Geochemistry of some lateritic nickel-ores with particular reference to the distribution of noble metals

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PLATINUM, palladium, gold, and iridium have been determined by radiochemical neutron-activation analysis in three lateritic profiles developed on serpentinized peridotite. In addition, a number of major, minor, and other trace elements have been estimated by conventional chemical, instrumental neutron-activation, and radiochemical methods. The fractionation of the elements as a result of the tropical weathering has been investigated as a function of depth. Each of the profiles L-Guatemala, BNC-New Caledonia, and BIP-Indonesia-has a lower decomposed serpentinite zone and upper zones enriched in iron^{III} oxides and hydroxides. There is marked depletion of silicon and magnesium, and sodium is also largely leached out as a result of the weathering. The deposits are of economic importance primarily in that they are enriched in nickel; this element is concentrated

in the ferruginous parts but also it is relatively plentiful in the intermediate saprolitic zones. Noble metals are concentrated in each of the profiles, particularly in the A and B horizons; it appears in the case of platinum and palladium that there has been some mobility as a result of the weathering and probably these elements have been brought into solution prior to subsequent redeposition.

The three profiles have many features in common, although the analytical and other information indicates that BNC is more mature than L. It appears that there is a fairly general sequence of differentiation in the development of laterites from ultrabasic rocks.

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it. It is unlikely that the titanomagnetite was actually pressed into con-tact mines the remainder of the pyrite periphery retains its spheroidal form and granular integument. Adhesion of the subplice molit to a titanomagnetic grain is even more convincingly shown in Fig. 2E where the grain only main-tains contact with a para-shaped gyrite by virtue of the latter's departure from a spherical form. Its present shape no doubt results from a recessive movement of the titanomagnetite relative to the mulphied globule while the host mesorials was still fluid. Fig. 27, on the other hand, appears to represent a subplied globule confined and distorted, while still fluid, by adjacent plagicolases displaced by movement in the host mesoriasis.

Summary and conclusions

The Imachar composite dyke is important as affording evidence of the em-placement and crystallization of two tholsitis members which, despite their openical similarity, show petrographic individuality which can only be a consequence of differing diroumstances of emplacement and the divergence of their subsequent cooling histories.

their makequent cooling histories. The outer and earlier amber shows textural svidmos of rapid intrasion followed by the immediate easts of crystallisation, the latter being initia-ded under temporary conditions of convolute with the state of the sec-sed and the supervised in the development of polkilitic overgrowthe on earlier-formed, probably intratelluring, plagicalese phenomysts and gloser-purpyritic removarystal groups. Continued crystallization produced further, earlier-formed, probably intratelluring, plagicalese phenomysts and gloser-purpyritic removarystal groups. Continued crystallization mode plagicalese phenomysts, while new individual of a seriet modersion of smiller plagica-clases were developed in the matrix. The ferromagnesian allocates joined plagicalese rather early in the crystallization sequence, while iron ores (itianoagnesite) are virually confide to the utimate mesostatis. These characters indicate crystallisation under essentially closed-system con-ditions, and are compatible with the failure of this member to reach the contagonary earth-surface. Its thermal effects on its country-rocks are sall, as is appropriate to a minor intrasive which served as a conduit to a limited volume of magna. The inner tholeits thows, in contrast, no evidence of chilling maging

a limited volues of magna. The inner tholeiite shows, in contrast, no evidence of chilling against its country-rocke which, where initially schistone-grite, have suffered transformation to cordierite-bunkle over a distance in excess of 20 cm from contact. This implies a major accession of best, supplied over a compar-tively protracted period. Petrographically the rock offerse widence of rester allow colling from a unusually high initial tengersture, since its compared in the state of the state of the state of the state orgets incompared to the state of the state of the state into the state of the state of the state of the state of the compared into the state of the state of the state of the state orgets incompared the state of the state of the state of the state orgets incompared to the state of the state of the state of the inner tholeiite which do show polkilition manifes have been derived from mobilised outer tholeitt, while the consectional place of the state rising magna from a crystallume basic mass at growthe depth. The early separation of these several and delayed appearance of augite indicate with the view that the immer tholeitte resched the contemporary earth-gurate and there several as feeder to fissure-orginion of instate of anythic as feeder to fissure-orgin of the state of growth the view of the static of anythic the static of state sufficient of states of the state of state of state of the state of state sufficient of states of state of state of state of state of state sufficient state of growth state of sta

group sometose-grine to userie is readily measured, The original connections of the terms "wariely and "warielite" have been lest sight of by a majority of petrologists active during the past century. The term warielite and the adjectivel "warielite" have been whely used in connection with rocks which have little or no tertural or structural simi-larity to the true varielites. Rocks having the characters implicit in the early usage do indeed exist, and for this reason a return to this usage is

For figs.1&2 see the synopsis (this vol.)

long overdus. In the inner, varialitia, thaleiite at Imaabar variales have resulted when droplets of buchitic melt became dispersed in the tholeitic magma, and it is concluded that it is only in this memore that they have been developed in the present association. The survival of the structure until the consolidation of the host is a consequence of the immissionility of acidic in basic melts at liquidus temperatures, a relation which fails only when advancing crystallisation of the host yields a mesostasis convergent on the composition of the intra-varialitic liquid.

