Redistribution of Metals in a New Caledonia Ferralsol After Microbial Weathering

C. Quantin, T. Becquer, J. H. Rouiller, and J. Berthelin*

ABSTRACT

Ferralsols from southern New Caledonia developed on ultramafic rocks are very rich in Fe, Mn, and in other transition metals like Cr, Ni, and Co. Bacterial weathering of Fe and Mn oxides performed in batch experiments increases metal solubilization particularly under reducing waterlogged conditions and when organic compounds are available as nutrients. Moreover, bacterial weathering can modify the metal distribution through the geochemical compartments of the soil. Bacterial reduction of oxides led to the solubilization of Fe, Mn, Ni, and Co and brought about a significant metal redistribution into the different geochemical compartments of the soil. Selective sequential extractions showed an increase in the metal (Fe, Mn, Co, Ni, and Cr) content of the most labile compartments (water-soluble and exchangeable) after microbial weathering. Metal concentrations of amorphous and poorly crystallized Fe oxides also increased significantly. This mineral phase acted as a strong sorbent promoting the coprecipitation of metals with Fe. The Mn oxide compartment decreased significantly, especially under high microbial activity. The metal contents of the well-crystallized Fe oxide and residual fraction were stable showing that microbial weathering have a limited effect on these compartments. Although the soluble Cr was always nil, Cr was also significantly redistributed into the various geochemical compartments (highlighting the rapid sorption of this element versus its solubilization). Such redistribution processes are important to be known and to be quantified to define metal behavior and improve risk assessment.

In southern New Caledonia, Ferralsols developed from ultramafic rocks are very rich in both Fe and Mn oxides (Nalovic and Quantin, 1972; Schwertmann and Latham, 1986). Other transition metals like Cr, Ni, and Co are also present in very high concentrations, either adsorbed on the oxides or incorporated into their mineral lattice. Recent mineralogical studies showed that most of the Ni and around 50% of the Cr were associated with Fe oxide (Becquer et al., 2001b), whereas Co was mainly associated with Mn oxides (Quantin et al., 2002). These observations confirmed that Fe and Mn oxides are major scavengers and reservoirs for metals and control their availability (McKenzie, 1989; Singh and Gilkes, 1992).

Bacterial reduction of Fe and Mn oxides increases metal solubilization when C is highly available as during simulated waterlogging conditions (Quantin et al., 2001). Other studies performed at a toposequence scale in New Caledonia have shown that both DTPA-extractable Ni and Ni contents of crops increased in plain soils submitted to waterlogging (Becquer et al., 1995; L'Huillier and Edighoffer, 1996). Depending on soil moisture, both redox potential and biological activity may control oxide solubilization (Patrick and Jugsujinda, 1992) and heavy metal release and redistribution (Hazra et al., 1987; Han et al., 2001).

Microbial transformation of both mineral and organic soil constituents leads to the solubilization of metals that can later be rendered unavailable by adsorption or precipitation phenomena (Quantin et al., 2001). Such process may lead to the removal of metals from the soil profile by leaching and to the modification of their form and distribution in the solid phase. The knowledge of these phenomena is important to understand the behavior of potentially toxic metals in soils, their potential uptake by plants and their leaching through the soil profile.

The aim of this study is to understand the partitioning and redistribution of metals in specific compartments of the solid phase after microbial weathering and particularly bacterial reduction and dissolution of Fe and Mn oxides. It provides information on mineral weathering by heterotrophic microorganisms.

MATERIALS AND METHODS

Soil Sampling and Analysis

Soil was collected in the Ouénarou forestry station in southern New Caledonia. It originated from the alluvio-colluvial soil of the sequence studied and described in details by Becquer et al. (1995, 2001b). Samples were taken in the subsurface horizon (4–10 cm) of a silt-clay Geric Ferralsol (FAO, 1998) and sieved at <2 mm.

