The occurrence and interpretation of carbonate and sulfate minerals in a sequence of Vertisols in New Caledonia

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Abstract

In the Tamoa Valley, on the western coast of New Caledonia, a Vertisol sequence shows a downslope transition from *calcimagnesic* Vertisols containing gypsum, aragonite, and magnesium-calcite, derived from flysch colluvium, to *hypermagnesic* Vertisols, rich in dolomite and magnesite, and derived from peridotite and serpentinite alluvium deposited by the Tamoa River.

Gypsum, magnesium-calcite and magnesite were probably formed during the dry period of the last glaciation, between 30,000 and 17,000 yr B.P. Magnesite nodules seem to be allochtonous, and were formed upstream by the weathering of serpentinite. During the more humid period of last Flandrian transgression (5000 yr B.P.), floods of the magnesium-rich waters of the Tamoa River over the alluvial plain brought magnesium to the soils and lead to fluctuations of the water table. These conditions favoured the formation of manganese deposits as mangans, calcite pseudomorphs after lenticular gypsum, crystallization of authigenic barite in *calcimagnesic* Vertisols, and dolomite formation in *magnesic* and *hypermagnesic* Vertisols. During the recent period, apparently drier, aragonite is forming in the lower part of *calcimagnesic* Vertisols.

1. Introduction

New Caledonia (166–168°E, 20–22°S) is a cratonic island 400 km long, 40 km wide, and oriented NW–SE. The west coast of New Caledonia is the leeward side of the island, and has a dry subtropical oceanic climate with a marked dry season. The yearly average rainfall ranges from 800 to 1100 mm.

Geologic strata, which range in age from pre-Permian to Late Eocene, are oriented parallel to the long axis of the island (Paris, 1981). During the Late Eocene, a sheet of peridotite (mainly dunite and harzburgite) overthrust the major part of the island (Recy, 1982) and presently covers more than 30% of the island (Fig. 1). Since the Miocene, intensive tropical
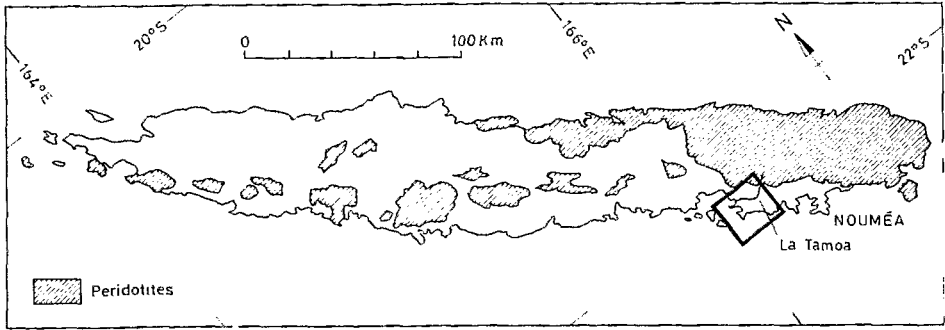
Fig. 1. Location of the studied area in New Caledonia.

weathering has affected the peridotite massif (Trescases, 1975; Latham, 1986) and the other geological formations. Peridotites are very sensitive to tropical chemical weathering which liberates high amounts of magnesium. Magnesium-rich soils cover large surfaces in New Caledonia, especially on the western dry coast, and a specific terminology for the soil classification has been developed by Tercinier (1962) and Latham et al. (1978). Applied to Vertisols (Podwojewski and Beaudou, 1991), this terminology is based on the exchangeable Mg^{2+}/Ca^{2+} ratio (MCR). When the MCR of the horizon located below the A horizon ranges from 0.5 to 3, the Vertisol is *calcimagnesic*, from 3 to 10 it is *magnesic* and over 10 it is *hypermagnesic* (Table 1).

The majority of streams are oriented perpendicular to the long axis of the island. Consequently, they rework many different geological strata, whose weathering residues are found in alluvial terraces. Two such alluvial terraces are present on the southwest coast. A pedological study of the left bank of the Tamoa River, southwest of New Caledonia, showed that the terrace system is connected to a piedmont beneath a hill composed of Middle to Late Eocene flysch (Fig. 2). From that hill to the river, seven soil profiles have been studied. Starting with the upper part of the catena and continuing in the downstream direction, the soil nature is as follows (Fig. 3): Brunisol (Référentiel Pédologique, 1992) to Vertisol over the flysch, *calcimagnesic* Vertisols in the transition colluvial deposits, and *magnesic* to *hypermagnesic* Vertisols on the old alluvial terrace. The recent terrace is composed of sandy-loamy Fluvisols.

During the late Quaternary, old *calcimagnesic* colluvium deposits were covered by magnesium-rich alluvial deposits (Podwojewski and Delaune, 1993). The Tamoa River, which drains peridotites in its upstream basin, contains very high amounts of dissolved magnesium carbonate. During cyclones or tropical depressions, the Tamoa River floods the alluvial plain, and is, thus, believed to be responsible for the high magnesium content in the Vertisols.

What is striking in this case is that gypsum, aragonite, magnesium calcite, dolomite and magnesite occur in the same soil sequence. Therefore, the objectives of this work were (1) to determine the form, composition and mode of formation of sulphate and carbonate minerals, (2) to estimate the consequences of magnesium inputs on these minerals, and (3) to establish a paleohydrological history of the area.

The study is descriptive in nature because the use of the thermodynamic modelling of the dissolution and/or precipitation of the calcium and magnesium is limited in the soil

Table 1
Some physical and chemical characteristics of the soils studied

Sample Hz	Depth	pH	Clay	Silt	Sand	Organic C	CEC	Ca	Mg	K	Na	Exchang. Mg/Ca
MER	(cm)				Texture (%)	(g/kg)	(cmol$^+$/kg)	Ca	Mg	K	Na	

Sample Hz	Depth (cm)	pH	Clay	Silt	Sand	Organic C (g/kg)	CEC (cmol$^+$/kg)	Ca	Mg	K	Na	Exchang. Mg/Ca
Calcimagnesic Vertisol												
52-1 A1	0–20	6.1	48	39	13	33.5	43.3	15.2	17.1	0.51	1.48	1.13
52-3 A3	40–65	7.5	63	23	14	6.8	44.3	17.1	24.8	0.19	4.05	1.46
52-5 V	100–155	6.6	65	23	12	3.0	43.1	14.3	24.7	0.21	6.10	1.73
52-7 C	170–180	6.1					32.9	17.1	22.5	0.07	7.04	1.32
Gypsum-bearing calcimagnesic Vertisol												
63-1 A1	0–15	5.9	49	34	17	30.4	36.2	12.0	14.7	0.84	0.65	1.23
63-3 A3	35–50	6.2	48	29	23	8.4	34.4	11.6	16.3	0.11	4.06	1.41
63-6 V	90–125	5.3	66	23	11		46.5	13.1	24.5	0.10	8.80	1.87
63-7 V$_{Gy}$	125–140	5.8	70	19	11		41.6	20.1	24.3	0.14	7.88	1.21
63-11 V1$_{Ca}$	195–240	8.2	66	18	17		46.2	21.4	28.6	0.12	8.83	1.34
63-12 V2$_{Ca}$	240–250	8.4	47	20	33		40.0	20.8	23.7	0.13	8.06	1.14
65-1 A1	0–15	5.8	52	31	16	17.4	35.5	8.96	13.8	0.34	2.14	1.54
65-3 A3	40–60	4.7	55	33	12	6.0	37.1	8.39	17.3	0.08	5.67	2.06
65-6 V	100–120	5.1	62	27	11		42.1	9.37	22.2	0.20	7.88	2.37
65-9 V$_{Gy, Ca}$	160–210	6.8	72	23	4		50.9	13.6	31.2	0.33	10.5	2.29
Magnesic Vertisol												
56-1 A1	0–12	5.7	55	38	7	23.5	38.5	8.75	18.2	0.40	2.26	2.08
56-3 A3	25–40	5.8	66	28	6	11.2	47.0	10.1	27.1	0.31	4.09	2.68
56-6 V$_{Mn}$	80–100	7.3	66	30	5		48.1	10.0	30.8	0.09	8.36	3.08
56-9 V$_{Ca,Mg}$	190–250	7.9	62	34	4		45.6	9.50	28.8	0.24	8.01	3.03
Hypermagnesic Vertisol												
71-1 A1	0–30	6.1	44	40	16	25.3	42.5	4.96	28.9	0.17	0.98	5.83
71-3 A3	50–72	7.2	59	29	12	6.0	51.4	3.78	44.4	0.07	2.41	11.75
71-5 C$_{Mg}$	90–200	8.1	41	27	32		35.5	3.19	32.1	0.30	1.72	10.06
72-1 A1	0–20	5.8	55	35	10	16.1	49.2	4.53	36.8	0.19	1.64	8.12
72-3 A3	37–52	6.7	60	30	10	6.9	52.9	2.00	45.1	0.09	2.45	22.55
72-5 V	70–95	8.0	62	28	10		54.4	1.47	52-1	0.06	3.19	35.44
72-8 C3$_{Mg}$	125–140	8.1	40	22	38		40.8	1.54	37.1	0.27	2.69	24.09
72-9 C4$_{Mg}$	140–180	7.9	60	27	12		51.0	1.02	46.6	0.32	3.11	45.69

Hz: Horizon.
CEC: Cation Exchange Capacity.

