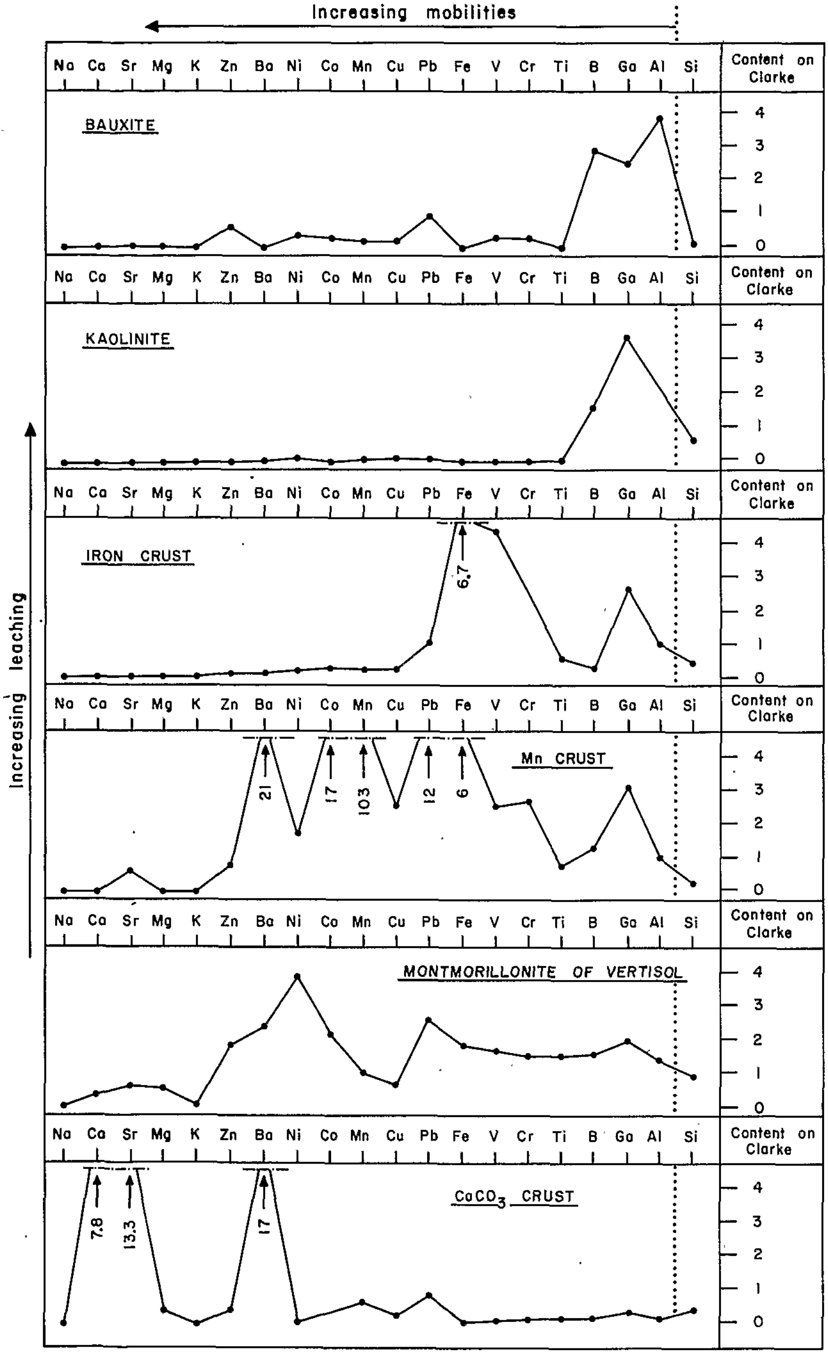

Fig. 15. Trace-element contents in the main weathering facies (after Tardy, 1969).

(a) Under tropical, very humid leaching climates, solutions are always highly diluted. Si is leached as easily as bases, Fe and Al which are not very mobile accumulate relatively, and neoformed minerals, such as gibbsite, $Al(OH)_3$, or boehmite, AlO(OH), and goethite, FeO(OH), are produced.