Total C and N in the sample were determined using a CHN 1108 Carlo Erba analyzer (Carlo Erba, Milan, Italy). Iron, Mn, Al, and Si concentrations in the sample were determined after alkaline fusion. One gram of lithium metaborate-tetraborate (80–20% [wt/wt]) mixture was added to 100 mg of fine crushed sample and heated at 1000°C. After the fusion, the resulting pellet was dissolved in 1% (v/v) HNO_3. The concentration of Co, Ni, and Cr were determined after acid (concentrated HNO_3/HCl; 2:1) digestion of 100 mg of finely ground soil in teflon vessels heated in a microwave oven. This procedure, that was used for metal analysis in the bulk soil and in the residual compartment (see below), was validated by analyzing a reference material (geostandard BX N, Govindaraju, 1995). The recovery rate for this sample was up to 93% (93.2% for Cr). Major and trace elements were measured by inductively coupled plasma atomic emission spectroscopy

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Abbreviations: CEL, shredded cellulose treatment; d (subscript), dissolved metals; DCB, dithionite citrate bicarbonate; EDXS, energy dispersive x-ray spectrometer; EXCH, exchangeable, FEOX1, bound to amorphous or poorly crystallized Fe oxides; FEOX2, bound to well crystallized Fe oxides; GLU, glucose treatment; ICP-AES, inductively coupled plasma atomic emission spectroscopy; MNOX, bound to Mn oxides; OM, associated with organics; RES, residual; SOM, soil organic matter treatment; SSE, selective sequential extractions; t (subscript), total element concentration; TEM, transmission electron microscope; WAT, water soluble.

Table 1. Selective sequential extraction (SSE) procedure.

Soil fraction (Abbreviation)	Extractant	Volume	Conditions
Water soluble (WAT)	ultrapure water	10 mL	20°C, 30′, end-over-end shaking
Exchangeable (EXCH)	0.1 *M* KCl	10 mL	20°C, 2h, end-over-end shaking
bound to Mn oxides (MNOX)	0.1 *M* $NH_2OH{\cdot}HCl$, pH 2	10 mL	20°C, 30′, end-over-end shaking
bound to amorphous Fe oxides (FEOX1)	0.2 M $(NH_4)_2C_2O_4{\cdot}H_2O$ + 0.2 M $H_2C_2O_4$, pH 3	10 mL	20°C, 4h, end-over-end shaking, in the dark
bound to crystalline Fe oxides (FEOX2)	CB: $Na_3C_6H_5O_7$, $2H_2O$ (78.4 g L^{-1}) + $NaHCO_3$ (9.82 g L^{-1}); $Na_2S_2O_4$, pH 7	50 mL CB 1 g $Na_2S_2O_4$	80°C, 15′ in CB and 30′ after adding dithionite, magnetic agitation
organics (OM)	1) 0.2 *M* HNO_3 − 35% H_2O_2 2) 3.2 *M* NH_4OOCCH_3 (20% v/v HNO_3)	1) 3 mL − 8 mL 2) 5 mL	1) 85°C, 5h 2) 85°C, 30′
residual† (RES)	1) alkaline fusion for major elements 2) diacid attack for trace elements		

† 100 mg.

(ICP-AES) (Jobin-Yvon 238). Total element concentrations are denoted Me_t.

Incubation Experiment

Batch incubations were performed with 50 g (or 25 g for controls) of soil in sealed 1000-mL (or 500-mL) glass bottles, supplemented with 750 mL (or 375 mL) of water as described by Quantin et al. (2001). All incubations were carried out anoxically, under O_2–free N_2 atmosphere, with four replicates per treatment.

Three treatments were performed with different sources of organic matter. The first received no organic matter supply, so that indigenous soil organic matter (SOM treatment) was the only source of C and nutrients (samples incubated with distilled water as liquid medium). To simulate organic input, the other treatments were supplied with 6 g C kg^{-1} of soil of either glucose (1 g L^{-1}; GLU treatment) or shredded cellulose (Whatman 40, 0.96 g L^{-1}; CEL treatment). Total C content was 3.2% in GLU and CEL treatments, whereas it was only 2.6% in the SOM treatment. Flasks with soil were incubated under biotic and abiotic conditions, to distinguish microbial and physicochemical processes. Abiotic conditions were obtained by adding 1 g L^{-1} of sodium thimerosal. Incubations were conducted in the dark at 28°C for 140 d, with only hand shaking prior to gas sampling.