studied for the following reasons: (1) the sampling of the soil solution in situ is very difficult in the Vertisols; (2) the ionic composition of water extract gives only a partial idea of the composition of soil solution because it induces dissolution and precipitation of some minerals and exchange with the adsorbed fraction on clays; (3) it is not certain that the current soil solutions are representative of the conditions under which calcite, dolomite, and magnesite were formed in the past.
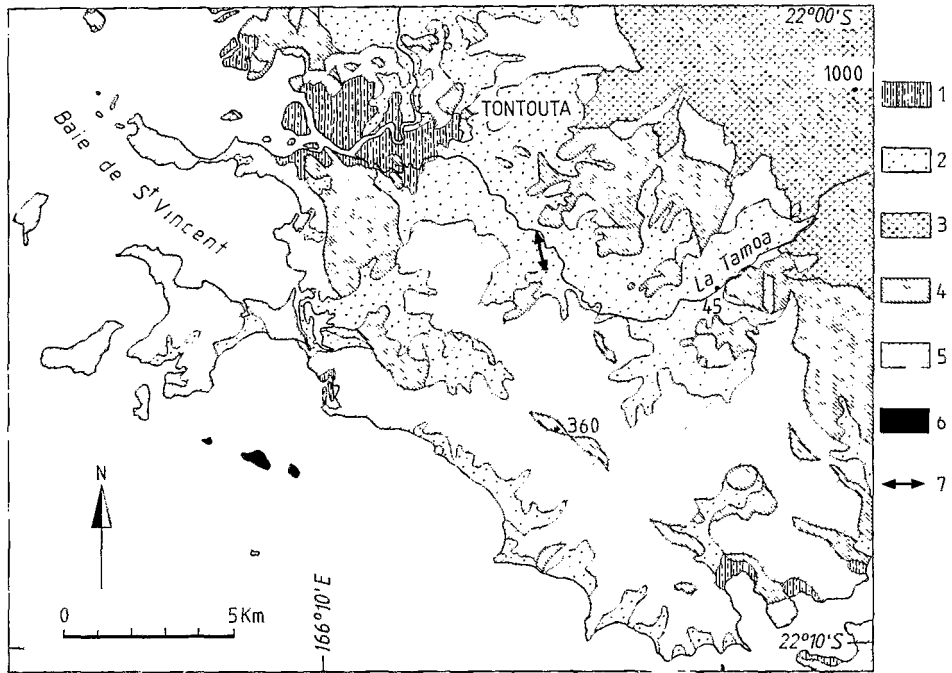
Fig. 2. Geological map of the Tamoa Valley and location of the soil sequence. 1: mangrove: 2: alluvial deposits; 3: peridotites and serpentinites (Oligocene): 4: terrigenous shales (Senonian) and phtanites; 5: basalts and flyschs (Eocene): 6: aeolianites (Plio–Pleistocene): 7: location of the studied sequence.

2. Materials and methods

2.1. The soils

Fourteen deep Vertisols were described according to the new French Référentiel Pédologique (1992) and seven of these were studied by macromorphological and micromorphical methods. The Vertisols evolve progressively from a *calcimagnesic* pole (MER 52) at the piedmont of the flysch hill, to a *hypermagnesic* pole in the middle of the alluvial plain (MER 71 and 72; Figs. 2, 3, Tables 1 and 2). The morphological properties of the different types of Vertisols are very similar. In particular, the variation in exchangeable Mg and Ca has no visible influence on the soil structure. These features are common to many Vertisols, which display a nutty structure (fine angular blocky) at depths of 0–20 cm, an intermediate horizon with a coarse prismatic structure, and below 60 cm depth, a sphenoid structure (Eswaran et al., 1988), with wedge-shaped aggregates and slickensides characteristic of a vertic horizon (FAO, 1971–1981; Dudal and Eswaran, 1988: Référentiel Pédologique, 1992). Vertical cracks are poorly visible at the soil surface. At about 1.50 m depth, a 10 cm thick black horizon is visible on the external edges of the terrace. This layer is rich in manganese oxides in the form of small concretions, dendrites, and mangans along the slickensides and around the tubular porosity. This oxide concentration indicates the upper limit of the fluctuation of an old watertable.
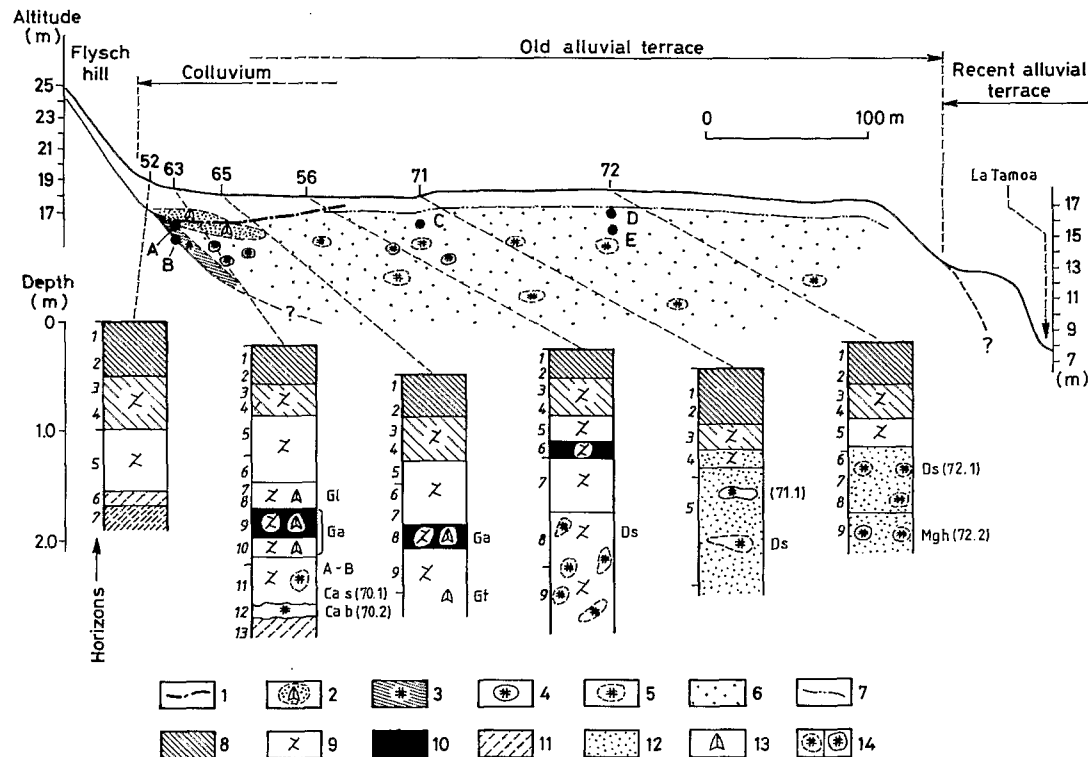
Fig. 3. Schematic location of the soil sampling. **The soil sequence:** Location of carbonate samples analyzed in Tables 3 and 4. A: MER 70.1, B: MER 70.2, C: MER 71, D: MER 72.1, E: MER 72.2. 1: black manganese-rich horizon, 2: gypsum-bearing horizons, 3: calcium-carbonate rich horizon, 4: hard carbonate accumulations (nodules), 5: soft carbonate accumulations, 6: colluvial or alluvial deposits, 7: limit of the penetration of the rain water in the alluvial plain. **The soil profiles (serie MER):** MER 52: *calcimagnesic* Vertisol, 63 and 65: gypsum-bearing *calcimagnesic* Vertisol, 56: *magnesic* Vertisol, 71 and 72: *hypermagnesic* Vertisol. 8: humiferous horizon, 9: vertic horizon, 10: manganese-rich horizon, 11: weathered parent-rock (flysch), 12: alluvial deposits (alternating of layers with variable texture), 13: gypsum bearing horizon, 14: carbonate accumulations in soft clusters/in hard nodules. A: aragonite, B: barite, Ca s: calcium carbonate in soft clusters, Ca b: calcium carbonate in continuous level; Ds: dolomite in soft clusters, Gl: gypsum in lenses, Ga: gypsum agglomerate, Gt: gypsum trapezohedron, Mgh: magnesite in hard nodules.

Table 2
Soluble salt compositions (mmol/l) from selected soil horizons of the Tamoa Valley. Soil:water ratio 1:2

Sample MER	Hz	Depth (cm)	pH	EC	Ca	Mg	Na	Cl	SO$_4$	HCO$_3$	Mg/Ca	Cl/SO$_4$
Calcimagnesic Vertisol												
52-1	A$_1$	10–30	–	–	–	–	–	–	~	–	1.83	34.00
52-3	A$_3$	50–80	6.0	400	0.25	0.43	5.45	4.80	0.40	0.50	1.70	12.00
52-5	V	125–160	5.2	1850	0.90	1.65	12.50	16.15	0.48	0.30	1.83	34.00
Gypsum-bearing calcimagnesic Vertisol												
63-1	A$_1$	0–20	–	–	–	–	–	–	–	–	–	–
63-3	A$_3$	40–55	4.8	890	0.25	0.40	6.95	5.75	0.90	–	1.60	6.39
63-6	V	95–125	4.3	3160	1.90	3.55	23.35	24.30	5.23	–	1.87	4.65
63-7	V$_{Gy}$	125–140	4.7	5940	15.78	14.48	27.00	18.35	34.58	0.05	0.92	0.53
63-11	V$_{1Ca}$	195–240	7.3	2940	1.83	3.13	21.80	19.05	5.48	1.05	1.71	3.48
65-1	A$_1$	0–15	–	–	–	–	–	–	–	–	~	~
65-3	A$_3$	40–60	4.2	1490	0.43	1.00	11.60	10.25	2.63	–	2.35	3.90
65-6	V	100–120	4.4	2930	1.23	3.28	22.40	18.15	6.75	–	2.67	2.69
65-9	V$_{Gy, Ca}$	160–210	5.1	5660	9.58	13.23	33.30	19.05	31.53	0.20	1.38	0.60
Magnesic Vertisol												
56-1	A$_1$	0–12	–	–	–	–	–	–	–	–	–	~
56-3	A$_3$	25–40	–	–	–	–	–	–	–	–	–	–
56-6	V$_{Mn}$	80–100	5.5	1850	0.33	1.18	15.50	16.00	1.30	0.20	3.62	12.31
56-9	V$_{Ca,Mg}$	190–250	7.1	2260	0.50	1.83	18.80	17.35	2.53	1.15	3.65	6.87
Hypermagnesic Vertisol												
71-1	A$_1$	0–30	6.3	110	0.18	1.08	0.65	0.20	0.10	0.55	6.14	2.00
71-3	A$_3$	50–72	6.9	317	0.03	0.40	2.20	1.45	0.28	1.05	16.00	5.27
71-5	C$_{Mg}$	90–200	7.9	293	0.05	0.45	1.85	1.10	0.10	1.60	9.00	11.00
72-1	A$_1$	0–20	6.5	298	0.05	0.65	2.35	0.85	0.38	1.15	13.00	2.27
72-3	A$_3$	37–52	6.9	357	0.05	0.23	2.90	1.40	0.40	0.90	4.50	3.50
72-5	V	70–95	7.3	340	0.03	0.23	2.90	1.25	0.25	1.40	9.00	5.00
72-8	C$_{3Mg}$	125–140	7.9	470	0.03	0.50	3.55	2.70	0.15	1.40	20.00	18.00
72-9	C$_{4Mg}$	140–180	7.4	804	0.03	1.28	5.00	6.40	0.08	0.50	51.00	85.33