the composition of the intra-verticities inquit: Reflected-light examination shows that the itianomagnetites of both dyke-members have homogeneous structure despite their quite high content of ulv8spine Molecule as revealed by obtained analysis. Their individual com-positions and deduced temperatures of crystallisation accord well with their textural relations to the respective host rocks. The textural evidence of sulphide immiscibility in both tholesites is of general interest, while in the present context the relations of the pyrite bodies to their host rocks is strikingly analogous to those of the variales in the inner tholesite. with their

The recognition of the inner tholeiite as a former feeder for lava extra sion is important in that it suggests the directly volcanic function of or more of the many dykes of the Hebridean Tertiary swarms (Holgate 1969, pp.133-134).

pp. 137-144. Acknowledgements. The writer wishes to record his thanks to Mr. Alex. Herricht for bringing to his notice the occurrence of buchite at Imachar; to Dr. N. R. L. Naccallum (Dept. of Mechanical Engineering, Thiversity of Glasgow) and to Dr. Donald Praser, for access to equipment for thermal con-ductivity determination; to Messre. D. L. Skinner, W. H. Reilson and G. W. Robb of this Department, for the obselfcal analyses; and to Mr. R. Cumberland, also of this Department, for the preparation of rock samples for the thermal conductivity determinations.

Specimens referred to in the present paper are identified by their access-ion numbers in the Geological Collections of the Hunterian Museum, The University of Glaegow.

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Ahmad & Morris: Noble metals in laterites

CEOCHEMISTRY OF SOME LATERITIC NICKEL-ORES WITH PARTICULAR REFERENCE TO THE DISTRIBUTION OF NOBLE METALS

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The definition of the term "laterite" and its origin is discussed in detail by Maignien (1966). Ferruginous deposits of this type occur in India, Malayata, Indonesia, Australia. Cuba, the Hawailan Flands, and the tropical regions of Africa and Central and South America. For laterization the following conditions appear to be prety essential:

(1) a warm humid tropical or subtropical climate conducive to extensive chemical weathering;

(2) a flat, or nearly level topography (peneplain) where water has relatively little power to wash away products of chemical weathering;

(3) sufficient time of exposure to the weathering process

(3) sufficient time of exposure to the weathering process. Nickel is enriched in various profiles which have originated from such weathering of ultrabasic rocks and, whilst sulphide minerals, particularly pentlandite, currently provide the major source of the elgeant, lateritic ores are worked on a large scale (Roldt and Quenesu, 1907; Skinner, 1976) and are considered to contain about 75 per cent of the haven reserves of nickel (Canterford, 1975). Plathum and palladium may exhibit similar spparent radii in crystals of analogous type [singl=-bond metallic r; pt. 1.295 Å; Pd. 1.283 : octahedral covalent r; PC(TV) 1.31; Pd(TV) 1.31; .1.295 Å; Pd. 1.283 : octahedral covalent r; PC(TV) 1.31; Pd(TV) 1.31; .1.295 Å; Pd. 1.283 : octahedral covalent r; NC(TV) 1.31; Pd(TV) 1.31; .1.295 Å; Pd. 1.283 : octahedral covalent r; NC(TV) 1.31; Pd(TV) 1.31; .1.295 Å; Pd. 1.283 : octahedral covalent r; NC(TV) 1.31; Pd(TV) 1.31; .1.295 Å; Pd. 1.283 : octahedral covalent r; NC(TV) 1.31; Pd(TV) 1.31; .1.295 Å; Pd. 1.284 : octahedral covalent r; N(TV) 1.39; Joint F; Nd²⁺ 0.30; Pd(2+2); and nickel (18.153) are of like order. Such similitude in properties led one of us to suggest that there might be a motable concentration on of plating main palladium (19.154); distance is an soutable concentration of plating main palladium (19.154); distance is an soutable concentration of plating main palladium (19.154); distance is an soutable concentration of plating main palladium (19.154); distance is an soutable concentration of plating main palladium (19.154); distance is an else of the souter. South soutable concentration of plating main palladium (19.154); distance is an soutable concentration of plating main palladium (19.154); distance is an soutable concentration of plating main palladium (19.154); distance is an soutable concentration of plating main palladium (19.154); distance is an soutable concentration of plating main palladium (19.154); distance is an soutable concentration of plating main palladium (19 notable concentration of platinum and palladium in lateritic nickel-ores.



The mimeralogy and geochemistry of lateritic weathering of ultra-basic rocks has been studied by several workers (Santos-Ynigo and Eaquerra, 1961; Notr, 1964; Schellman, 1964; Zeiseink, 1969, 1971). Using the colorimetric method of analysis developed by Grimaldi and Schnepfe (1968), Zeissink (1971) determined platium and palladium in two Australian profiles; the distribution of the two elements in the overlying weathering zonce appears to be somewhat erratic, but there seems to be some possibility of concentration in the nickeliferous deposits. In general, relatively little is known about the geochemical behaviour of noble metals during weathering (Crocket, 1969, 1974).

The present paper reports on three lateritic profiles of different degrees of development and from widely separated localities. Each of the occurrences represents a useful source of nickel. The discribution of platinum, palladium, gold, and iridium as a function of depth has been determined. For the analysis of these trace elements neutron-activation has been the preferred method. In addition, the fractionation of several major, minor, and other trace constituents has been examined.