(b) Under tropical but less intensely leaching conditions, solutions are not so highly diluted. Si is not released so easily, a part of it combines with Al to give 1/1 clays (kaolinite), and the Fe continues to assume the hydroxide or oxide forms.

(c) Tropical but drier conditions favour 2/1 clays, such as montmorillonites of steppe soils or vertisols in which Fe and Mg can enter.

(d) In true arid regions, where the solutions can reach high concentrations through evaporation, siliceous neoformations, calcareous crusts and fibrous clays are mainly found (Millot, 1964; Millot et al., 1969; Dutil, 1971), with salt deposits, such as Ca-sulphates, Na-carbonates, Na-chlorides and silicates (Hardie, 1968; Eugster, 1970; Maglione, 1974). These deposits are observed on the fringes of salt lakes, playas and sebkhas, where the most mobile elements leached from the surrounding landscapes may accumulate.

In actual fact, the neoformed mineral zonality is not sharply defined: gibbsite and kaolinite, for example, co-exist in most ferrallitic soils, kaolinite and 2/1 clays occur in most fersialitic soils, 2/1 clays and carbonate minerals in most steppe soils. Indeed, the climatic zonality is greatly complicated by the action of the other factors of soil formation, such as parent rock and topography.

Development of amorphous-mineral products often bears a relationship with a particular parent rock. So, for example, many amorphous silico–aluminous products (allophanes) are observed in soils derived from volcanic rocks having an unstable glassy structure (Bates, 1962; Sieffermann, 1969). Also, amorphous products rich in Fe, Mn, Co and Ni (limonites, wads, psilomelanes) are found in alterites from ultra-basic rocks. In soils with very acid humus (podzols), favouring an intense Fe and Al cheluviation, amorphous oxides are also more or less linked with organic matter.

Trace elements become selectively concentrated in these different minerals and weathering products, as shown by Fig. 15, established by Tardy (1969). In bauxites and kaolinites, Ga and B are the most retained elements; in ferruginous crusts, they are V and Cr; in manganiferous crusts, Ba, Co, Pb; in vertisol montmorillonites, Ni, Ba, Pb and Zn; and in calcareous crusts, Ba and Sr.

These results confirm those published by some other authors. The elements concentrated in bauxites are often: Ti, Fe, V, Ga, Cu, Zr, B, Cr, Co and Ni (De Chetelat, 1947; Bardossy, 1958; Gordon et al., 1958; Maksimovič, 1968). In kaolinites there are very few trace elements enclosed in the network, except perhaps Ti (McLaughlin, 1957). Sherman, (1952), Lajoinie (1964) and Worthington (1964) report enrichments of Ti, Cr, V, Ni, Co and Mn in ferruginous concretions. Taylor et al., (1964) and Taylor (1968) report concentrations of Ni, Co, Cu, Ba and Li in manganiferous concretions. In vertisol montmorillonites and generally in ferriferous or Mg-phyllosilicates, Ti, V, Ni and Cr are relatively concentrated (Paquet, 1969; Trescases, 1973b).

Comparing the behaviour of U, Cu, Zn and Pb in different weathering processes, Samama (1972) concludes that U and Cu are concentrated under allitization processes (giving bauxite facies), Cu and Zn under monoziallitization (giving 1/1 clay minerals facies) and Zn and Pb under bisiallitization (giving 2/1 clay minerals facies). As and Sb are but slightly mobile and seem relatively enriched in oxidizing environments of lateritic soils and derived siderolitic sediments (Chakrabarti and Solomon, 1971; Guillou, 1971 and personal communication, 1974). In reducing environments, rich in organic matter, high concentrations of Pb, Zn, Cu, Ni, V, Co, Mo and Sn are also to be noted (Perel'man, 1967) and the fixation of U by organic matter is also well known[1] (Barbier, 1974).

The amorphous weathering products may also play an important role in the selective entrapping of some elements: Perruchot (1973) illustrates this by showing that a Si–Mg-gel obtained by an experimental weathering of a peridote is able intensively to concentrate transition elements, such as Mn, Fe, Co, Ni, Zn and particularly Cu.