Sample 52-1: No. of the profile-No. of the horizon.
Hz: Horizon.
EC: Electrical Conductivity (μS cm^{-1}).

There are, however, some differences between the main soils types: deep clay-rich horizons from *calcimagnesic* Vertisols on old colluvium are more than 4 m thick, contain 50% of smectitic clay, and have a homogenous yellowish brown (10YR 5/3 to 5/4) colour, while clay-rich horizons from *magnesic* or *hypermagnesic* Vertisols on alluvium contain up to 70% smectitic clay and generally have an olive brown colour (5Y 5/2 to 5/3). *Hypermagnesic* Vertisols at depths below 1 m show an alternating of alluvial strata with a variable sandy clayey to clayey texture.

A major difference between the Vertisols is the nature of the pedogenic carbonates and sulphates. In *calcimagnesic* Vertisols, gypsum accumulates down to a depth of 80 cm within

horizons containing more than 50% smectitic clays. At a depth of 2 m, gypsum gradually gives way to a transitional horizon, 20 cm thick, which contains some rare, spherical, soft carbonate clusters of 1 to 2 cm in diameter. Beneath this transition, carbonate accumulations appear in larger clusters, or soft or spongy nodules, similar to those described by Seghal and Stoops (1972). The proportion and the hardness of the carbonate nodules increase with depth. At the base of the profile a hard continuous carbonate layer, 20 cm thick, is found between the clay-rich vertic horizons and the weathered rock.

Towards the river, *calcimagnesic* Vertisols evolve to *magnesic* Vertisols and gypsum crystals gradually disappear from the upper part of the profile. In the middle of the alluvial terrace, *hypermagnesic* Vertisols occur. Down to a depth of 1 m, white soft dolomitic clusters, about 1 cm in diameter, appear and gypsum is completely absent. In some places, there is a succession of old alluvial strata consisting of an alternation of clayey and sandy layers. In some coarse sandy layers, small pebbles of serpentinite and magnesite are visible.

2.2. Methods

Disturbed samples from each horizon were air-dried, then passed through a 2 mm sieve. The clay content was obtained by the usual pipette method after removal of gypsum and carbonates. Major cations and anions, pH, and electrical conductivity were determined in the soil solution after a soil:water extraction at 1:2. Exchangeable cations and CEC (cation exchange capacity) were determined using a NH_4Cl method (Tucker, 1985).

Undisturbed samples were collected for micromorphological and morphometrical studies. The thin sections were made on air-dried samples and an oil-base lubricant was used to avoid clay swelling. The micromorphological features were described using the terminology of Brewer (1972, 1976). Staining methods of carbonate identification (Friedman, 1959) was unsuccessful because these aqueous solutions promote swelling of smectites and damaged thin-sections.

The mineralogy of carbonates was determined by particle X-ray diffraction (XRD) using $CuK\alpha$ radiation. Nodules and calcans were studied using a JEOL 840 scanning electron microscope (SEM)' coupled with a TRACOR TN 5000 energy dispersive spectrometer (EDS). Electron diffractograms were obtained by a Philips EM 300 transmission electronic microscope (TEM) and peaks were compared to the American Standard for Testing and Materials (ASTM) for mineral identification.

Aragonite was determined by one or more of the the following: (1) SEM microphotographs; (2) micrographs made with a TEM; (3) X-ray diffraction from a thin section. Dolomite was indentified by X-ray diffraction and by TEM micrographs. Magnesite was identified by X-ray diffraction. Barite was initially identified by SEM with a back-scattered electron image and subsequentially the identification was confirmed using the EDS of the heavy element fraction.

3. The mineral morphology

3.1. Calcite

The features of the calcitic accumulations in New Caledonian Vertisols are not very different from those described in other soils (Blokhuis et al., 1968/1969; Wieder and
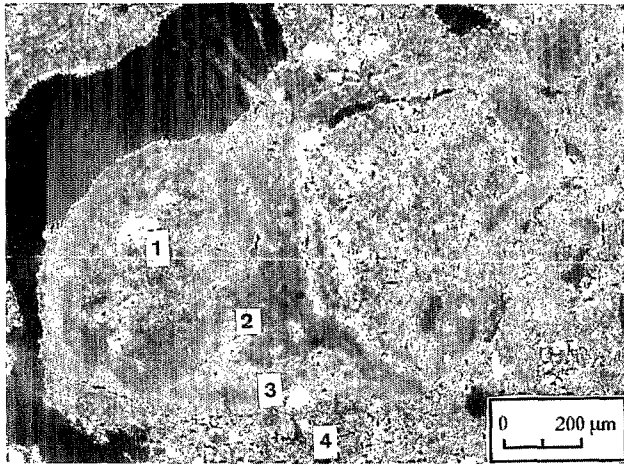
Fig. 4. Profile MER 63. horizon 11. Polygenic nodule of magnesium calcite (1) with cortex (2) recovered with aragonite (3); clay matrix (4).

Yaalon, 1974, Blokhuis, 1982; Wieder and Yaalon, 1982; Drees and Wilding, 1987). In the Tamoa Valley, magnesium-calcite nodules occur in *calcimagnesic* Vertisols (MER 63 and 55) beneath both gypsum and aragonite-bearing horizons. In the upper part of their accumulation (MER 63.11, 55.9) they occur as small nodules from 500 μm to 5 mm in diameter and in clusters with diffuse external boundaries from 2 to 10 cm in diameter. Below these accumulations, hard nodules appear with sharp boundaries with the clay-rich matrix, or within the soft carbonate accumulation zone. Many nodules have a 20 μm thick gray cortex and are formed by an assemblage of smaller nodules and contain a lot of skelletal grains and clay inclusions (Fig. 4). These nodules consist of micritic (crystals less than 5 μm long) magnesium-calcite with less than 10% $MgCO_3$, as confirmed by X-ray diffraction and partial chemical analysis (Fig. 5. Table 3). The nodules are often impregnated with a centripetal accretion of manganese dendrites or neosesquans. The porosity of the nodules (vesicular and tubular voids) is much greater than the porosity of the clay matrix (planar voids). Vesicular porosity is often observed around the carbonate (or iron-manganese) nodules.

At depth, in horizon 63.12 (Table 1), the carbonate accumulation increases and forms a 10 cm thick continuous layer between the vertic clay-rich horizon and the weathered flysch. Thin neocalcans are oriented parallel to planar or tubular voids, and alternate with thin clay-rich layers, forming 10 to 100 μm thick laminae. Small calcite crystals of 2–3 μm have invaded the clay-rich matrix to form a calciasepic structure (Seghal and Stoops, 1972; Wieder and Yaalon, 1982). At depth, at the base of horizon 63.12, calcite exhibits a sparry texture (Folk and Land, 1975) or crystic fabric (Brewer, 1976).