The localities are as follows:

The localities are as follows: <u>Guatemain</u> - Samples coded L were obtained from a profile in eastern <u>Guatemain</u>, some 50 miles inland from Puerto Barrios on the Caribbean coast. Latefile material occurs over a large area in association with hills of partly segnetivized periodite on the sides of Lake Iabal. The pattern of distribution at various elevations on gentle to fairly steep siopes and on III-defined terraces is probably partly due to block faulting. The climate is tropical and the vegetation developed on the ultramafic rock area is parse in comparison with the developed on the covering surrounding regions.

<u>BEN - New Caledonia</u>, - This deposit occurs at Lat. 22⁰17'S and Long. 166⁰30'E. Most of the area consists of peridotits and its alteration products. The peridotic is believed to have been introduced during the tertiary pariod. Lateritic type weathering evidently took place on a peneplain or mature land form that was being subjected to uplift and block faulting.

<u>BLP - Indonesia</u>. - This profile is located in the Pomalea district, Lat. 4³10'S, Long. 121⁰37'E. In this region large areas of ultra-basic rocks are in part overlain by nickel-bearing laterites. Topography is rugged, although there are plateaux. The climate is tropical, with heavy rainfall and dry intervals.

A description of the samples investigated is given in Appendix 1. The nomenclature used in our study to describe the various horizons in the profiles is as follows:

A - horizon: the eluviated (leached) top layers.

B - horizon: the illuviated (enriched) intermediate layers.

C - horizon: weathered parent material.

D - horizon: largely unaltered parent material.

 $\Lambda_{\rm h}$ idealized section through the kind of ore-body that we have studied is illustrated by de Chétalat (1967) and by Roorda and Queneau (1973).

Mineralogical information obtained from microscopic examination was Inadequate because the samples were supplied in a very finely powdered form. A further complication was the presence of an iron oxide coating on most

of the grains. Such coating was removed by chemical treatment with 0.03M acetic acid prior to electron-microscopic examination.

0.03, acetic acts prior to electron-microscopic examination. The mineral assemblages of the profiles comprised: serpentine minerals, limonite, goethite, chlorite, montmortillonite, and calc. Minor emounts of other minerals, such as magnetic and chronite, were identified. Goethite is microscopically recognisable as anisotropic fiskes, and diffraction patterns corresponding to a mixture of amorphous to poorly crystalline material (limonite, goethite, and hematite) were characteristic of all the profiles. Quartz was identified in very small amounts and was of chalcedonic type.

Although nickel was a significant constituent of the samples analysed, no specific mineral of the element was identified. In each profile the deepest or "least weathered zone" is mainly serpentinized perodotite.

Analytical Methods

The radiochemical neutron-activation method (RNAA) for determination of platinum, palladium, gold, and iridium has been described elsewhere (Ahmad, Ahmad, and Horris, 1977).

(Ahmad, Ahmad, and Morris, 19/7). Conventional chemical methods were used for quantitative analyses of silica, magnesium, chromium, iron, sanganese (Maxvell, 1968), copper, cobalt, (Sandell, 1959), and nickel (Vogel, 1962). In addition, chromium, cobalt, copper, iron, manganese, nickel, scandium, sodium and zinc were estimated by instrumental neutron-activation analysis (INAA) (Ahmad and Morris, 1977a). Determinations of total chiorine content and water-leachable chlorine were made by a nondestructive neutron-activation procedure (Ahmad and Norris, 1977b). Uranium was determined by an adaptation of the radiochumendar budiestic schemes (1975), and involved beta-counting at a suitable time interval (~ 1 day) after separation. separation.

Leaching experiments were made by adding $50cm^3$ of distilled water (PH 6.5) to 10g of powdered lateritic sample in a polytheme tube. The sealed tube was agitated for 1 hour, and, 24 hours later, measurements were made with an SIL direct reading pH meter, model 23A.

Results

The analytical results for the elements platinum, palladium, gold, and iridium in the three profiles are summarized in Table I. Contents of other elements are listed in Table II.

General Interpretative Procedures

Various procedures have been used as general aids to interpretation of the distribution of the elements in the profiles.

of the distribution of the elements in the profiles. (i) Plots have been made of molar concentration of element, expressed as mole per kg of sample, as a function of depth - cf. Reiche (1950). (ii) An indication of relative concentration in the profiles was gained by taking the ratio of the concentration of an element in a sample relative to its concentration in the <u>U.S. Geological Survey Reference</u> peridotic Procl (riangan, 1973; Amad, Amad and Morris, 1977). This is not so satisfactory as the use of concentration factors related to freeh unaltered rock underlying the laterites, cf. Zeissink (1971), but regrettably we did not possess samples of such material]. (iii) Correlation coefficients have been computed for the distribution of pairs of constituents in order to identify geochemical coherences. (iv) Resctine pH measurements were made to gain some indication of the effects of weathering on the composition of natural waters. Of course,

the data obtained, and listed in Table III, should be considered as giving only a rough guide to field conditions.

