GEOCHEMISTRY OF WATERS AS RELATED TO WEATHERED ULTRAMAFIC ROCK IN NEW CALEDONIA

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INTRODUCTION - CHEMICAL COMPOSITION OF WATERS IN THE NEW CALEDONIAN ULTRAMAFIC MASSIFS

In order to complete the study of weathering of the ultramafic rocks under tropical climate in New Caledonia (TRESCASES, 1969a; 1973a), rivers, springs and ground waters were systematically sampled in the peridotite massifs of this island. These rocks are mainly composed of harzburgites, with a low content (10 %) of very magnesian orthopyroxene SiO_3 $Fe^{2+}_{0.08}$ $Mg_{0.92}$, 30 to 50 % of olivine SiO_4 $Fe^{2+}_{0.15}$ $Mg_{0.85}$ and 60 % to 40 % of serpentine (lizardite) Si_2O_5 $Fe^{2+}_{0.07}$ $Mg_{2.93}$ $(OH)_4$ (GUILLON, 1973; TRESCASES, 1973b).

The sites of sampling were chosen according to the morphology, in order to compare waters from different environments:
- lateritic high plateau with a serpentinous deep layer;
- steep slopes where weathering lets a serpentinous residue remain;
- piedmonts, which are nontronitic at the bottom of the profiles, and lateritic at the top;
- swampy lowlands and alluvial plains, mainly nontronitic.

On each sites the author sampled several times, according to the seasons: hot and rainy season (December to March); little dry season (April to May); cool and a little wet season (July to August) dry season proper (September to December). This study is based on about 700 water analyses, sampled over four years (1966-1970) (TRESCASES, 1969b; 1973b).

The average chemical composition of the spring and ground waters, in each topographic area and each season, is in tab. 1. These waters include chiefly bicarbonate, magnesia and silica: The amounts of magnesium, always high, change just a little through the year, but the range of variations of the silica amount is large; the dissolved silica exportation is higher in the wet season. These waters carry away the s o l u b l e   p h a s e   of weathering. Their composition is in conformity with what could be expected from the chemical composition of rocks and weathering profiles, progressively leached in silica and magnesia towards the top (tab. 2).

THERMODYNAMIC EQUILIBRIA BETWEEN SOLUTIONS AND MINERALS

The mineralogical study of weathering profiles show the following transformations of primary minerals:

$$\text{enstatite} \longrightarrow \text{talc + quartz + goethite}$$

$$\text{olivine} \begin{cases} \longrightarrow \text{opale + ferric gel} \\ \longrightarrow \text{nontronite} \end{cases} \longrightarrow \text{goethite} \quad \begin{array}{l}\text{(well drained areas)} \\ \text{(poorly drained areas)}\end{array}$$
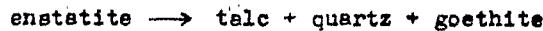
serpentine, first inherited, is dissolved next.

The hydrolytic reactions of the different minerals, primary and secondary, provisionally considered as exclusively magnesian, give the equilibrium equation of each mineral with a solution of silica and magnesia. The equation of each equilibrium line is computed by applying the mass action law, the equilibrium constant of which is deduced from the standard Gibbs free energies of formation ΔG^o_f of the final and initial products (GARRELS and CHRIST, 1965; ROBIE and WALDBAUM, 1968; HELGESON et al., 1969; TARDY, 1969). This calculation was carried out for each mineral observed in the weathering profiles, as well as for some minerals, the formation of which was expected:

peridot SiO_4 Mg_2	($\Delta G^o_f = -491.9$ Kcal/Mole)
orthopyroxene SiO_3 Mg	($\Delta G^o_f = -349.4$ Kcal/Mole)
serpentine Si_2O_5 Mg_3 $(OH)_4$	($\Delta G^o_f = -964.7$ Kcal/Mole)