3.2. Aragonite

Aragonite occurs rarely and only in *calcimagnesic* Vertisols, in the transition area between the gypsic horizon (MER 63.10) and the calcic horizons (MER 63.11). It appears in very porous spherulitic accumulations from 1 to 2 cm in diameter and has a fibrous texture (Folk,
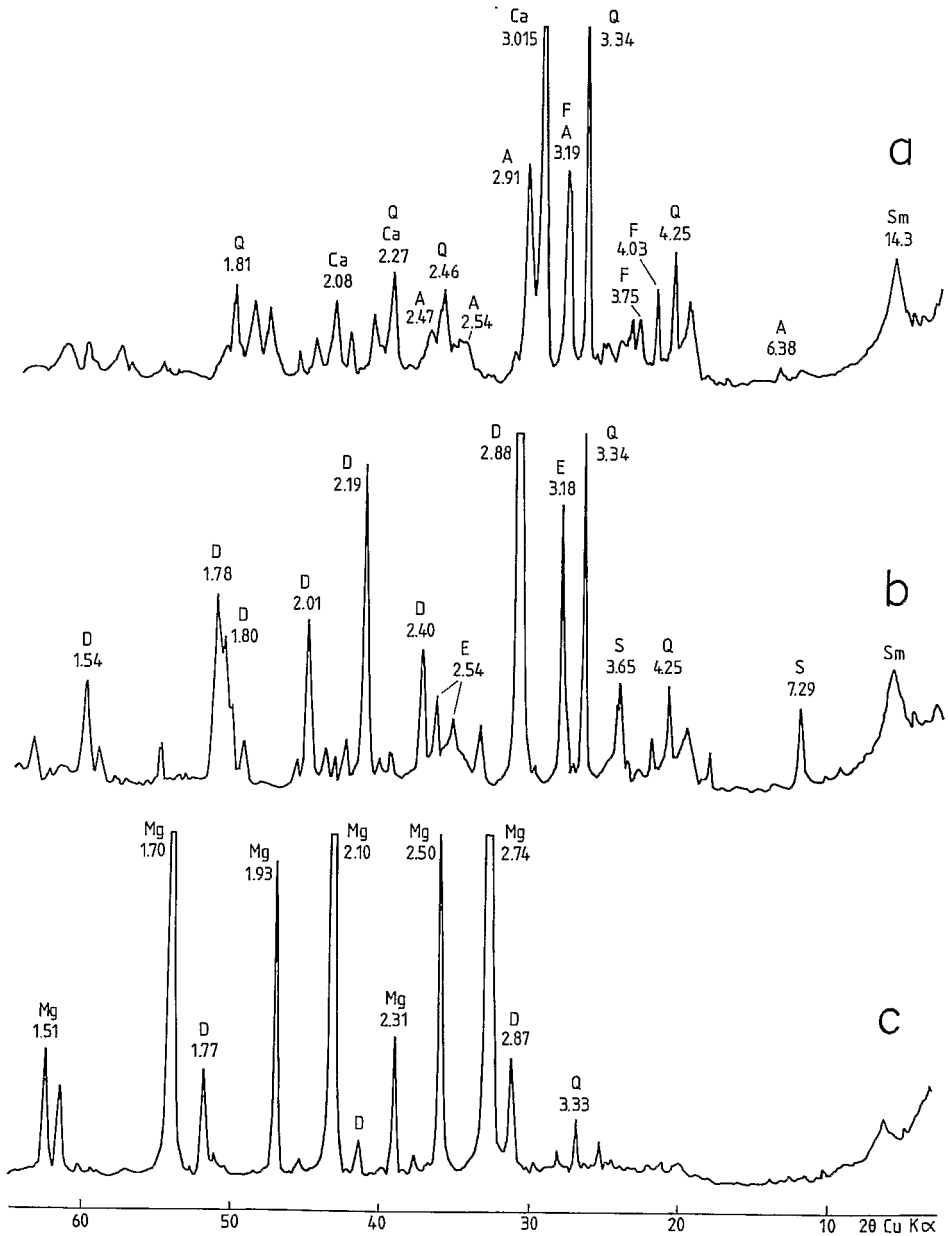
Fig. 5. X-ray powder diffraction patterns of the selected carbonate glaebules from the soils studied. Location: see Fig. 3. (a) Magnesium calcite — sample 70.1; (b) dolomite — sample 71.1; (c) magnesite — sample 72.2. A: Augite; Ca: Calcite; D: Dolomite; E: Enstatite; F: Feldspar; Mg: magnesite; Q: Quartz; S: Serpentinite; Sm: Smectite.

Table 3
Chemical composition (%) of selected carbonate glaebules from the soils studied

Sample	Nature	LOI	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	TiO$_2$	CaO	MgO	K$_2$O	Na$_2$O	BaO	Mg/Ca (mol)
MER 70.1	hard nodule: Mg calcite	15.59	47.90	10.90	7.80	0.27	0.83	10.90	3.50	0.34	1.33	0.08	0.45
MER 70.2	hard nodule: Mg calcite	22.49	33.30	7.60	6.60	0.11	0.62	21.80	5.26	0.28	1.22	0.03	0.38
MER 71	soft glaebule: dolomite	29.77	25.60	3.50	5.30	0.08	0.31	17.60	17.60	0.14	0.55	0.02	1.40
MER 72.1	soft glaebule: dolomite	17.89	46.80	7.90	7.30	0.12	0.63	4.60	13.30	0.34	1.13	0.04	4.05
MER 72.2	hard nodule: magnesite	45.18	3.00	0.50	0.80	0.06	0.06	3.10	46.60	0.05	0.09	<0.01	21.05

LOI: Loss on ignition.
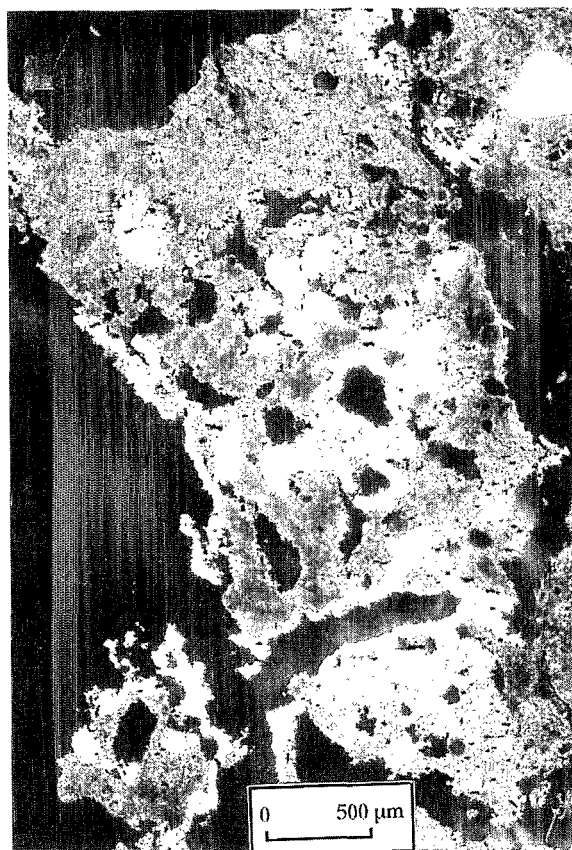
Fig. 6. Profile MER 63, upper part of horizon 11. Needles of aragonite organized in a thin clay-rich matrix and forming a pseudo-hexagonal alveolar porosity.
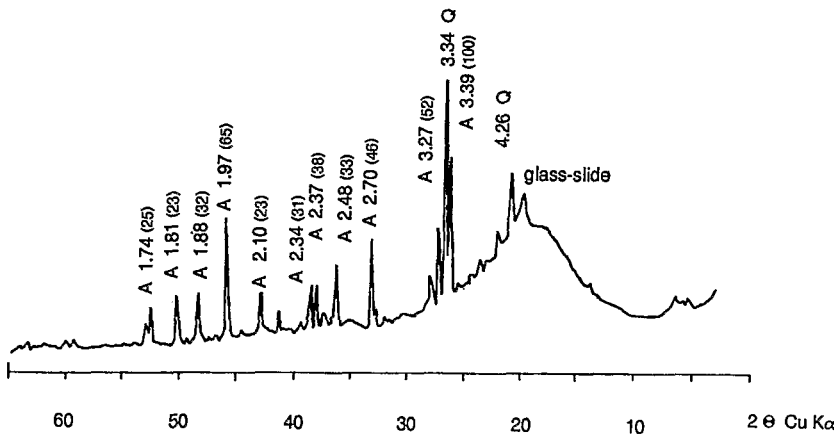
Fig. 7. Profile MER 63, horizon 11. X-Ray powder diffraction patterns on a thin section, along a pore coated with aragonite. $d_{hkl}(I)$, after Brindley and Brown (1984).

1974) formed of 1 to 5 μm needles, organised around a thin clay-rich matrix. This matrix forms a 100 to 200 μm pseudo-hexagonal alveolar porosity (Fig. 6).

At depth (horizon 63.11), aragonite occurs as microsparitic calcans or as 10 to 50 μm long needles perpendicular to the surface of planar voids, and around old calcitic nodules (Fig. 7). An X-ray transect on a thin section oriented parallel to the planar void, shows all the characteristic peaks of aragonite (Fig. 8). A thin dark gray clay layer separates the calcitic nodules from the aragonite microsparitic crystals, thus demonstrating that magnesium-calcite crystals are not a nucleus base for the neoformation of these carbonate crystals (Fig. 9).

3.3. Dolomite

Dolomite appears in the alluvial plain, in the lower part of the sequence, in *magnesic* and *hypermagnesic* Vertisols (profiles MER 56, 71 and 72), below 1 m depth. Dolomitic glaebules occur, generally as clusters of micritic crystals from 1 to 20 cm in diameter, which are sometimes hardened in their core. The boundary between the dolomite and the clay matrix is always diffuse. Dolomite is very poorly crystallized and the rhombohedric network is not clearly visible by TEM, but the X-ray peaks are characteristic (Fig. 5). The dolomitic glaebules contain many impurities such as clay and weakly weathered minerals (serpentinite, enstatite), which give the glaebules a light beige colour.