Discussion

UISCUSSION General - An examination of the analytical results as a function of depth reveals many characteristics in the geochemical behaviour of major and trace elements which recur in each of the profiles investigated. The weathering of the ultramafic rocks has resulted in relative depietion of silicon and magnesium and enrichment of iron, cobalt, nickel, copper, zinc, and scandium. Moreover, the concentration of noble metals is enhanced in the lateries.

enhanced in the laterices. Reaction pit through the profiles increases with overall depth, although the variations from monatomic behaviour shown in Table III may be of some consequence. Top surficial horizons are acidic in SNC and BIP, and in the relatively well developed New Caledonia profile magnesium and silicon have been practy thoroughly leached out. On the other hand, in the case of the L-profile the resction pH for the A-horizon is dightly basic, and the higher magnesium concentration is compatible with the fact that some weathered serpentine remains in this part of the laterite.

weathered serpentine tomains in this part of the interite. The basicity of a metal ion is a relevant factor affecting its distribution in a lateritic profile. Britton (1962) suggested that the basicities of metal ions be measured by the precipitation pl values of their hydroxides to oxides. In many cases of weathering, however, deposition arising from correctipitation processes, involving either isomorphous replacement or surface adsorption, or both, scher than separation of pure hydroxides, is important. Norton (1973) has described the conditions favouring the formation of laterite and bouxite as indicated by Bu-pH diagrams.

The distribution of the individual elements in the nickeliferous lateritic profiles is discussed below.

lateritic profiles is discussed below. Platinum and palladium. - In the three profiles there is a notable enrichment of both platinum and palladium relative to the parent rock. Results for the Gustemaina L-deposit demonstrate a striking correlation between the occurrence of platinum and nickel and also some correspondence between the distribution of palladium and nickel (Fig. 1). On the other hand, there does not appear to be geochemical coherence between either of the two noble metals and nickel in the New Caledonian weathering site -BNC. In all three profiles the contents of platinum metals are enhanced in horizons where the concentration of hydrows irroll¹¹¹ oxide is high. Rasin <u>et al</u>. (1965) suggested that platinum metals released from decomposed minerals are sorbed by freshly formed bydrated irroll¹¹¹ hydroxides and demonstrated such an effect with laboratory experiments. Stability constants for the formation of anionic platinum and palladium

hydroxides and demonstrates such an miract with importancy experiments. Stability constants for the formation of anionic platinum and palladium chloro-complexes are large (Sillén and Martell, 1964, 1971) and such complexes in aqueous solution may be of consequence in the transport of the elements (Otreman and Augustithis, 1967; Cousins, 1973a, b). Fuchs and Rose (1974) have suggested that in an area containing aqueous media the higher the chloride content the greater the mobility of the precious metals, and although chloride may not necessarily be essential for their migration it can certainly promote it.

Formation of organogaliadium complexes could have an influence on the distribution of pailadium. The Pd-content of a tree-sample has been reported by Fuchs and Rose (1974), who have suggested a possible pailadium mobility in an organic cycle - see also Cousins and Vermaak (1976). Iridium. - This element has a very low abundance in the lithosphere and

there is relatively little reliable information on its geochemical distribution (Crocket, 1969). Iridium is not readily attacked by acids, and the metal appears to be rather resistive towards chemical reaction in nature. In each of the three lateritic profiles there is a concentration of iridium relative to freeh rock, particularly in the A and B horizons.

The first first for the first first

in the more mature New Caledonian profile. Gold, like the platinum metals, is noble, and its compounds are readily reduced to metal. Hence, it is largely found in the native state, and because of its high density it often tends to become concentrated in placer deposits - again showing resemblance to platinum metals Nevertheless, gold may be dissolved and transported in aqueous medium, either as a complex ion, such as AuCL, or in colicial solution (Crocket, 1974). Tenyakov, Rakovskiy and Fillpova (1970) have noted that if gold is dissolved as an ionic species in the weathering process, adsorption on hydrous iron or aluminium oxide or clay minerals may effectively limit its prolonged leaching by ground water. Also it is appropriate to point out that the ion AuCl₄ and complex chloro-anions of platinum metals are strongly ported at low acidities and chloride concentrations by synthetic anion-exchangers (Diamond and Whitney, 1966).

anion-exchangers (Diamond and whitney, 1990). Silicon, - The geochemical distribution of silicon in the three profiles conforms to tendencies reported previously for laterites developed on ultramafic rocks. Silicon is depicted in all the weathered samples. There may be some discontinuities in this overall trend; thus near the surface of the BRC-deposit there is a residual concentration of difficulty soluble silicates, and this is borne out by mineralogical examination which revealed minute particles of the resistant group of silicates, typified by quartz.

The transport of silicaceous material takes place both in the colloidal state and in true solution (Krauskopf, 1959). A hydrous silica sol can undergo extensive mägration, because it is very insensitive to the floculation caused by electrolytes in solution. Moreover, additional relativisation may be brooght about by protective colloids of organic origin.