Bacterial activity was monitored by measuring the C mineralization (infrared analysis of the CO_2 content of the flask headspace) and metal solubilization at various times of incubation (see details in Quantin et al., 2001). Metals were determined in biotic and abiotic treatments by ICP-AES analysis of 0.2-μm filtered samples. Dissolved metals are denoted Me_d.

Selective Sequential Extraction Procedure

The partitioning of metals among the compartments of the soil solid phase was investigated indirectly by selective sequential extractions (SSE). The SSE procedure (Table 1) was a seven-step procedure adapted from Leleyter and Probst (1999), modified from Tessier et al. (1979) and Shuman (1985). The SSE was performed with 1 g of ground soil in 50-mL polypropylene centrifugation tubes to minimize losses of material. All extractions were performed in duplicate on three replicates of each treatment. In each extraction series, a standard sample (initial one) was introduced to follow the reproducibility of the procedure.

After each extraction step, the tubes were centrifuged at 5200 × *g* for 20 min. The supernatants were then filtered through 0.45-μm membranes (Sartorius), whereas the residues were washed with 10 mL of ultrapure water, centrifuged again, and then the supernatants were pooled. The leachates (extract and rinsing) were then stored in polypropylene bottles or glass vials at 4°C until chemical analysis. The residues were dried at 40°C prior to the next extraction step.

All reagents were of analytical grade or of better quality. Blanks without a soil sample were done for each extraction step to determine the purity and quality of the procedure.

No satisfactory physicochemical and chemical methods exist to determine unambiguously the distribution of elements within the solid phase (see above). Nevertheless, this extraction procedure provides an operationally defined soil-phase fractionation that is convenient for comparison of treatments. The chemical forms were labeled according to the targeted geochemical compartments during each extraction step: water soluble (WAT), exchangeable (EXCH), bound to Mn oxides (MNOX), bound to amorphous or poorly crystallized Fe oxides (FEOX1) or to well crystallized Fe oxides (FEOX2), associated with organics (OM), residual (RES).

Each element in the different fractions was expressed in micrograms extracted per gram of soil and in total amount percentage of the metal extracted after the seven steps (Me_7). Elements were analyzed by ICP-AES. Calibration was done with standard solutions analyzed at the beginning of series and after each 15 sample series.

Transmission Electron Microscopy Observations and Microanalysis

Air-dried samples were suspended in ethanol under ultrasonication. A drop of suspension was then evaporated on a carbon-coated copper grid and the preparation was observed with a Transmission Electron Microscope (TEM Philips CM 20, Philips, Eindhoven, the Netherlands) at an accelerated voltage of 200 kV. Microanalysis of selected particles were carried out using an EDAX energy dispersive X-ray spectrometer (EDXS) associated to the TEM.

Statistical Analysis

The effects of microbial weathering treatments on the different fractions were evaluated with an analysis of variance (ANOVA) that allows comparison of samples before and after

Table 2. Main characteristics of the soil sample.

pH	C_{org}	C/N	Fe_2O_3	MnO_2	SiO_2	Al_2O_3	Cr_2O_3	NiO	CoO
	mg kg^{-1}		mg kg^{-1}						
4.6	2.6	21.7	568	6.04	86	63	15.9	10.9	0.92

incubation. The comparisons of means were made with the Fisher's PLSD test (least significant difference) ($p < 0.05$) using Statview 4.02 (Abacus Concepts, Inc., Berkeley, CA).

RESULTS

Soil Characteristics

Total element analysis showed a very high content of Fe and relatively high contents of Mn, Cr, Ni, and Co in the soil sample (Table 2). Iron was mainly present as goethite and Mn as a nonidentified mixed-layers Mn oxide (Becquer et al., 2001a; Quantin et al., 2002). Dithionite citrate bicarbonate (DCB) and hydroxylamine extractions as well as TEM observations and EDXS analysis showed that Ni and Cr were mainly associated with goethite whereas Co and <1% of Ni were associated to Mn oxides (Becquer et al., 2001a; Quantin et al., 2002). The Si content was very low in this soil sample and mainly present as talc mineral with traces of chlorite and quartz. The SOM content reached 5% and the C/N ratio was close to 22.