3.4. Magnesite

Magnesite occurs in the lower part of the sequence in a deep horizon (MER 72.8) at 1.30 m below a dolomite-bearing horizon. The magnesite-bearing horizon has a very coarse texture and contains small sepentinite pebbles. Magnesite appears as very hard, kidney-shaped nodules from 1 to 10 cm in diameter and composed of euhedral micritic crystals (1–2 μm) (Figs. 5, 10). These nodules resemble cauliflowers, and the cores are always pure white.
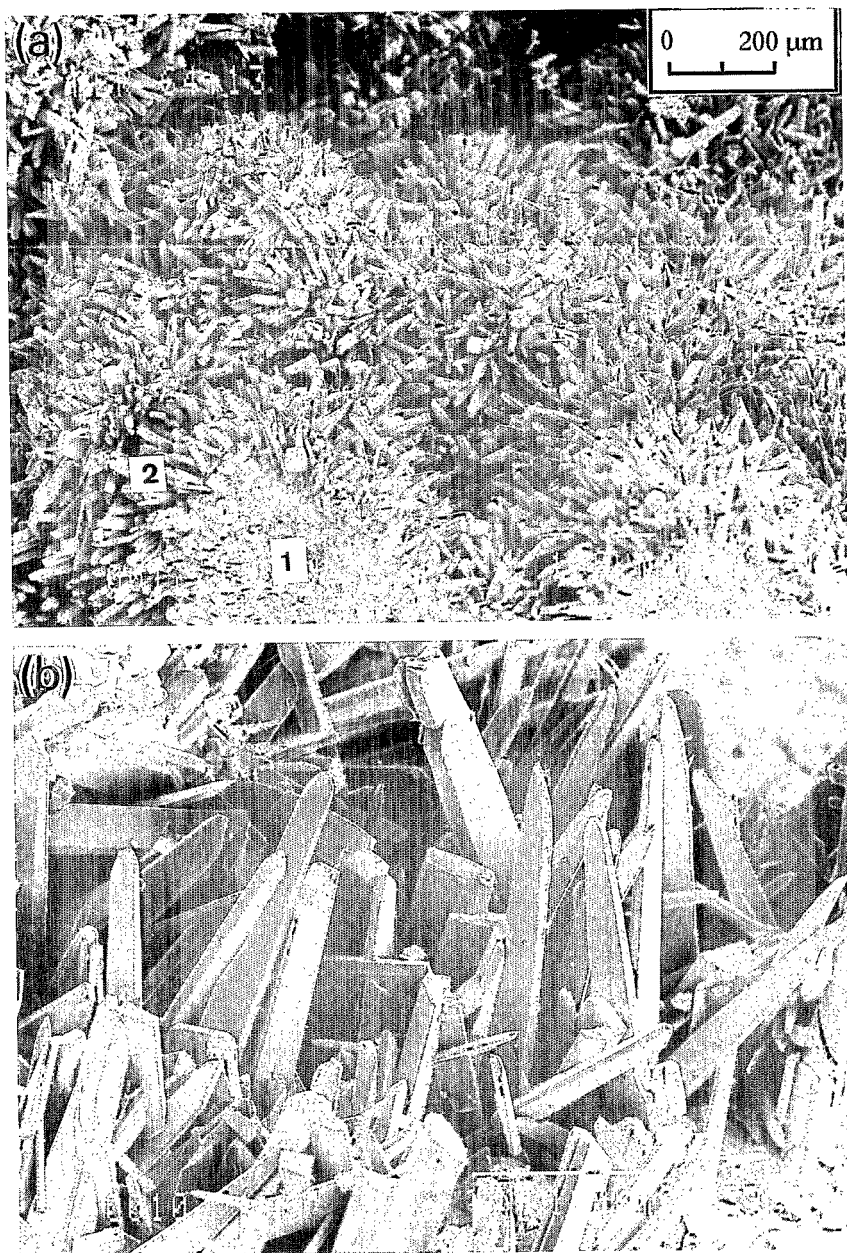
Fig. 8. (a) Profile MER 63, horizon 11. SEM image of nodules (1) recovered with aragonite crystals (2). (b) Detail of (a).

3.5. Gypsum

Gypsum occurs in the profiles located downslope, on the glacis area, in *calcimagnesic Vertisols* (MER 63 and 65). Upstream gypsum crystals appear down to 1 m depth (horizons
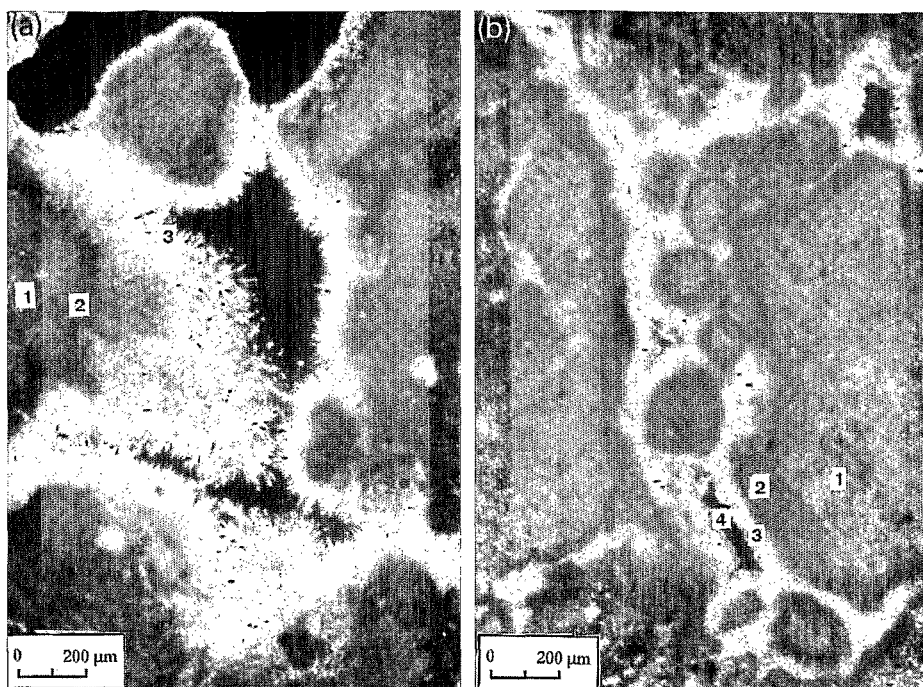
Fig. 9. (a, b) Profile MER 63, horizon 11. Nodule of magnesium calcite (1); a thin clay layer (2) separates the nodule from the external crystals of aragonite (3); pore (4).

63.7 and 63.8), as lenticular lenses, isolated in the clay matrix, above the black manganese-rich horizon. In this black horizon (63.9) and beneath (63.10), gypsum occurs as 1 to 10 cm spheric crystal agglomerations. In air-dried soil, the gypsum constitutes very large quantities of the soil weight. Downstream (profile MER 65), when the slope becomes nil, the proportion of gypsum decreases and agglomerate crystals appear down to 1.60 m depth (horizon 65.9), as very small spheric agglomerate crystals, or as millimetric trapezohedron crystals, in the clay matrix, just beneath the surface of the slickensides. In both profiles, gypsum disappears when calcite appears at around 2 m depth.

3.6. Barite

In the lower Tamoa Valley, barite is present among the detrital heavy minerals of the sandy fraction of the middle part of the gypsum-bearing Vertisols, especially at the base of the profile MER 52 and in the middle of profile 63 (63.4 to 63.8) (Podwojewski and Delaune, 1993). However, some very small isogranular microcrystals of barite from 5 to 10 μm long seem to be idiomorphic. They appear as agglomerate crystals in the lower part of *calcimagnesic* Vertisols, in the transition zone between gypsic and calcic horizons (63.10–63.11), around the spherulites of aragonite, and within the clay matrix (Fig. 11).
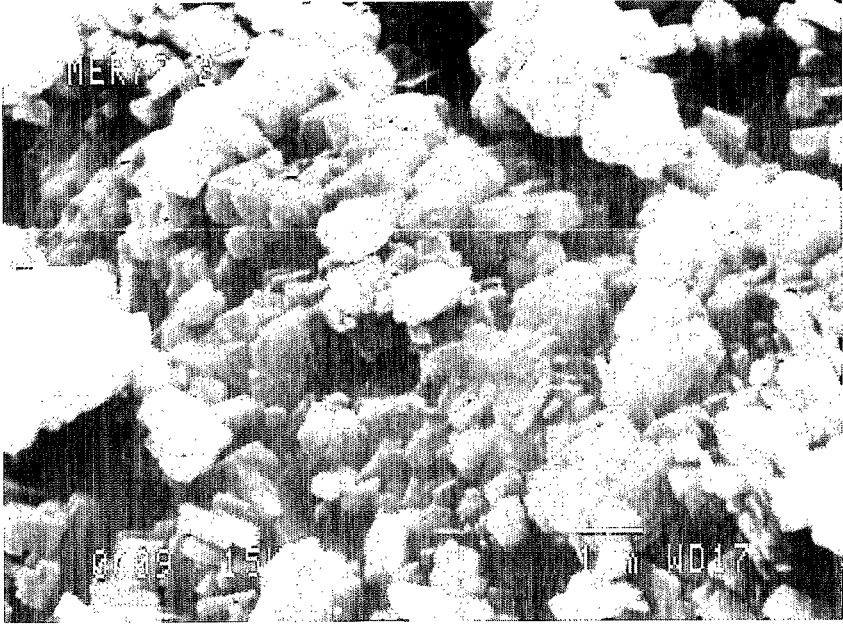
Fig. 10. Profile MER 72, horizon 9. SEM image of a hard nodule of magnesite. Well formed rhomboedral magnesite crystals.
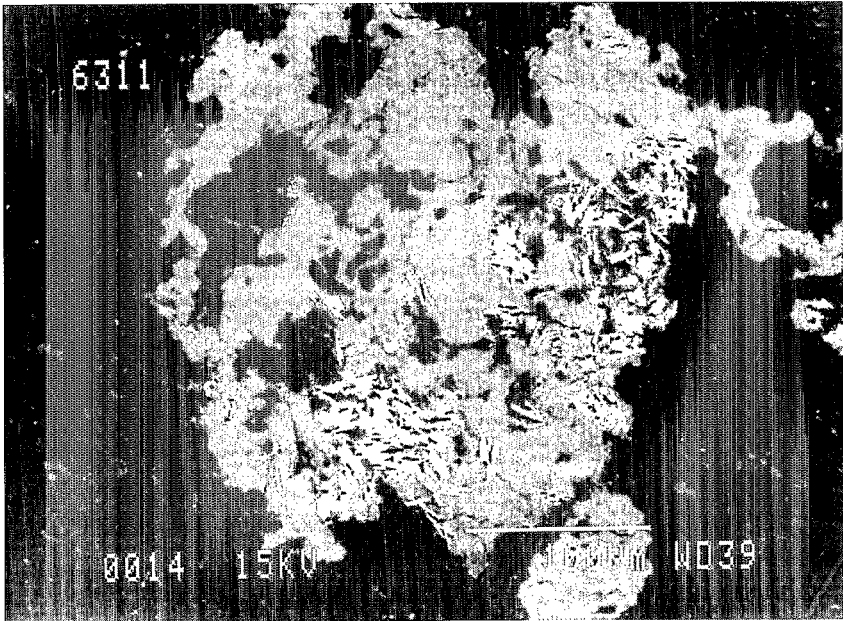