Magnesium. - Depletion of magnesium accompanying the transformation of rock to laterite is a pronounced feature of each of the profiles investigated. This trend appears to be a usual one, e.g., see Harriss and Adams (1966), Zeissink (1969). It is generally accepted that reinwater, containing carbonic acid, attacks olivine, which may contain 25% Mg (Goldschmidt, 1954), and leaches out the magnesium as bicarbonate

22% Mg (Goldschmidt, 1954), and leaches out the magnesium as bicarbonate. Our correlation coefficients show a marked coherence between the distribution of magnesium and silicon [Mg-Si; for L, +0.88; NNC, +0.93; BIP + 0.99]. The effect of rock-weathering on the composition of natural waters begins when rain-water comes in contact with mineral surfaces. It is apparent that alkaline conditions are produced, as indicated by the reaction pR of fresh rock, even when the rock is "acidic" in character -Marriss and Adams (1960). The higher the pR the more silica goes into solution, and magnesium, once brought into equeous solution, will only more then 10: reprecipitated independently as the hydroxile at a pR of more than 10.

The depletion of magnesium in the BNC-profile is more complete than

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n the L-profile, and this agrees with the conclusion that the former has ndergone more thorough weathering.

undergone more thorough weathering. Iron - Upper parts of the three profiles are rich in from^{III} oxide and hydroxide minerais, such as gosthita, hematice, and limonite. This very marked concentration may be regarded to some extent from the point of view that depletion of iron^{III} occurs at a slow rate in comparison with other constituents. However, in the New Caledonian profile there is somn indication that from has been dissolved in the uppermois layer and been redeposited at greater depth. Hydrous iron^{IIII} hydroxide has the low precipitation pR value of 2, but hunto or Tuivit acids could play a part in bringing about such solubility through complexing and reduction (Maingien, 166). The several factors affecting the solubility of iron in nature are discussed by Garrels and Christ (1965) and Berner (1970).

(Maignier, 1966). The several factors affecting the solubility of iron in mature are discussed by Garrels and Christ (1965) and Berner (1970). Mickel = Each of the three lateritic deposits that we have studied is a commercially important source of nickel (Boldt and Dueneau, 1967). In the Guatamaian profile nickel is most concentrated in the 3-burianos, and there appears to be correlation between the distribution of nickel moliton. A relationship between goethite and nickel in interviewas pointed out by Gombes (1963). Turner (1968) showed that high nickel values are senocited with zoned goethite concretions which contain high economic of anogames; this corresponds with the correlation coefficient for the contamany of the source of the source of the source of the nickel is initially sorted on the iron¹¹¹ hydroxide, bur bably the nickel is initially ached on the iron¹¹¹ hydroxide, bur bably the nickel has migrated downward until it is fixed, e.g., in serpentine. Redeposition may occur in small cracks and interrices in serpentine (Goldschmidt, 1954). The nickel magnesium hydroxilicate, garnierite, has been frequently reported at various localities in New Caledonia, but it was not identified in the BNC-profile from our mineralogical examinations. Cobalt, _ Undownhedly could ¹¹¹ and nickel¹¹¹ any undergo some substitution for iron¹¹¹ in lattice positions of constituent nilicate minerals in serpenting perioditie, and such isomorphous reprimers heat result of lateritic westering, and a parallelism in behaviour between cobalt and nickel is quice apparent in che case of the profile - 1. On the other hand there is negligible similarity between the distribution of cobalt and nickel is due to apparent in che case of the profile - 1. On the other hand there is negligible similarity between the distribution of cobalt and nickel is due to profile similarity between the distribution of cobalt and nickel is due apparent in che cobalt apparent and cobalt and there are very close association between cobalt and manganese

(cobaltion wad). <u>Chroquium</u>. - The usual amount of chromium in fresh serpentine is 0.31 per <u>Cert - De Wall</u> (1971). In primary rock the element occurs as accessary chronite, and it is also incorporated in minor quentities in clivine and chlorite. The lateritie samples contain only relatively small amounts of chromite and olivine, and some of the chromium in the profiles may well be affiliated with chlorite. Roorda and Queneau (1973) have demonstrated association of chromium with limonite. Our concentration factors for Cr as a function of depth indicate a loss of chromium from the shallow, horizon and strong concentration at intermediate depths. Chromium¹¹¹ forme an insolubile hydroxide, but under strong oxidizing conditions soluble chromate (Santos-Ynigo and Equerra, 1961; Wolfreden, 1965). Santos-Inigo uses this argument to explain the tendency for chromium to be concentrated near the base of the iron-rich zone in Phillipino - and be concentrated near the base of the iron-rich zone in Phillipino - and Cuban laterites.

Cuban laterites. The fresh ultramafic nocks mangenese probably occurs <u>Mangeness</u>. - In the fresh ultramafic nocks mangenese probably occurs predominantly as Mm²¹ (g = 0.80h), substituting for g^{-1} (g = 0.76h). Enrichment of the shown is noted in the <u>lifericas</u>, particularly in mangeness^{III} is probably unitally leached from the <u>lifericas</u> was the second bicarbonate, and in this respect it behaves like $tron^{II}$. The mangeness^{III} is oxidired to the quadrivalent state quite readily and such oxidation may take place in the weathering solution. Mangenese^{II} may remain first in solution as colloidal hydroxid and later may precipitate as wad or finely divided Moj; mangenomelane has been identified also by Zeissink (1971) in material from Australian nickeliferous lateritic profiles -(incidentally, he also recognized lithiophorite). Mangenese^{II} bydroxide has a weakly scidic character, whilst Fe(OH)₀ is weakly basic. Therefore, Mn(OM)₀ hydrosol is negatively charged and pe(OH)₀ hydrosol is positively charged. If the two sols are brought into contact with sach other, their charges are neutralized, and they flocculate together. Hence a mixture of hydroxides is formed. When there is an excess of one of the sols, the least abundant one will be recharged (Rankama and Sahma, 1950) and may migrate in ground water and surface water under auitable conditiona. This may account, at least in part; for the dereues in monitoment of mangenese in comparison to in observed in the auficial layer of profiles L and BNC. Copper. - Faust and Pahve (1963) reported copper contents of freeh