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Table 1

Chemical composition of springs and ground waters

	Plateau				Slope				Piedmont					Lowland		
	1a	1b	1c	1d	2a	2b	2c	2d	3a	3b	3c	3d	4c	5a	5c	6d
pH	7.5	7.5	7.5	7.5	7.6	7.8	7.8	7.5	7.6	7.6	7.1	7.6	7.7	7.5	7.3	7.5
ρ	12000	12000	12000	12000	9960	10700	10100	9950	12300	11200	11100	12300	8300	6200	5050	1400
HCO_3^-	50.0	50.0	50.0	50.0	67.3	53.7	53.9	56.0	41.8	41.3	42.7	46.0	66.3	109.8	134.0	356
Cl^-	6.0	6.0	6.0	6.0	6.7	5.9	6.7	6.2	8.3	11.7	11.2	15.7	11.1	5.7	9.7	29.1
SO_4^{2-}	-	-	-	-	3.9	3.3	6.8	7.9	2.2	4.5	2.9	-	6.5	8.9	8.2	2.5
CaO	1.5	1.7	1.5	2.1	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.5	3.7	5.0	20.4
Na_2O	4.0	4.0	4.0	4.0	3.6	3.6	3.5	3.6	7.6	8.2	7.9	7.1	6.9	5.1	5.8	17.0
K_2O	0.1	0.1	0.1	0.1	0.5	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.3	0.2	0.3	0.2
MgO	12.4	12.9	12.8	13.6	21.8	20.3	19.5	19.9	14.8	15.7	15.9	17.6	23.1	37.0	35.7	207.0
SiO_2	12.3	10.6	11.3	7.7	19.8	17.7	16.9	17.1	14.7	13.4	12.6	11.0	21.5	29.7	25.5	25.4
n	14	14	14	14	16	11	5	21	7	13	8	5	3	3	3	1

1 to 4 : Springs (1 : Dumbéa Est; 2 : Couvelée; 3 : Prony; 4 : Plum). 5 and 6: ground waters in alluvial plain (5 : Dumbéa; 6 : Tontouta). a : hot and wet season; b : little dry season; c : cool and wet season; d : dry season. ρ : Ω cm; HCO_3^- to SiO_2 : mg/l; n : number of samples.

Table 2

Chemical composition of weathering profiles

| %	Rock	Plateau			Slope		Piedmont			Lowland	
		3	2	1	2	1	3	2	1	2	1
H_2O^+	11.5	13.0	13.7	13.5	10.2	11.0	13	13	13	6.5	13.1
SiO_2	37	33	1.2	0.5	38.1	30.1	33	3.5	2	28.2	2.3
FeO	5	2	1	0.3	26.3[M]	37.7[M]	2	1	0.3	29.0[M]	64.7[M]
Fe_2O_3	3.5	17	72	74			18	71	73		
Al_2O_3	0.4	2	4.5	5	4.5	4.5	1	4	6	15.4	11.7
CaO	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MgO	41	29	0.9	0.5	18.2	12.5	29	1	0.7	9.1	0.7
Cr_2O_3	0.4	0.8	4.0	5.5	0.5	1.2	0.8	3.8	3.8	9.7	3.4
MnO_2	0.14	0.29	1.0	0.5	0.28	0.45	0.5	1.0	0.4	0.4	0.6
NiO	0.40	2.5	1.0	0.4	0.33	1.45	2.5	1.0	0.3	1.5	0.7
CoO	0.02	0.08	0.2	0.07	-	-	-	-	-	-	-

[M]   total iron as Fe_2O_3.

1 : Superficial layer; 2 and 3 : deep, weathering layer (saprolite)

talc $Si_4O_{10} Mg_3 (OH)_2$ $(\Delta G_f^o = -1320$ Kcal/Mole$)$

sepiolite $(Si_3O_{7.5}) (OH) Mg_2 (H_2O)_3$ $(\Delta G_f^o = -1105.6$ Kcal/Mole$)$

brucite $Mg (OH)_2$ $(\Delta G_f^o = -199.5$ Kcal/Mole$)$

magnesite $Mg CO_3$ $(\Delta G_f^o = -246.1$ Kcal/Mole$)$

The lines calculated in this manner are plotted in fig. 1, with the solubility lines of quartz (6 ppm SiO_2) and silicic gel (130 ppm SiO_2). For magnesite the equilibrium line depends on the partial pressure of CO_2. In the weathering profiles $[pCO_2]$ is close to $10^{-2.7}$ probably with extreme values of about 10^{-3} and $10^{-1.5}$.