Total Microbial Activity

In abiotic treatments, CO_2 production was negligible and only because of chemical degassing (Fig. 1). The values were the same in all the abiotic treatments. In contrast, in biotic treatments, C mineralization was significant and reached 13.8, 16.8, and 18.9 g C-CO_2 kg^{-1} of the total C content for SOM, GLU, and CEL treatments, respectively, after 140-d incubation (Fig. 1). Kinetics of mineralization were quite different for the three treatments. In the SOM treatment, organic matter mineralization increased slowly with time and reached a maximum rate of 0.107 g C-CO_2 kg^{-1} C d^{-1} (Quantin et al., 2001). In the GLU treatment, C mineralization increased very fast after a 2-d lag-period. Mineralization rate was 0.714 g C-CO_2 kg^{-1} C d^{-1} during 22 d and then decreased to zero after 75 d.

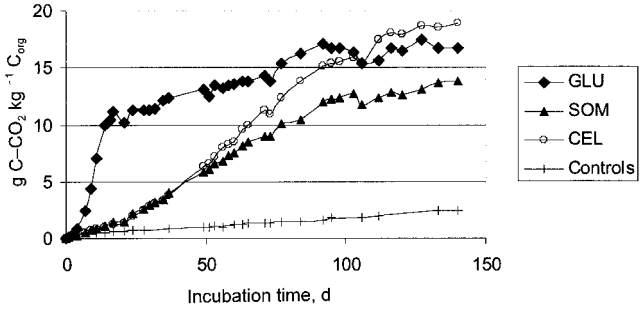

Fig. 1. Carbon mineralization in experiments with (GLU and CEL) and without (SOM) organic addition under biotic conditions and in controls.

For the CEL treatment, the CO_2 production was low and similar to that of the SOM treatment during the first 3 wk. After this period, C mineralization increased from 0.064 to 0.164 g C-CO_2 kg^{-1} C d^{-1}. At the end of incubation, the cumulative quantity of mineralized C became higher than in the GLU treatment (Fig. 1).

Metal Solubilization

In abiotic treatments, metal solubilization was low especially for Fe and Mn (Fig. 2 and Table 3). For Co and Ni, <1.5 and 0.1% of total metals was solubilized, respectively, and this was ascribed only to exchange with the added sodium thimerosal (Quantin et al., 2001).

Iron and Manganese

In the SOM treatment, maximum solubilization of Fe was close to 0.2% of Fe_t whereas solubilized Mn reached 17% of Mn_t (Table 3). A decrease of soluble Mn was observed at the end of the experiment corresponding to sorption phenomena (Fig. 2). In treatments where microbial activity was greatly stimulated by hydrocar-