in the surficial layer of profiles L and BNC. <u>Copper</u>. - Rauts and Fahey (1963) reported copper contents of fresh screpentinities ranging from 4 to 32 ppm, while the parent rocks under two Australiam mickeliferous lateritic profiles studied by Zetasink (1971) where found to contain 23 and 7 ppm, respectively. Wedepohl (1974) in his taview has stated that olivine from abundant peridotitic rocks is ampacted to have an average copper content between 40 to 50 ppm and that other common constituent minerais will not contribute much Cu. It follows from this information and our analyses that copper is considerably enriched in the laterites in the A,B, and C horizons.

enriched in the laterites in the A,B, and C horizons. Sorption of coppeII from acycous solutions has been studied experimentally by Corress (1924) and by Krouehopf (1956), and it has been percenter by corress (1924) and by Krouehopf (1956), and it has been percented by corress (1924) and by Krouehopf (1956), and it has been percented by corress (1924) and the solution of the solution basic carbonate or be sorbed by irouIII bydroxids. Moreover, the high copper values in the top parts of profiles may be connected in part to association with organic material. Krauskopf's experiments demograted that at pH 7.1 to 8.2 the following extents of removal of copper limay be achieved by different adsorbents: montmorillonite, 99.4%; freshly precipitated hydrous ferric oxide, 98%; reshly percipitated hydrous manganese dixide, 95%; dead plankton, 42%; peat, 95%; lighte, 66%.

manganese dioxide, 96%; dead plankton, 42%; peat, 98%; lignite, 66%. <u>Scandium</u>. - Frycklund and Plaitecher (1963) estimate the abundance of scandium in the lithosphere as 30 ppm and Faust and Fahey (1962) report values in the range of 1-19 ppm Sc in serpentinites. It follows, therefore, that the element 1*a* quite enriched in the surficial and aballow horizons of the laterites. There is a striking correlation between the distribution of scandium and iron in the watering profiles. [correlation coefficient Sc-Fe: for L-profile 40.96; for BNC 40.90; for BIP 40.94 J- Fig. 2. The ionic radii Sc²⁺ z = 0.81% and Fe²⁺ <u>x</u> = 0.64, according to Pauling (1960), are not similar, but it has been reported by Frondel (1966, 1970) that a more representative value for the radius of 6 - coordinated Sc⁻, avitable for most generalised geochemical purposes, is ca. Q.738 or possibly less. A diadochic relation between Sc⁻ and Fe³⁺ is thus understandable. Following

extensive tropical weathering, scandium probably becomes largely associated with goethics. The ion Sc²⁺ is quite generally believed to be adsorbed by bydrous ironli and alumnium oxides and by colloidally divided clays (Lange, 1957; Turekian and Wedepohi, 1961; Vissov, 1968). It has been found experimentally to be strongly probed from artifical seawater by bydrous iron¹¹ oxide and clay, reaching 90-100 per cent at pH 7-8 (Yoshimut and Tatega, 1961). The carrying by ferric hydroxide starts at a pH rather above, 4 and reaches a maximum in the range where complete bydray bydray of 5c². (Gueebanchikova and Produdina, Yoshimut and Scherner, pH -6.5 (Greebanchikova and Produdina, Yoshimut and Scherner, pH -6.5 (Greebanchikova and Produdina). 1963)

<u>Sodium</u>. - Stueber and Goles (1967) determined sodium in a total of 113 ultramefic rocks by neutron-activation analysis. The arithmetic mean of the results was 0.104 per cent Na, and the highest concentrations of the element were in the more pyroxene-rich rocks.

Sodium content of the lateries generally decreases as a result of the transformation of rock and significant leaching occurs. Fluctuations in the general trend of depletion way be largely because of the occurrence of the element in detrical phases, such as clay minerals, but inevitably at least some sodium is present adopted on mineral phases and ion-exchange sites and as dissolved Na⁺ in interstital fluids.

exchange sites and as dissolved Na in interstital fluids. <u>Uranium</u>. - The concentration of uranium in ultramsfit rocks (dunites, serpentinites, etc.) is extremely low, 10-80 ppb (Rogers and Adams, 1969). Heier and Carter (1964) give the average figure as 14 ppb. In the lateritic profiles there is some increase in concentration in B and C-horizons, relative to that in fresh rock. During weathering, for uranium most probably has been brought into solution as uranium³⁷ (uranyl ion, 105^{25}_{3})²⁸ and been somewhat leached out of the shallow horizon. The soluble uranyl species are readily sorbed on hydroxide gels of iron, aluminium, and manganese, and on silica gel (Ramkama and Sahama, 1950).