Adsorption on the colloidal fractions of soils. Ion exchanges between the solutions and the adsorbing organo–mineral complexes of the soils (clay, humus, and amorphous products) interfere in a very complex way with the element mobility (Ermolenko, 1966; Duchaufour, 1970). Most of the adsorbing constituents of the soils are electro-negatively charged. The exchangeable elements are then cations, mainly Ca, Mg, Na, K, Al, and among the trace elements, B, Mn, Zn, Cu and Mo.

In neutral or alkaline soils, the adsorbed elements are mainly basic cations, while in acid soils, Al and H prevail in relation with the respective ionic activity in solution. The selective exchange reactions proceed through dynamic equilibria, following some general, mostly empirical, rules which apply only to very dilute solutions:

(1) All these ions are not adsorbed with the same intensity. The adsorption is less intense for hydrated ions (Na, for example) than for but little hydrated ones.

(2) The adsorption intensity increases generally together with the valency. The order of increasing adsorption is as follows:

$$K^+, Na^+ < Ca^{2+}, Mg^{2+} < Al^{3+}, Th^{4+}$$

(3) For a particular valency, the adsorption increases with the atomic weight of the element and the heavy cations Mn, Cu and Zn tend to be adsorbed more tightly than light cations. Thus, uranyl cation UO^{2+} and perhaps other complex ions of this element can be strongly adsorbed by clays or humic products.

Reversely, positively charged colloids, chiefly hydroxides and oxi-hydroxides of Fe, Al and Mn, are liable to adsorb anions, such as PO_4^{3-}, VO_4^{3-}, ASO_4^{3-}, SO_4^{2-}, (Ermolenko, 1966; Perel'man, 1967). In certain circumstances, the adsorbed elements may form stable compounds with the colloids and even progressively crystallize. Thus, the adsorption processes are an important mechanism of concentration of some elements. Therefore, the

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[1] See also Chapter 5, by Saxby in Vol. 2.

adsorbed cations and anions may be transported in the surface and subsurface waters, in the form of colloidal suspensions of clays and humus, as seen above (p. 158).

Fixation by plants and living organisms. The role played by living organisms and particularly by plants in the supergene cycle of elements, must also be mentioned.[1] The total mass of organic matter over the globe is considerable and its relative importance compared with the mass of mineral matter in soils is not to be neglected in regions of dense vegetation. Moreover, the living organisms are perpetually renewed. The living matter concentrates mainly C, P, S, N and Ca and plants which accumulate Si, Fe or Al or even trace elements are also known (Lovering, 1959; Ermolenko, 1966). The ability of the plants to adsorb and/or absorb certain elements selectively is well defined by the coefficient of biologic accumulation (Perel'man, 1967). This coefficient is the ratio of the element content in the plant-ash to its content in the soil on which the plant grew. A classification of chemical elements on the basis of the value of this coefficient is given in Table XII (after Perel'man, 1967, p. 9).

The elements concentrated in living matter return to the soil during the decay of this matter, in a form permitting easy mobilization. Thus, there is a perpetual cycling of the elements from the soil to living matter and from living matter to soils (biogeochemical cycle), but the system is not closed; some losses of elements occur by erosion (wind, runoff) or by leaching, and the plants compensate for these losses by taking up the mineral reserve of the soil.

The biological mobilization of elements is one of the basic features of the pedogeneses (Duchaufour, 1968) and also of the supergene geological phenomena (Perel'man, 1967; Erhart, 1973a). It governs the distribution of many elements in the soil profiles, C, N and Ca, especially. The selective action of each plant or vegetal association must be taken into account in the establishment of rules of geochemical exploration. Sometimes, the biological mobilization favours a behaviour of elements entirely independent of the physicochemical laws. Therefore, the genesis of some either residual or sedimentary mineral deposits cannot be explained without referring to it. More essentially, by the continual consumption of the atmospheric CO_2 and by the release of O_2, plant activity is directly responsible for the major changes in the weathering conditions and during sedimentary processes from Precambrian times to the present.

Conclusion

At the end of this discussion, an order of the element mobility during chemical weathering proves difficult to establish because too many and, often contradictory, factors interfere during the successive processes of hydrolysis, solubilization, secondary-mineral formation and exchanges in the soil. Not the least of these is the foremost factor

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[1] See Chapter 5 by Saxby, in Vol. 2.