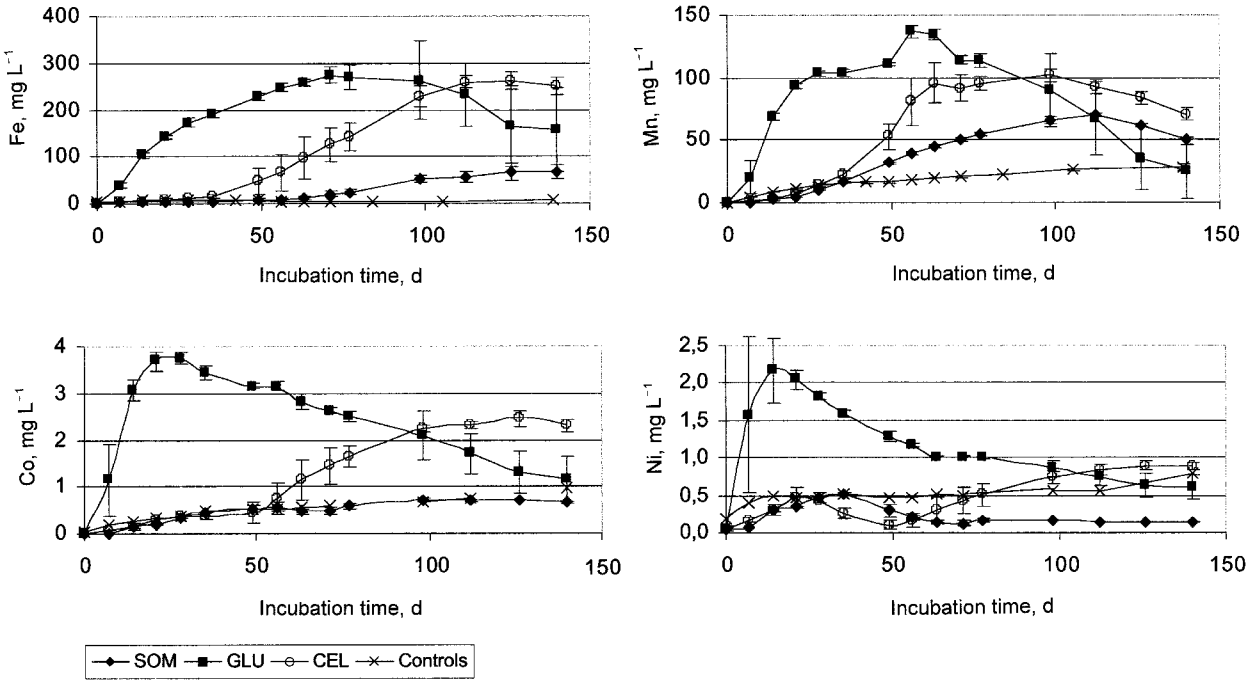

Fig. 2. Metal solubilization in GLU, CEL, and SOM treatments under biotic and abiotic anoxic conditions.

Table 3. Percentage of maximal solubilization of Fe, Mn, Co, and Ni in soil organic matter (SOM), glucose treatment (GLU), and shredded cellulose treatment (CEL) biotic and abiotic treatments and percentage of metal solubilization at 140 d of incubation.

		Fe_d/Fe_t		Mn_d/Mn_t		Co_d/Co_t		Ni_d/Ni_t	
		max	140 d	max	140 d	max	140 d	max	140 d
SOM	bio	0.19 ± 0.05	0.18 ± 0.04	17.2 ± 0.2	11.9 ± 0.2	1.16 ± 0.06	1.0 ± 0.02	0.09 ± 0.01	0.02 ± 0.00
	abio	0	0	4.56 ± 0.4	4.56 ± 0.4	1.11 ± 0.21	1.11 ± 0.21	0.09 ± 0.00	0.08 ± 0.02
GLU	bio	0.77 ± 0.05	0.38 ± 0.22	32.0 ± 1	5.1 ± 4.5	7.08 ± 0.26	1.57 ± 0.66	0.48 ± 0.02	0.08 ± 0.02
	abio	0	0	5.95 ± 0.02	5.95 ± 0.2	1.38 ± 0.09	1.38 ± 0.09	0.1 ± 0.0	0.08 ± 0.01
CEL	bio	0.75 ± 0.04	0.69 ± 0.05	26.0 ± 4.5	16.4 ± 1.1	2.49 ± 0.66	2.49 ± 0.66	0.09 ± 0.03	0.07 ± 0.03
	abio	0	0	4.62 ± 0.6	4.62 ± 0.6	1.06 ± 0.15	1.06 ± 0.15	0.09 ± 0.00	0.08 ± 0.01

bon input, Fe and Mn release reached 0.75% of Fe_t and 32% and 26% of Mn_t for GLU and CEL, respectively. The solubilization kinetics were quite different between treatment as metal solubilization started earlier in the GLU treatment than in CEL (Fig. 2).

At Day 140, the amounts of dissolved metals decreased markedly for Mn and slightly for Fe, and the metals were assumed to be sorbed onto the solid phase either adsorbed or precipitated. The decrease of dissolved metal contents at the end of the experiment shows that, at this period, metal solubilization becomes slower than the sorption processes (Fig. 2).

Cobalt, Nickel, and Chromium

Cobalt and Ni release was low for all treatments (Fig. 2 and Table 3). However, in the GLU treatment, Co solubilization reached 7% of Co_t after 24-d incubation (Quantin et al., 2001) after which the Co content in solution decreased. In the CEL treatment, Co release reached 2.5% of Co_t, whereas in the SOM treatment it was only 1.2%. For Ni, a similar tendency was observed. The maximum release (0.48% of Ni_t) occurred in the GLU treatment after 14 d whereas in the other treatments it was not significantly different from abiotic controls.

Chromium was never detected in solution for any of the treatments (detection limit: 1 mg L^{-1}).