 $^\circ$ It is of interest to note that the main hydrolyzed species of $\mathrm{UO}_2^{2.4}$ in water at 25°C are UO_20H⁺, (UO_2)_20H⁺, (UO_2)_20H⁺, (AD)_3, although the formation of polymerized hydrox-o-tridged species may not be very relevant at the ultramicro-concentrations of uranium that pertain in ground waters in the lateritie norfiles. lateritic profiles

<u>Zinc.</u> - In peridotites the average abundance of zinc is 56 ppm and serpentinites contain about the same mount, indicating no general loss or gain on serpentiniscion (Medaolity). The redistribution of zinc during weathering follows a pattern simily 0.08, spr ao.08, jn nthe (overlation coefficients Zn-Mn L-0.81; NMC - 0.96, spr ao.08, jn nthe Guardiation coefficients Zn-Mn L-0.81; NMC - 0.96, spr ao.08, jn nthe Guardiation coefficients Zn-Mn L-0.81; NMC - 0.96, spr ao.08, jn nthe duardiant of indonesian profiles there is correlation hetween sinc and iron [corr. coef. Zn-Fe: 1 - 0.96; SPF -0.9A] and the zinc is probably largely sorbed by goathite. On the other hand, in the profile-NMC the element is most concentrated in C horizons. This difference in distribution from that in profile-L, where the zinc is richest in the ferruginous A and B, horizone, again illustrates a greater extent of weathering in the New Caledonian occurrence. Chlorine. - Several workers have noted the bigh chlorine content of

Callering in the set Calebook Dynamic Dynamics of the high chlorine content of sergentinized ultramafic rocks (Foge, 1974). Earley (1958) has suggested that this has arisen during seepneiningation by chloride-rich solid solutions. Rucklidge (1972) has shown that the chlorine may occur in solid solution in sergentine, being absent from chlorine. However, there is evidence to suggest that chlorine may play a significant role in the alteration of olvine.

alteration of olivine. Goldachmidd (1954) assumed that during the process of weathering all of the shlortime in magnetic rocks would be released. According to Nem (1970), children assumed that during were released. According to Nem (1970), children assumed that during were released of the short of the release of the second second of the short of the second of the second concentrated considerably by only a few groups of organisms. Hence, the enrichment of chlorine in intermediate and deeper zones of the laterizes is perhaps rather supriming. Garcels (1967) has suggested that much of the chloride in ground waters has been derived from rain water, small mounts possibly being added from chloride-rich fluid inclusions. The greatest source of chlorine in rainfall is the sea, and the chloride-content of rain water is greater near the coast than inland (Eriksson, 1952; Junge and Werby, 1958). It is possible that chlorine may be lost from assume sealution

It is possible that chlorine may be lost from aqueous solution because of its incorporation in such minerals as chlorite (Johns, 1963). A conversion of montmortlinite to chlorite away arise because of assimilation of CI ions together with OH ions in intermediary layers of the chlorite, as magnessum hydroxychloride.

As mentioned earlier, the possibility of complexing platinum and palladium by chloride under oxidizing conditions may well affect the distribution of the two prectous metals in lateritic profiles. Moreove Krauskopf (1967) has shown by calculation that gold may be disaolved as AuCL in the presence of oxygen or Mhog under natural conditions.

Concluding Remarks

The mechanism of formation of laterities is still incompletely understood (Alexander and Cady, 1962; Maignien, 1966). Thorough aqueous leaching is funolved, because laterities are best devoloped where drainage is good and where rainfall is heavy for at least part of the year. Moreover, the higher temperatures that pertain in the hundl dropi. (equatorial) beit are clearly relevant to the intense weathering -PickerIno 1962). tropical lckering 1962).

It has been emphasized by Krauskopf (1967) that clay minerals are not true end-products of weathering but they are metastable substances formed as intermediates in the alow breakdown of rocks into constituent oxides. Hence in tropical mgions, where conditions of rainfall and topography are particularly favourable for thorough leaching, reactions may go beyond the clay-mineral stage. Evidence for this hypothesis is provided by the fact that normal clay soils are found in the tropics where leaching is leas commlere complete.

A comparison of our geochemical results with those for different major lateritic deposits studied by others (e.g., Hotz, 1964; Santos-Yrágo and Bequerer, 1961; Zeissih, 1969; 1971; Schellam, 1972; Reynolda, et.al., 1973) indicates many common trends in development, although the extent of weathering may be different in the various localities.

Note

Pauling's (and Ahrens's) crystal ionic radii have been cited in this article, and we consider that they provide a generally convenient numerical description for geochemical purposes, e.g., for appreciation of diadochic relationships. Nowever, it must be pointed out that they are not compatible with electron density distributions in 'ionic crystals' as

determined by X-ray differation membry distributions in "ionic crystals" as determined by X-ray differation methods (Norris, 1968). On the other hand, radii derived from electron density minima are probably only realistically applicable to alkali halides and similar crystals, and even among theirs asls the interionic distances show small deviations from strict. The savent Kasinir Pajane (1969) once exclaimed;"ionic radii - simple -tay do not axis:"



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TABLE I. <u>Distribution of noble metals as a function of depth through</u> <u>lateritic profiles.</u> Values in ppb $(\underline{\mu}g, \underline{k}g^{-1})$