TABLE XII

Biologic accumulation series of chemical elements[1]

		Coefficients of biologic accumulation					
		100*n*	10*n*	*n*	0.*n*	0.0*n*	0.00*n*
Elements of biologic capture	very strong	P, S, Cl					
	strong		Ca, K, Mg, Na, Sr, B, Zn, As, Mo, F				
Elements of biologic accumulation	moderate			Si, Fe, Ba Rb, Cu, Ge, Ni, Co, Li, Y, Cs, Ra, Se, Hg			
	weak					Al, Ti, V, Cr, Pb, Sn, U	
	very weak						Sc, Zr, Nb, Ta, Ru, Rh, Pd, Os, Ir, Pt, Hf, W

[1] After Perel'man (1967).

involved, that is the stability of the primary minerals in which elements are enclosed.

The problem of the relative mobility is complicated by the existence of some threshold effects and the effect of many interactions. For example, below a certain drainage rate, the hydrolysis mobilizes the bases rather than the Si, whereas above this rate, the Si may be preferentially mobilized, so that a slight quantitative variation is sufficient to modify the nature of the processes. The decrease or the increase in solubility of some elements when additional ions are present illustrates well the interaction phenomenon. Another example is afforded by the influence of the development of secondary minerals on the solubility equilibria between the primary minerals and the solution.

Owing to this complexity, only some general laws applicable to the common weathering environments can be offered. The most-mobile elements are those which are rapidly released from unstable primary-minerals and which are later entrapped in secondary minerals. The least-mobile elements are those which are retained a long time in resistant primary-minerals, and which, being less soluble, are consequently rapidly entrapped in secondary minerals. Therefore, however unsatisfacory it may be, only a simple classification of the elements into large mobility categories is possible. The more recognized categories are the four groups proposed by Polynov (1937) or the classes defined by Goldschmidt (1954), mentioned above (p. 150 and p. 156), or still from a naturalist view point the two Erhart (1956) "phases": the migrating soluble phase (alkaline cation and cations of the alkaline earths, combined silica) which is removed during the pedogenesis process and the residual phase (Si from quartz, Al, Fe, Ti) which becomes accumulated in soils. The partial accumulation of combined Si in the clay minerals of most soils corresponds well with the intermediate position of this element between the classes 2 and 3 of Goldschmidt. But the Erhart classification applies principally to the pedogenesis of humid-tropical type.

The most general classification of the migrational ability of elements in the supergene processes has been established by Perel'man (1967), on the basis of the mode of migration (aerial or aqueous), of the intensity of migration and of contrast of the element behaviour. This classification scheme, given in Table XIII, is applicable to the supergene

TABLE XIII

Geochemical classification of elements on the basis of their supergene migration[1]

A. Aerial migrants

A_1. Active (forming chemical compounds)
O, H, C, N, and I
A_2. Inactive (not forming chemical compounds)
A, Ne, He, Kr, Xe, and Rn

B. Aqueous migrants

B_1. Very mobile anions, with K_x between 10 n and 100 n
S, Cl, B, and Br
B_2. Mobile, with $K_x = n$
  B_{2a}. Cations: Ca, Na, Mg, Sr, and Ra
  B_{2b}. Anions: F
B_3. Weakly mobile, with $K_x = 0.1n$
  B_{3a}. Cations: K, Ba, Rb, Li, Be, Cs, and Tl
  B_{3b}. Mostly anions: Si, P, Sn, As, Ge, and Sb
B_4. Mobile and weakly mobile in oxidizing media ($K_x = n$ to $0.1n$), and inert in strongly reducing media (K_x less than $0.1n$)
  B_{4a}. High mobility in acid and weakly acid oxidizing waters and low mobility in neutral and alkaline waters (predominantly cations): Zn, Ni, Cu, Pb, Cd, Hg, and Ag
  B_{4b}. Energetic migration in both alkaline and acid waters – more energetic in alkaline than in acid (predominantly anionic): V, U, Mo, Se, and Re
B_5. Mobile and weakly mobile reducing, colloidal media ($K_x = n$–$0.1n$) and inert in oxidizing media ($K_x = 0.01n$): Fe, Mn, and Co.
B_6. Poorly mobile in most environments ($K_x = 0.1n$ to $0.01n$)
  B_{6a}. Weak migration resulting in formation of chemical compounds: Al, Ti, Zr, Cr, rare earths, Y, Ga, Cb, Th, Sc, Ta, W, In, Bi, and Te
  B_{6b}. Not forming or rarely forming chemical compounds: Os, Pd, Ru, Pt, Au, Rh, and Ir