For nontronite the composition of which is

$$(Si_{3.73} Al_{0.27}) (Fe_{1.66}^{3+} Al_{0.07}^{3+} Mg_{0.25}^{2+} Ni_{0.16}) O_{10} (OH)_2 Mg_{0.135}$$
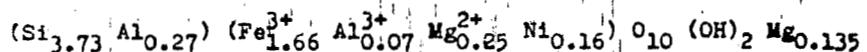
the calculation cannot be carried out in the same way: this mineral includes iron, and its free energy ΔG_f^o value was not known. However, the author used an indirect way: this mineral appears at the bottom of the piedmont profiles, where it replaced olivine, and it weathered into goethite next; nontronite also forms in the swampy lowlands where goethite is deposited and resilicified, through an amorphous stage (TRESCASES, 1973b). There is thus a reversible transformation nontronite $\rightleftarrows$ ferric gels, goethite. Ground waters sampled at PLUM (see tab. 1) were considered in equilibrium with nontronite, massively present in the weathering profile. The equilibrium line nontronite $\rightleftarrows$ ferric gels (goethite) (fig. 1) divides the field of ground waters from the alluvial plains (nontronitic), and the field of waters sampled in the upper part of the piedmont profiles (goethitic layers). For the concentrations of H^+, Mg^{2+} and SiO_2 in the PLUM water, the calculation from the reaction ferric (Al, Ni) gels $\rightleftarrows$ nontronite yields the equation of the line plotted in fig. 1, and the standard Gibbs free energy value of formation for this nontronite: $\Delta G_f^o = -1081$ Kcal/Mole[1].

The location in fig. 1 of sampled waters shows, for each mineral, the direction of the transformation in process, neoformation or hydrolysis, according to whether the water is situated inside the stability field of the mineral or not.

Therefore, the composition of waters shows that the three primary silicates are unstable with regard to these solutions, and are hydrolysed in the following succession: olivine first, enstatite next, and lastly serpentine. This succession is in good agreement with the mineralogical data about the weathered profiles. The sampled solutions are too diluted to allow sepiolite or brucite to form. On the other hand, magnesite precipitation takes place in the driest alluvial plains: the concentrations reached by ground waters explain this process. The equilibrium line of talc shows that sampled waters are close to stability with regard to this mineral. However, talc would be stable only in concentrated waters of the bottom part of the weathered profiles; more diluted solutions of the upper layers hydrolyse talc. The following should be pointed out: the concentration of the intra-crystalline solutions is expected to exceed the concentration in intercrystalline solutions, and a fortiori that of the sampled waters; indeed, precipitation of silicic gel takes place in weathering olivines, in the bottom part of the plateaux profiles, though fig. 1 does not show this process.

RELATIVE SPEEDS OF LEACHING AND WEATHERING PARAGENESES

The chemical study of ground waters permits one to consider the time factor: this gives an estimation of the p r e s e n t dynamics of weathering.

Outline of the calculation

The relative speeds of leaching have been used by PEDRO (1964; 1968) and TARDY (1969; 1971) to rediscover the principal ways of weathering. These works were applied to granitic or basic rocks, by using aluminium as an insoluble reference. For ultramafic rocks, where