A11

Pr Pd

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Depth

Des éd 1 a

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riorite	o amp 2 o		1			
	No.	m				
Guatemala	1	1.5 - 2	11,8+0.8	140+4	84+3	8.2+0.1
L	2	2.5 - 3	13.8+0.7	145 + 1	79+4	13.9+0.4
	3	3.5 - 4	8,9+0.1	173+9	57+1	15.2+0.5
	4	5.25-5.75	5.9+0.4	135+1	93+3	13.2+2.2
	6	8 - 8.5	5.6+0.4	101+1	50+1	7.4+0.1
	5	8 - 8.5	8.8+0.1	97+1	46+2	6.7+0.4
	7	10.25-10.75	3.2 + 0.2	68+2	37 <u>+</u> 1	5.040.6
New Caledonia	1	0 -2	30,4+3.7	108+9	80.0+2.1	8.0+0.7
BNC	2	2 -7	31.7+2.2	164 + 3	52.5+3.1	5.4+0.4
	з	7 -11	40.5+0.6	151+5	80.2+1.2	5.2+0.5
	4	11 -13	11.3+0.3	190+5	27.5+1.3	5.7+0.7
	5	13	8.0+1.3	131+2	24.6+1.0	6.5+0.3
	6	14	9.5+0.5	11073	21.5+0.5	5.1+0.6
	7	17 - 20	6.3+0.3	83 <u>+</u> 2	21.0+0.5	4.8+0.7
Indonesia	1	11 -13	14 ±1.9	67 <u>+</u> 3	52 <u>+</u> 2	16 ±1.3
BIP	2	13 -17	8.5+1.5	43+5	45 +3	7 +1.2
	3	18 -19	6.2-1.9	18-3	30 - 3	5.3 <u>+</u> 1.2
Results are bas deviation for a	ed on qu single	adruplicate a determination	nalyses of s is quoted.	samples	and the s	tandard

Fig. 1. Relationship between platinum and palladium and nickel in samples from the Guatemalan profile - L.

TABLE II. <u>Distribution of elements in lateritic profiles.</u> Contents in per cent unless indicated elsewhere. Singly underlined figures refer to INAA and doubly underlined figures are from radiochemical analysis.



M7

M8

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 <u>APERDIX 1</u>
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APPENDIX 1

Description of	weathering	g profile L lo	ocated near Lake Izabal,	Guatemala
Location and sample no.	Depth	Weathering borizon	Description	Moisture content %
L-1	1.5-2	A	Red-brown soil with organic matter and iron ^{III} oxide pellets. Slight amount of weathered serpentine.	4.9
L-2	2.5-3	^B 1	Highly weathered red- brown soil of plastic iron ^I LIoxides with some organic material. Fine earthy appearance.	5.6
L-3	3.5-4	Во	Yellow-orange soil with less iron oxide than L-2 and with saprolitic texture and some fragme of soft peridotite.	n 5.7 ents
L-4	5.25-5.75	°ı	Yellow-brown soil. Saprolitic texture with boulders of peridotite-serpentine.	5.7
L-5 Coarse L-6 Fines	8-8.5	С "о	Gray-yellow colour. Slightly weathered serpentine fragments and fine grained soil containing iron ^{III} oxide	8.0 8.1
L-7	10.25-10.	75 D	Slightly weathered peridotite-serpentine.	3.4

Description of weathering profile BNC located in southern New Caledonia,

Location and sample no.	Depth 1 m h	eathering orizon	Description	Moisture content	5
BNC-1	0 - 2	A	Ferricrete surficial soil, consisting mainly of iron ¹¹ Loxide (limonit Red-brown colour. Sligh amount of organic matter and some fragments of serpentine are present.	4.5 e). t	
BNC-2 BNC-3 BNC-4	2 - 7 7 -11 11 -13	A	Yellow-brown soils with texture analogous to BNC-1 but containing less organic matter. Textural resemblance begins to disappear in BNC-3 and BNC-4.	6.3 4.6 2.5	
BNC-5	13-14	8	Highly weathered, dark red soil rock completel disaggregated. Mostly limonite with asbolite.	y 2.7	
BNC-6	14-17	c	Yellow-brown colour; mai consists of saprolite an asbolite with less limon Some partly weathered serpentine rock fragment are also present in this horizon.	nly 2.6 d ite. B	
BNC-7	17-20	с	Grey-yellow colour; slig weathered rock with saprolitic texture.	htly 1.2	
Description of S	of weatherin ulawesi, 1	ng profile B Indonesia, L	IP located in the Pomalea at. 4° 10' S and Long. 12	-Kolaka 1º 37' E	
Location and sample no.	Depth	Weatheri horizo	ng Description	Moisture content	%
BIP-I	11 - 13	A	Red-brown colour with saprolite limonite, ambolite enstatite, and some grains of quar	1,7 Lz.	
BIP-2	13 - 14 16 - 17	В	Dark red saprolite, with ironIIIoxides enriched in base elements; asbolite.	2.0	
BIP-3	18 -19	с	Grey-yellow saproli serpentinized peridotite with guarte horwork	te; 2.5	

quartz powerk. Moisture content was estimated by the following procedure. - About 1g of sample was accurately weighed and transferred to a tared 30 cm³ -platimum crucible. This was placed in an oven, covered with a filter paper of 7.em.-diam., and heated at 105-110°C for 1 hour. The crucible was placed in a desiccator and allowed to cool for 30 min, before reweighing. The loss in weight was taken as representing the moisture content of the sample.