Fig. 11. Profile MER 63, upper part of horizon 11. SEM with a backscattered electron image, where barite crystals appear bright.
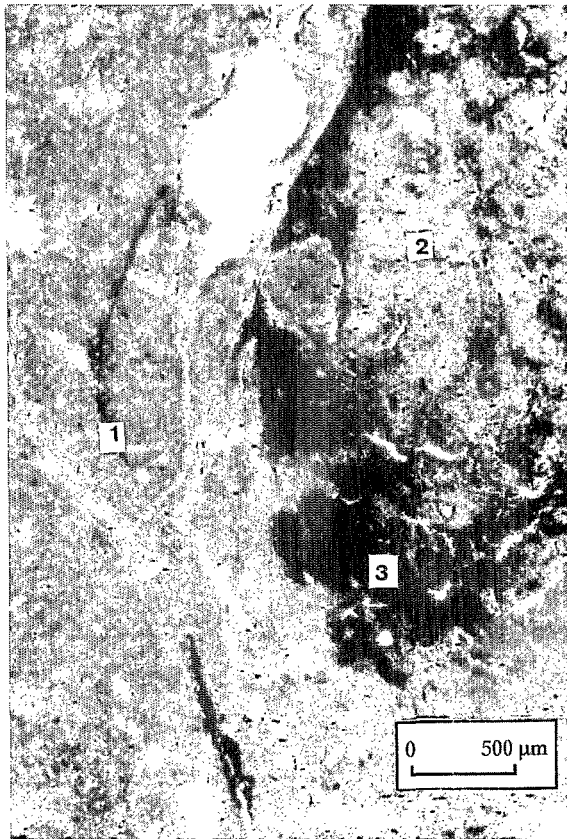
Fig. 12. Profile MER 63, lower part of horizon 11. Clay matrix (1) with a planar porosity underligned by mangans; calcitic nodule (2) with a high tubular and vesicular porosity. Centripete diffusion of manganese oxyde (3) within the nodule.

4. Discussion

4.1. Calcite

The formation of the nodules with sharp boundaries probably requires several steps. In a *per descensum* carbonate accumulation model, soft nodules accumulate first, in the smectitic matrix (Goudie, 1983), probably by filling pores beneath the root fringe or by centripetal accretion (Seghal and Stoops, 1972; St. Arnaud, 1979). In a cracking clay environment, the smectitic matrix shrinks during dry periods and swells when it becomes moist or wet, generating slickensides and planar voids. Carbonaceous accumulations do not shrink and swell, and during dry periods, a circum-nodular peripheral cavity appears. This produces favorable conditions for further carbonate accumulations growth (Nahon, 1991).

In the base of MER 63 (63.12), in the piedmont area of the soil sequence, a continuous calcareous layer is forming between the weathered flysch and the deepest vertic horizon. The preferential accumulation of carbonate in this zone appears to be controlled by à textural

Table 4
Inorganic radiocarbon ages and stable isotope characteristics of selected carbonate glaebules from the soils studied

Sample	Nature	Age ^{14}C	δ^{13}C PDB	δ^{13}O PDB	δ^{18}O SMOW	Mg/Ca (mol)
MER 70.1	Mg calcite	$26,740^{+2080}_{-1660}$	−10.60	−2.53	28.25	0.45
MER 70.2	Mg calcite	$28,710^{+1930}_{-1560}$	−10.13	−2.87	27.91	0.34
MER 71	dolomite	5390^{+180}_{-170}	−7.12	−1.28	29.54	1.4
MER 72.1	dolomite	4150^{+450}_{-430}	−3.94	−1.47	29.35	4.05
MER 72.2	magnesite	$17,690^{+950}_{-850}$	−9.38	−0.23	31.10	21.04
L-BOU 950	magnesite	19,600 ± 250				
L-BOU 420	magnesite	22,075 ± 300				
L-P.G. 60	magnesite	20,400 ± 800	−8.66	+1.56		
L-LO 2	magnesite	26,680 ± 1500	−6.16	+1.10		
L-L.O. 8	magnesite	24,170 ± 1200				

Analyses were realised by M. Fournier, in the isotope laboratory at ORSTOM, Bondy, France.
L-: data from Latham (1986).

discontinuity, and lateral drainage. At the interface between clay-rich horizons and weathered flysch, there is a change of porosity and permeability such that carbonate concentrates at the interface (Drees and Wilding, 1987). In the upper part of this layer, the clay matrix inhibits the crystallization of calcite spars (Wieder and Yaalon, 1974, Wieder and Yaalon, 1982). The alternating of calcans and argillans forms laminae locally because the bonding between calcite and clays is strong (Halitim et al., 1983). The calcareous layer is indurated in its lower part, and contains calcite sparitic crystals, probably because the soil texture is coarser (Wieder and Yaalon, 1982).

The radiocarbon ages of the magnesium-calcite nodules from *calcimagnesic* Vertisols on colluvium samples 70.1 and 70.2 located in horizon MER 63.11 and 63.12 are respectively 26,740 and 28,710 yr B.P., and are greater than the ^{14}C ages from magnesite nodules occurring in the hypermagnesic Vertisols on alluvium (< 18,000 yr B.P. for sample 72.2) (Table 4), in agreement with the relative dates of Podwojewski and Delaune (1993). These ages suggest that the formation of carbonates was probably contemporanous to their enclosing material. Many nodules are polygenetic and their growth should have been irregular. In New Caledonian Vertisols, ^{14}C ages of hard nodules range from 29,000 yr B.P. to 17,000 yr B.P. (Table 4). This wide range could be interpreted as resulting from climatic fluctuations during the dry period of the last glaciation. Fluctuations have also been noted by Latham (1986) on the basis of the composition of iron-manganese concretions in *hypermagnesic* Vertisols, where iron deposits alternate with those of manganese. In Latham's concretions, iron precipitates more readily during drier periods than does manganese. In the Vertisols of the Tamoa Valley, an inverse relationship between Fe and Mn in soil nodules is confirmed, as suggested earlier by Acquaye et al. (1992).

At approximately 5500 B.P., rainfall was more abundant both in northeastern Australia and also in New Caledonia (Kershaw, 1974; Bowler et al., 1976) and the sea-level was 1.5 m higher in New Caledonia (Cabioch et al., 1989), corresponding to the Flandrian Transgression. The accumulation of manganese oxide at the top of this paleo watertable level was probably contemporaneous with this period. Mangans cover gypsum crystals and

carbonate nodules. Manganese seems to be transported easily within the nodules, probably because of their higher porosity and permeability. Black carbonate glaebules described by Mermut and Dasog (1986) in Indian Vertisols are older than white glaebules probably for the same reason as in New Caledonia, because the formation of the first generation of glaebules was followed by a humid period favourable to the precipitation of black manganese oxides.

4.2. Aragonite

In the New Caledonian Vertisols, needles of aragonite occur in horizon MER 63.11 at a depth of more than 1 m, beneath the major root rims in horizons with a very low organic matter content. It is therefore unlikely that the aragonite observed in the Vertisols from the Tamoa valley was formed by biologic activity, as suggested by Nahon et al. (1980) and Ducloux and Dupuis (1987).

Aragonite needles are only found in these Vertisols in intervals where Mg^{2+} is abundant, as in the case of seawater (Folk, 1974; Bathurst, 1976). Mg^{2+} increases the nucleation time for calcite and inhibits calcite growth on preexisting surfaces (Cailleau et al., 1977 Cailleau et al., 1979). The supersaturation of the soil solution with respect to aragonite that results from the inhibition of the calcite precipitation leads to the precipitation of the less stable secondary phase (Fyfe and Bischoff, 1965; Bischoff and Fyfe, 1968; Bischoff, 1968; Berner, 1975).

Generally, in soils, aragonite forms in a Mg-rich environment, like the weathering of dolomite (Sticher and Bach, 1971; Laya et al., 1992) or is associated to marine shells and beach rocks like in some Australian calcretes (Milnes and Hutton, 1983). In the Tamoa Valley, the continuous weathering of feldspars from Eocene flysch provides the source of calcium for the sulphates and carbonates. The source of magnesium could be rainfall (mol. $Mg/Ca \approx 5$), or Mg-rich waters from the Tamoa river (mol. $Mg/Ca \approx 45$) produced by the weathering of peridotites and serpentinites (Table 5), and which recover the alluvial plain and infiltrate the soil during and after each flood.

Aragonite crystallizes on the external part of calcitic concretions and mangans (Fig. 13). This aragonite indicates their recent formation, in a drier regime than existed during the Flandrian Transgression. The soft spheric aragonitic glaebules are not affected by soil shearing or by lateral constraints occurring in "active Vertisols." This observation supports the hypothesis that shrink and swell Vertisol processes are no longer active (Podwojewski and Arnold, 1994).