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[1]By calculation from the reaction goethite (Al, Ni) $\rightleftarrows$ nontronite ΔG_f^o Nontronite $=$ -1094 Kcal/Mole
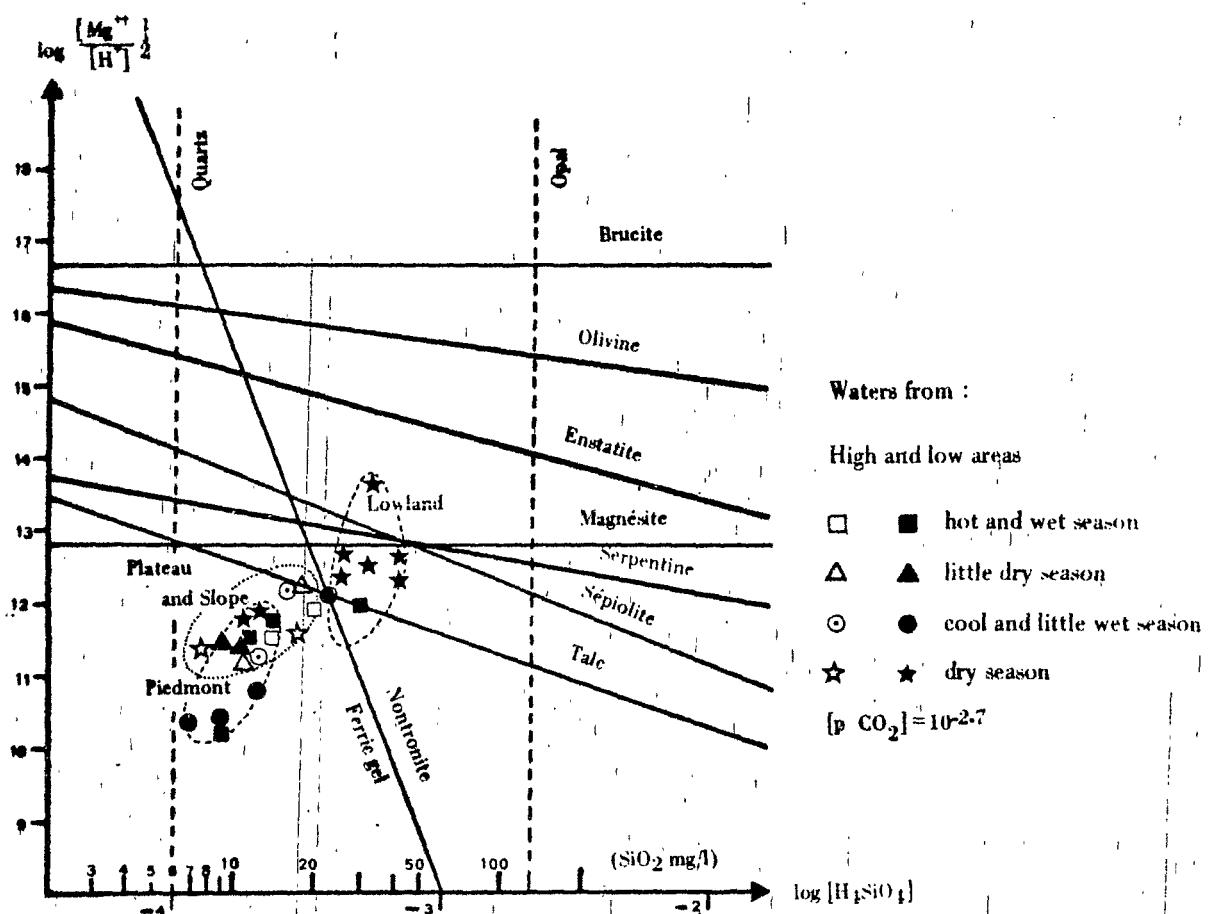
Figure 1. Stability fields of minerals and chemical composition of spring and ground waters
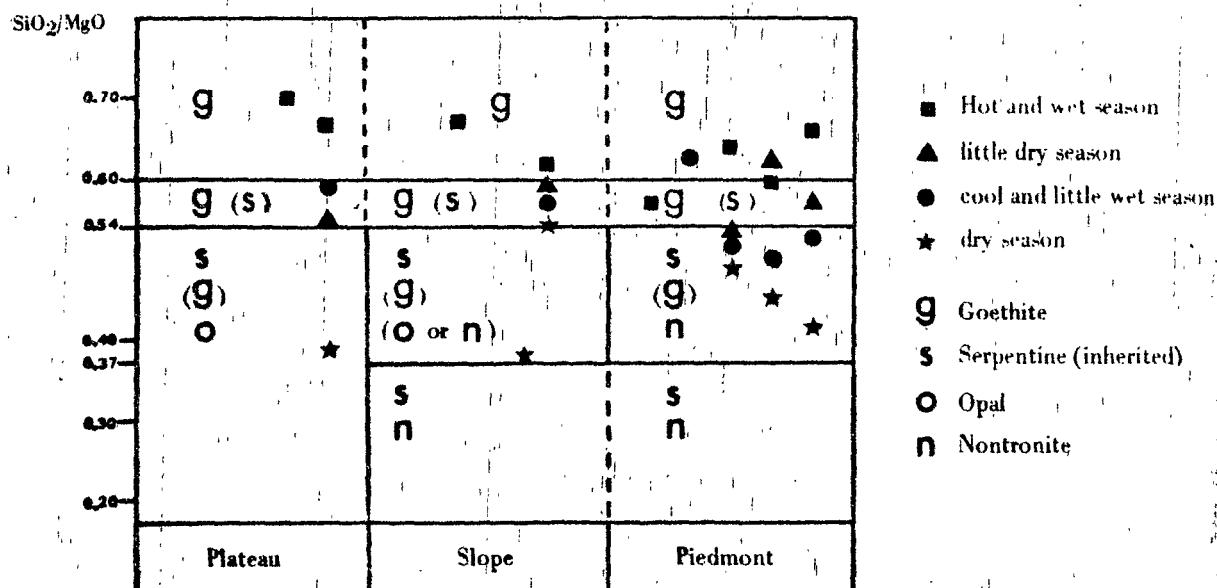
Figure 2. Values of L = SiO₂/MgO in the sampled waters, according to climatic and morphologic factors, and correlative minerals in weathering profiles