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[1] After Perel'man, 1967. The coefficient of aqueous migration K_x is defined on p. 150.

continental zones. In each category, the elements are classed in decreasing order of abundance. In particular cases, important variations in the behaviour of some elements may be observed. Perel'man (p. 153) indicates: "Co is placed in the B5 group together with Fe and Mn, but because of certain peculiarities of its behaviour in the supergene zone, it could be placed together with Cu, Zn and others in the group B4a. Cr, placed in the B6 group of poorly mobile elements, acquires considerable mobility in deserts, and is then analogous to the elements of the B4b group. Some poorly mobile elements like Zr or Y may move in the form of organic complexes. The intensities of their migration increase in tundra, swamps and similar environments. The migration of metals of the B4, B5 and B6 groups intensifies in the sulphatic waters of the oxidation zone of sulphide ore deposits".

The mobility of elements depends also on the scale considered: it might vary according to whether a local evolution restricted to a particular soil profile is considered, or a general evolution over a large area. The mobile elements leached out of a profile may be laterally fixed after a more or less prolonged migration together with drainage waters (lateral geochemical redistribution); these elements, which are mobile on the scale of the soil profile, must be considered rather stable on the scale of the landscapes.

In practice (e.g., during metallogenic exploration projects), the mobility of the chemical elements must be first considered at the scale of large areas. A significant geographical zonation of the weathering facies exists along the earth's surface, in relation to the bioclimatic zonation. Inside each zone, petrogenetic and topographical variations induce more or less marked changes of the weathering type. The main weathering facies are regularly ordered in a sequence between two extreme environments:

(1) The most intensely leached and chemically very acid environments (evolving through "subtractions" of mineral matter, Millot, 1964), which are located in the top layers of soil profiles in equatorial regions, where the least mobile elements, Al and Ga, concentrate.

(2) The most confined and chemically very basic environments (evolving through "addition"), which are located in the depressions and are temporarily water-logged, in the arid regions, where the more soluble elements Mg, Na, Ca, Rb and Li, etc., accumulate and precipitate with Cl^-, SO_4^{2-}, NO_3^-, etc.

Between the above two extremes, one finds a wide range of weathering facies which correspond to less and less leached and more and more confined environments, where the concentrated elements are of increasing mobility. The different facies are defined in Table XIV from data given by Tardy (1969). This weathering sequence may be observed entirely on the large scale of continents from the equatorial regions to the deserts. It may be partially observed on the limited scale of toposequences (succession of soil types along a slope) where the upper, relatively well-drained-part, shows the most intensively leached facies and where the lower and relatively poorly-drained-part shows the most confined facies.

This general scheme permits of predicting the haloes of dispersion of chemical ele-

TABLE XIV

Partition of chemical elements between the main facies of weathering: oxi–hydroxides, clay minerals, salts and alkaline silicates

Bauxite Al–Ga–B	Iron crust Fe–Ti–V–Cr–Mo	Manganese crust Mn–Fe–Co–Pb–Ba–Sn–Ni–Cu	Calcite crust Ca–Sr–Ba–Zn	Sulfates Ca–Sr–Ba	Sodium carbonates Sodium chlorides Na–Rb–Li
	Kaolinite Al–SiO_2–Ga–B		Montmorillonites SiO_2–Ti–Al–Fe–Mg–Ni–Zn–Pb–Cu		Zeolites Magadiite Mg-montmorillonite SiO_2–Mg–Na–Ca
Humid climate Upstream Top of the profiles			increasing mobilities →		Arid climate Downstream Bottom of the profiles

ments according to the characteristics of the landscape and, inside each landscape, according to the topographical conditions. Nevertheless, the lateral geochemical differentiation is often unapparent, because of the superposition of the effects of mechanical erosion, the processes of which are entirely distinct from the chemical migration processes.

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