4.3. Dolomite

In the Tamoa Valley, dolomite occurs in the *magnesic* and *hypermagnesic Vertisols* and is linked to the presence of magnesite. High Mg/Ca solution ratio is an important controlling factor in dolomite formation (Folk and Land, 1975; Warren, 1990). In a non-marine environment, the dolomite occurrence has generally a sedimentary origin like in the Coorong lakes of Australia (Alderman and Skinner, 1957; Von der Borsch, 1976) or is a product of physical weathering of dolomitic rocks (Doner and Lynn, 1989). The Mg/Ca ratio of the exchangeable cations in the dolomite-bearing *hypermagnesic* Vertisols ranges from 3 to

Table 5
Chemical composition of waters from selected rivers and watertables near the studied site. Yearly average (mmol / l)

No.	NB	pH	EC	Ca	Mg	Na	Cl	SO₄	HCO₃	Si	Mg/Ca	Cl/SO₄
1	21	7.4	259	0.03	1.34	0.22	0.24	0.03	2.49	0.56	44.67	8.00
2	39	7.7	177	0.06	0.87	0.13	0.21	0.05	1.43	0.36	14.50	4.20
3	104	7.9	154	0.02	0.82	0.07	0.21	0.04	1.71	0.33	41.00	5.25
4	3	7.7	120	0.01	0.58	0.11	0.31	0.07	1.09	0.36	58.00	4.43
Underground waters												
5	3	7.3	198	0.09	0.89	0.10	0.27	0.08	2.20	0.42	9.89	3.38
6	1	7.5	714	0.36	5.17	0.28	0.82	0.03	5.84	0.42	14.36	27.33
Seawater												
				10.2	53.7	486	542	28	2.5		5.2	19.4

1: Tamoa River (P. Podwojewski); 2: Ouenghi River (Hydrologie, ORSTOM, Nouméa); 3: Couvelee River; 4: Source of Dumbea River; 5: Pumping station, alluvial plain of the Dumbea River; 6: Pumping station, alluvial plain of the Tontouta River (3 to 6: Trescases, 1975).
NB: Number of samples.
EC: Electrical conductivity (μS cm^{-1}).

more than 20 (Table 1). This ratio corresponds to the ratio found in the water table aquifer of the leeward coast and is lower than the ratio of surface waters of the Tamoa River (Table 5). In an entirely magnesic environment, magnesite or hydromagnesite should crystallize instead of dolomite (Usdowski, 1968; Lippman, 1973; Danduran and Schott, 1977).

In the case of *magnesic* Vertisols of the Tamoa Valley (MER 56), it is suggested that dolomite crystallized preferentially from groundwater slighly enriched in calcium by a lateral drainage of the upstream part of the soil sequence. In the case of *hypermagnesic* Vertisols (MER 71 and 72), dolomite could be formed by surface Mg-rich waters from the Tamoa River (mol. Mg/Ca ≈ 45) during floods further enriched in calcium by rainfall (mol. Mg/Ca ≈ 5) and/or organic matter (mol. Mg/Ca ≈ 1). Hutton and Dixon, (1981) also suggested that rainwater favours the formation of dolomite in some Australian calcretes. In all *magnesic* and *hypermagnesic* Vertisols of New Caledonia, exchangeable calcium is more abundant in the surface horizons (Table 1). In the tissues of plants growing on magnesium-rich soils, the Mg/Ca ratio is close to 1, which is much lower than the ratio found in soils (Jaffré, 1980). Thus, organic matter and the leachate of these surface horizons are relatively enriched in Ca compared to waters and deep horizons.

The ^{14}C dates from Tamoa Valley dolomite indicate an age of formation around 5000 yr B.P. This was a rainy period with a higher sea level, during which the alluvial plain from the lower Tamoa Valley was probably often inundated, and the water table was higher. Saline environments subjected to episodic flushing by fresh water with a high Mg/Ca ratio is an ideal place to form dolomite (Folk and Land, 1975). This period was also favorable to hydromorphic conditions and/or a higher biologic activity, which probably caused an increase in the partial pressure of CO_2 in soils and controlled the reduction of MnO_2 (Mermut et al. 1988; Acquaye et al., 1992). Under these conditions, calcium and magnesium ions were leached from the topsoil, into the deeper horizons where the Mg/Ca ratio is high (over
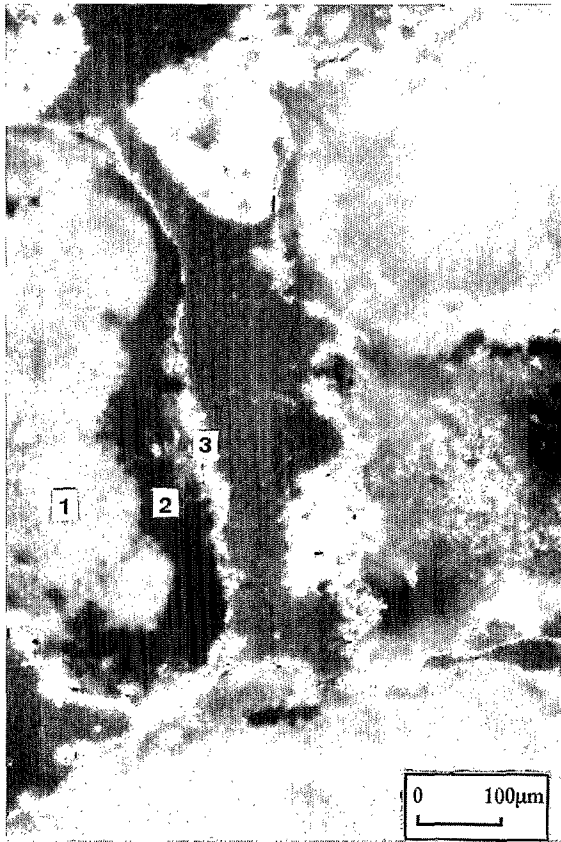
Fig. 13. Profile MER 63, lower part of horizon 11. Calcitic nodule (1); aragonite (3) cristallizes on external part of the nodule and recovers mangans (2).

20). All these conditions could have been favourable to the precipitation of dolomite at depths down to 1 m.

4.4. Magnesite

In the Vertisols of the Tamoa Valley, magnesite appears only as isolated round nodules, at depths down to 1 m. In New Caledonia, magnesite is frequently found on the leeward coast, in soils, in colluvium or alluvium that are derived exclusively from the weathering of serpentinites and peridotites. However, today, magnesite is forming in situ exclusively in association with the alteration of serpentinites (it has not been observed on peridotites) in hypermagnesic Brunisols (Mollisols), as pure white veins from 1 to 20 cm thick. In that case, it may be a secondary product of the weathering of brucite which occurs preferentially in serpentinite rocks (Trescases, 1975; Neal and Stanger, 1985). Brucite does not appear in New Caledonia because it is unstable in the local conditions of rainfall, and magnesite, unstable in the presence of dilute waters, does not appear in the surface horizon (Trescases, 1975).

The radiocarbon age of a nodule of magnesite in the Tamoa Valley is 17.690 yr B.P. This corresponds to the ages of other magnesite nodules described by Latham (1986) which range from 26.700 to 19.600 yr B.P.(Table 4). The magnesite nodules have been formed during the dry period of the last glaciation. Precipitation of magnesite, however, has been observed accompanying dolomite and hydromagnesite in some lakes of the Coorong area in South Australia (Rosen et al., 1988). The neoformation of magnesite by the fluctuation of a watertable is unlikely in arid conditions and in a period where the sea level was 120 m lower than today. In the *hypermagnesic* Vertisols from the lower Tamoa Valley, the relatively high concentration of calcium suggests that the neoformation of magnesite in situ is unlikely. The presence of pure magnesite, as hard round nodules, in a sandy-clayey horizon rich in pebbles of serpentinites and peridotites could be explained by an allochtonous formation. Magnesite nodules may have been formed upstream in the weathering horizons of serpentinites, at the base of the peridotite sheet, and transported in an old channel of the Tamoa River to the soils, during major flooding, in an arid environment.

4.5. Gypsum

The $\delta^{34}S$ analyses of many gypsum crystals of New Caledonia suggest that the major source of the sulfur in gypsum is rainwater and sea sprays (Podwojewski and Arnold, 1994). Gypsum layers typically mark the depth of water penetration in a leached soil horizon (Sonnenfeld, 1984). The accumulation of gypsum at depths greater than 1 m in the Tamoa valley is also linked to the presence of vertical cracks, which permit the surface water to penetrate rapidly to depth, when the cracks were deeper and the climate drier and windier than today (Podwojewski and Arnold, 1994). Gypsum crystals have also been reworked at the water table during the last humid period. In the black manganese-rich horizon, gypsum crystals are agglomerated and are coated by thin mangans.

In *calcimagnesic* Vertisols, gypsum crystals progressively diminish in size and in abundance with depth. When they disappear, calcium carbonate accumulation takes their place. At the boundary of the gypsum and calcite glaebule-bearing horizons, calcite pseudomorphs after lenticular gypsum crystals are visible. Such a pheneomenon has been described by Watson (1985, 1988), Drees and Wilding (1987), Gumuzzio and Casas, (1988), and Sullivan (1990). In the case of the Tamoa Vertisols, large monocrystals of lenticular gypsum (100 to > 500 μm) have been dissolved and microsparitic calcite crystals (< 10 μm) have precipitated in the pores (Fig. 14). In some tubular pores, gypsum has crystallized on the external part of the void. Calcite cristallized later in the internal part of the voids, pseudomorphic after lenticular gypsum crystals (Fig. 15).