main part of the components (SiO_2 and MgO) is soluble the author used magnesium as the reference, considering that this element was completely and always removed by weathering, as is true in most cases.

In order to compare speeds of leaching S of silica and magnesia, the molecular ratios SiO_2/MgO calculated in water (L) and in fresh rock (R) are used. Theoretically, three cases can be defined:

$$L = R \quad \text{that means} \quad S_{SiO_2} = S_{MgO} \quad (1)$$

$$L > R \quad \quad\quad\quad\quad S_{SiO_2} > S_{MgO} \quad (2)$$

$$L < R \quad \quad\quad\quad\quad S_{SiO_2} < S_{MgO} \quad (3)$$

In case (1) the rock is simply dissolved. In case (2), magnesia would be relatively increasing in the weathered profiles; this is inconsistent with the observations of the profiles. In case (3), silica is relatively increasing during weathering; this occurs at the bottom of the profiles, with precipitation of silicic gel and preservation (inheritance) of serpentine. In fact, when L is higher than R, the ratio SiO_2/MgO of the hydrolized material is higher than the a v e r a g e ratio R of the fresh rock: when silicic gel and serpentine are dissolved, L becomes higher than R.

The author calculated all the limiting values of L in every case of weathering of peridot and serpentine, with the following hypotheses (supported by the mineralogical study of weathering profiles):
- the dissolution of serpentine begins when olivine is completely weathered;
- magnesium is always wholly removed.
These limiting values of L depend on the ratios SiO_2/MgO in minerals and rock.

In order to compare all the waters, relative speeds of leaching were calculated in regard to an average peridotite (10 % enstatite, 44 % serpentine, 46 % olivine). The ratio SiO_2/MgO equals 0.54 for olivine, and 0.60 for the olivine + serpentine mixture. When all the iron of olivine is combined with silica to form nontronite, L equals 0.37.

Application

The different ways for weathering in the successive morphological environments are illustrated in fig. 2. Values of $L = SiO_2/MgO$ in the sampled waters are plotted along the ordinate axis: the a c t u a l evolution of peridot and serpentine according to the climatic and morphologic factors is shown (tab. 3). Opal and nontronite, formed to the detriment of olivine, and inherited serpentine only constitute a temporary residue in the bottom part of weathering profiles; this residue is preserved u n d e r t h e f a - v o u r a b l e c o n d i t i o n s of the dry season. During the hot and wet seasons, weathering is more complete in the less deep layers; serpentine, opal and nontronite are dissolved. In gently sloping areas, evolution becomes complete and ends by total ferrugi- nization.