This pseudomorphosis is the opposite of that observed by Halitim (1985) in southern Algeria. He observed calcite crystallized on the external part of the tubular pores and gypsum in the internal part. The pseudomorphosis could be caused by an increase in downward-moving solutions, saturated with respect to calcite but capable of dissolving gypsum (Watson, 1988; Sullivan, 1990). In New Caledonia, a similar phenomenon occurred at about 5000 yr B.P., when the rainfall was much greater than today. The high carbonate contents of the Tamoa River flood waters contribute to this process. On contact with the carbonate solution, calcium sulfate dissolves and calcium carbonate precipitates in its place, while sulfate is exported out of the profile according to the reaction:
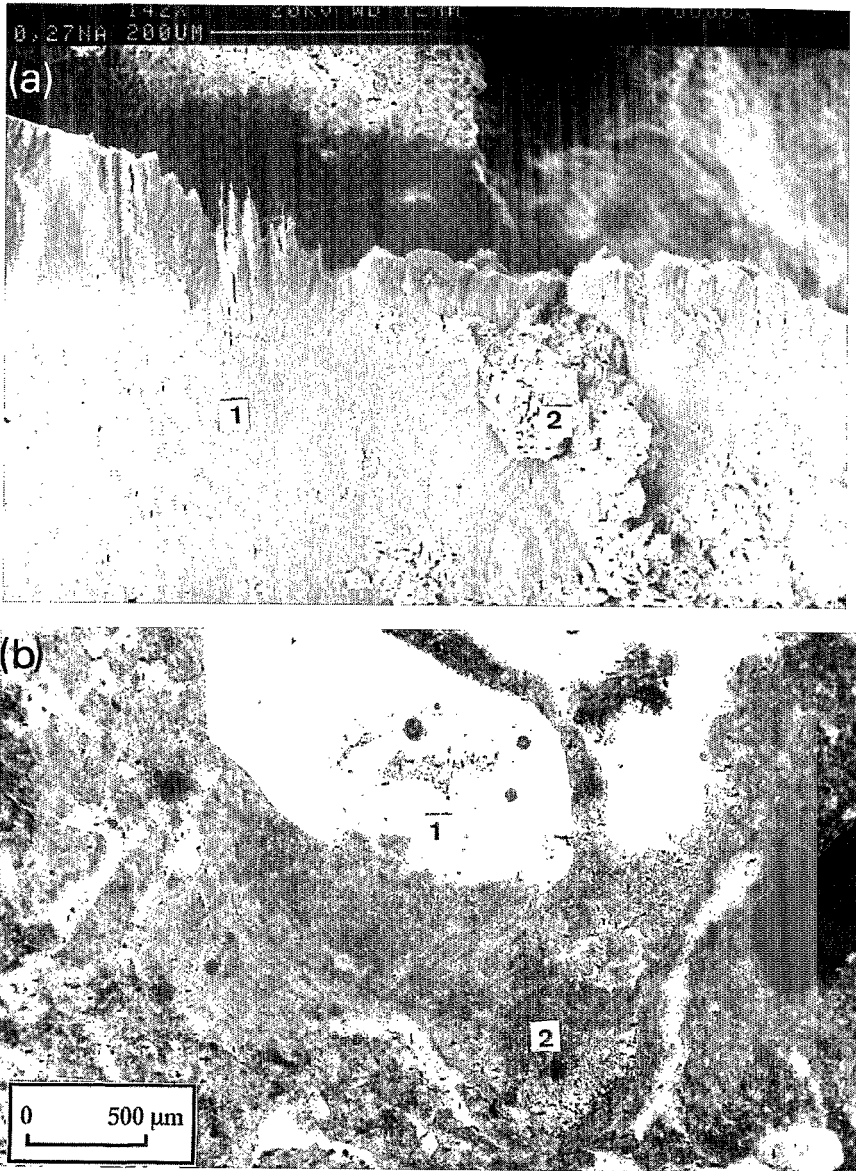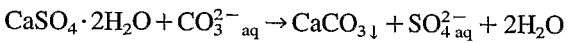
Fig. 14. (a, b) Profile MER 63, lower part of horizon 10. Calcite pseudomorphs (2) after lenticular weathered gypsum crystal (1).

$$CaSO_4 \cdot 2H_2O + CO_3^{2-}{}_{aq} \rightarrow CaCO_{3\downarrow} + SO_4^{2-}{}_{aq} + 2H_2O$$

4.6. Barite

Detrital barite crystals are derived from the physical weathering of Senonian terrigenous shales. However, the isogranular barite microlites developed close to aragonite accumula-
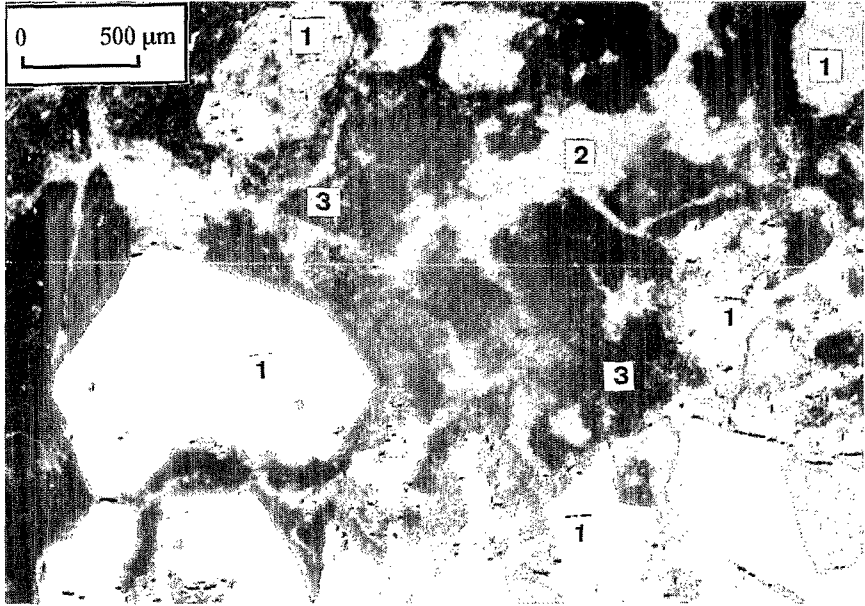
Fig. 15. Profile MER 63, lower part of horizon 10. Weathered gypsum crystals (1). Calcite pseudomorphs (3) after weathered gypsum crystals developing from the central tubular pore (2) to the external part of the void.

tions seem to be authigenic. Barite does not crystallize in direct contact with aragonite, probably because of a small inhibition effect from Ba^{2+} on the transformation of vaterite into aragonite (Cailleau et al., 1979). Authigenic barite in soils is rare because of the mineral's very low solubility. The formation of authigenic barite could be attributed to the presence of a saline watertable (Stoops and Zavaleta, 1978). After Carson et al. (1982), barite formation in soils seems to occur in a matrix that is highly smectitic, high in cation concentration, and low pH. Barite formation under such conditions has also been observed by Lynn et al. (1971) or Stoops and Zavaleta (1978). In the *calcimagnesic* Vertisol of the Tamoa valley (MER 63), all of these preceding conditions are present. The CEC's of the gypsum-bearing horizons (63.7, 63.8, 63.9) are saturated in cations, the soil pH is close to 5.0 at 70 cm depth (Table 1), and the water table fluctuated during the humid period of the last Flandrian transgression.

4.7. Chemical and mineralogical evolution by magnesium inputs

There are three potential inputs of dissolved and reactive magnesium to the Vertisols of the Tamoa Valley: (1) by rainfall and seasprays, (2) by the chemical weathering of alluvial deposits composed of peridotites and serpentinites. The weathering of these ultrabasic sediments liberates high amounts of magnesium ions, and (3) by the flooding of the Mg-rich waters of the Tamoa River.

The magnesium inputs have the following effects: They promote the precipitation of aragonite and dolomite, and they help to form calcite pseudomorphs after lenticular gypsum crystals. In magnesium-rich Vertisols, high Mg^{2+} inputs displace some Ca^{2+} present on

the exchangeable complex and concentrated by the organic matter in the surface horizons. This calcium is easily leached down the profile and contributes to the neoformation of dolomite.

5. Conclusion

The Vertisols of the Tamoa Valley, in New Caledonia, have recorded the climatic changes during the recent Quaternary period. Gypsum and calcium carbonate most likely crystallized during the dry period of the last glaciation, which reached its maximum at around 18,000 yr B.P. Magnesite nodules appear to be contemporaneous with the alluvial terrace, but are allochthonous and originate from the mechanical weathering of soils on serpentinites found upstream. During the Flandrian Transgression, at about 5500 yr B.P., the rainfall increased and fluctuations of the water table favoured the reworking and the dissolution of gypsum and calcium carbonate. Manganese accumulations coated carbonate nodules and gypsum agglomerate crystals. During this period, hydromorphic conditions may have promoted the formation of dolomite by increasing biological activity and leaching conditions. The formation of barite is also likely to have been contemporaneous with this period.

Today the climate is drier than it was during the Flandrian Transgression, but the Vertisols of the alluvial plain are regularly flooded by the Mg-rich waters from the Tamoa River. Modern flooding on the alluvial plain favors the formation of dolomite, the formation of calcite pseudomorphs after lenticular gypsum crystals, and the formation of aragonite. Today vertical cracks are rarely observed at the soil surface and the aragonite crystals are not affected by soil shearing effects. These facts suggest that the Vertisol movement is not effective today, probably because of the too high rainfall and/or a less contrasted climate than existed during the dry period of the last glaciation, in the early stages of Vertisols development.

Acknowledgements

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The occurrence and interpretation of carbonate and sulfate minerals in a sequence of Vertisols in New Caledonia

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