GEOCHEMICAL BALANCE OF WEATHERING, IN EACH ENVIRONMENT

The use of hydrological data allow one to calculate a quantitative reconstruction of the weathering balance, for a river basin, or for a morphological unit. The geochemical balance of weathering is expressed by two values:
- mean annual tonnages exported in the solution from a river basin (chemical erosion);
- rate of lowering of the weathering front.

Outline of the calculation

C h e m i c a l e r o s i o n :

Calculation is carried out using the inter-annual mean values of silica and magnesia in waters. For each element, annual tonnage exported in the solution (t/km^{2}year) is

obtained by multiplying the amount (g/m^3) of this element by the amount of flowing waters per 1 km^2 of basin area. This last datum is calculated from the mean annual discharge (river), or from the height of rain-fall, corrected by the flow coefficient.

Rate of lowering of the weathering front:

Reactions of mineralogical transformations which occur by weathering are applied, and the balance of silica and magnesia is computed. For example, for weathering on slopes, the calculation was applied to the mountainous Dumbea Nord river basin. If we consider x to be annual amount (kg) of weathered peridotite per 1 km^2, the mineralogical content of x is:

3.15 x moles olivine + 1.5 x moles serpentine + 0.95 x moles orthopyroxene

The weathering reactions can be expressed as (TRESCASES, 1973b):

- 3.15 x olivine $\longrightarrow$ 2.52 x SiO_2 (dissolved) + 5.83 x MgO (dissolved)

  $+ 0.63$ x SiO_2 (residual) + 0.47 x goethite
- 0.95 x orthopyroxene $\longrightarrow$ 0.15 x SiO_2 (diss.) + 0.30 x MgO (diss.)

  $+ 0.19$ x talc + 0.04 x quartz + 0.076 x goethite
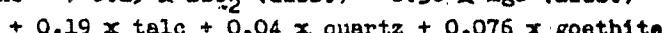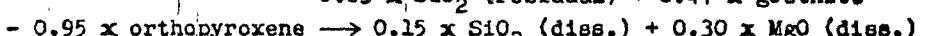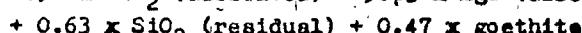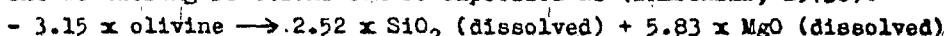
If y moles serpentine are hydrolysed out of 1.50 x moles:

- 1.50 x serpentine $\longrightarrow$ 2 y SiO_2 (diss.) + 2.93 y MgO (diss.)

  $+ (1.5 x - y)$ serpentine (inherited) + 0.25 y goethite.
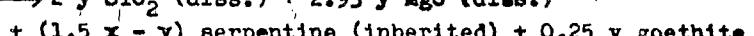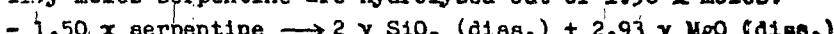
If z moles of residual silica are redissolved:

- 0.67 x SiO_2 $\longrightarrow$ z SiO_2 (diss.) + $(0.67 x - z)$ SiO_2 (res.)
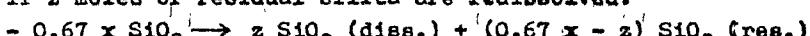
If w moles of talc are hydrolysed:

- 0.19 x talc $\longrightarrow$ 4 w SiO_2 (diss.) + 3 w MgO (diss.) + $(0.19 x - w)$ talc
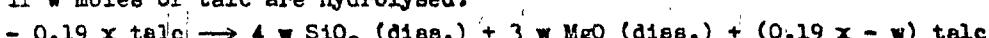
On the whole:

2.67 $x + 2$ $y + z + 4$ w = Total amount of SiO_2 exported in the solution (mole/km^2/year)

6.13 $x + 2.93$ $y + 3$ w = Total amount of MgO exported in the solution

Thus, we have two equations with four unknown quantities. This system is solved by testing several hypotheses. In fact, z and especially w are always low as compared to y. In the case of the Dumbea Nord river basin, the ratio $L = SiO_2/MgO$ in water equals 0.44; therefore, the latter shows (see fig. 2) that the weathering of serpentine is very weakly y must be low. Thus, one can consider z and w as negligible. The solution of the system of equations yields values of y and x, the annual amount of weathered peridotite per 1 km. The chemical composition of this rock is known, which allows one to reconstruct the geochemical balance of weathering completelly (tab. 4). By dividing the value of x (t/km^2/ year) by the rock density (d = 3), the rate of lowering of the weathering front can be inferred.

Application

The previous calculation was carried out for representative areas of each of the four types of morphology. The results, plotted in tab. 4, give the geochemical balance of weathering for each environment.

The very high values of chemical erosion show that peridotites are very liable to weathering under the hot and wet climate of New Caledonia. Their almost soluble characteristic, in some cases, explains the evolution of the landscape towards a "peridotitic karst" (WIRTHMANN, 1970; TRESCASES, 1973b).

The comparison between the values of chemical erosion and the rate of lowering of the weathering front shows that:

- on plateaus weathering is rapid and complete;
- on slopes it is more rapid, but less complete;
- on piedmonts in contrast, it is less rapid than on the plateaus, but as complete as there;
- in the swampy lowlands, it is slow and remains uncomplete (on account of the confinement).

Table 3

evolution of olivine and serpentine with climatic and morphologic factors

	Dry season	Hot and rainy season
Well drained high areas (plateau, slope)	Olivine ⟶ opal + ferric gel	Olivine ⟶ opal + ferric gel ⟶ goethite
	Serpentine is preserved (inherited)	⟶ Serpentine is dissolved
Poorly drained areas (piedmont, lowland)	Olivine ⟶ nontronite	Olivine ⟶ nontronite ⟶ goethite
	Serpentine is preserved (inherited)	⟶ Serpentine is dissolved

T a b l e 4

Geochemical balance of weathering (in t/km^2/year)

		Plateau	Slope	Piedmont	Lowland
Mean annual value of the tonnage of peridotite subject to weathering (t/km^2/year) ⟶		87.0	138.0	56.9	37.6
Soluble phase	SiO$_2$	33.3	22.7	21.7	10.7
	MgO	38.7	34.7	24.8	15.9
	CaO	0.09	0.23	0.10	0.06
	Na$_2$O	0.09	0.14	0.06	0.04
+					
Residual phase	Serpentine (inherited)	2.5	59.1	0	0
	Opal and Quartz	1.3	5.56	1.13	0.61
	Talc	0	9.94	2.15	1.43
	Nontronite	0	0	0	7.48
	Goethite	7.10	6.87	4.66	3.06
	Al$_2$O$_3$	0.26	0.27	0.17	0.11
	Cr$_2$O$_3$	0.42	0.39	0.28	0.18
	MnO$_2$	0.10	0.08	0.06	0.04
	NiO	0.35	0.30	0.21	0.14
Chemical Erosion (t/km^2/year)		72.2	57.8	46.7	26.6
Rate of lowering of the weathering front (mm/1000 years)		29.0	46.0	19.0	12.5

CONCLUSIONS

The thermodynamic reasoning allowed us to study the equilibrium state of the diffe-rent minerals in regard to the sampled ground waters. The succession of relative stabili-ties is shown by the diagrams, but the neoformation of some secondary products is not al-ways in evidence. Indeed, the sampled waters generally come from the upper part of the aquifer. They are more dilute than waters from the bottom layers, and, a fortiori, than intracrystalline solutions.

The study of the relative speeds of leaching of silica and magnesia showed for each season the mineralogical nature of the secondary products which neoformed. Thus the che-mical study of waters completed the mineralogical study of the weathering profiles: the study of waters allowed us to explain that the vertical succession of several secondary parageneses inside profiles was the result of the alternation of dry and wet season, a characteristic alternation of the subtropical climate of New Caledonia.

Lastly, the calculation of the weathering balance showed the role of the morphologi-cal environment. The intensity of the chemical processes of weathering is higher in high areas than in low ones thus their actions lead to a progressive flatteness of the land-scape. Of course, the mechanical processes of erosion (TRESCASES, 1973b) magnify this flattening tendency very much.

Remark: For further particulars on calculations, in paragraphs II, III and IV, see
TRESCASES, 1973b.

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