Partitioning of Metals in the Soil

The cumulative amounts of elements recovered during the seven-step SSE procedure were up to 85% of that obtained by a single-step total analysis.

Only small changes in metal distribution were observed in controls where bacterial activity was inhibited by thimerosal (data not shown). In these abiotic treatments, water soluble and exchangeable metals increased slightly during incubation because of the effect of sodium thimerosal, whereas other compartments remained constant. So, in the results below, only the distribution of the metals in the geochemical compartments at the end of the biotic treatments were presented and discussed in comparison to the initial distribution.

Iron

Iron was intimately associated with the reducible fraction corresponding to well-crystallized Fe oxides (40.8% of Fe_7, Table 4). Iron quantified in the residual fraction (53.5%) was overestimated because the DCB extraction was not complete as indicated by the colored residue suggesting that some goethite was not dissolved by the conventional extraction of crystallized Fe oxides adopted in this experiment. However, more than 95% of Fe can be extracted by DCB during a 772-h extraction at room temperature (Becquer et al., 2001b). After incubation,

Table 4. Concentrations of Fe, Mn, Ni, Co, and Cr in the solid compartments of the initial and incubated soils.

		WAT†	EXCH	MNOX	FEOX1	FEOX2	OM	RES
		mg kg^{-1}						
Fe	Initial	0.44 ± 0.21a#	0.41 ± 0.42a	115 ± 37b	9 100 ± 1 999a	139 300 ± 20 960a	31 ± 36a	193 246 ± 22 802b
	SOM‡	27 ± 4a	18 ± 10c	67 ± 12a	10 763 ± 347a	158 767 ± 13 822a	73 ± 9b	201 671 ± 1 299b
	GLU§	35 ± 8a	11 ± 9bc	193 ± 27c	30 567 ± 4 457c	163 700 ± 21 482a	114 ± 38c	157 291 ± 4 423a
	CEL¶	4.2 ± 0.8a	5.6 ± 3ab	130 ± 21b	15 590 ± 1 154b	163 800 ± 19 974a	102 ± 16bc	191 912 ± 16 695b
Mn	Initial	14 ± 3a	146 ± 1a	2 330 ± 210a	500 ± 63a	823 ± 169a	0.99 ± 1.1a	624 ± 103ab
	SOM	84 ± 3c	648 ± 74c	885 ± 26b	1 103 ± 29b	1 069 ± 79a	4.2 ± 0.5b	748 ± 27c
	GLU	45 ± 3b	430 ± 47b	601 ± 78c	2 073 ± 263c	1 108 ± 210a	4.1 ± 2.1b	551 ± 25a
	CEL	110 ± 7d	587 ± 59c	616 ± 41c	1 154 ± 61b	981 ± 95a	4.5 ± 1.6b	662 ± 28bc
Ni	Initial	0.82 ± 0.13a	8.5 ± 0.6a	63 ± 24b	99 ± 18a	3 170 ± 525a	13 ± 10a	4 486 ± 350b
	SOM	3.0 ± 0.2a	18 ± 2b	40 ± 5a	279 ± 9b	3 650 ± 348ab	25 ± 2b	5 509 ± 84d
	GLU	6.5 ± 1.0b	56 ± 11d	101 ± 17c	501 ± 45d	4 117 ± 619b	35 ± 7c	3 980 ± 154a
	CEL	8.5 ± 0.9b	46 ± 4c	70 ± 4b	320 ± 14c	3 890 ± 518b	33 ± 5c	4 867 ± 149c
Co	Initial	0.53 ± 0.11a	6.5 ± 0.2a	337 ± 17a	93 ± 18a	132 ± 22a	0.31 ± 0.32a	145 ± 20a
	SOM	3.6 ± 0.3b	26 ± 4b	73 ± 6c	247 ± 8c	240 ± 16b	0.97 ± 0.13b	203 ± 4c
	GLU	4.5 ± 0.7c	42 ± 8c	85 ± 13b	253 ± 7c	219 ± 32b	0.96 ± 0.39b	156 ± 8a
	CEL	9.2 ± 0.9d	48 ± 5c	81 ± 4bc	222 ± 7b	239 ± 26b	1.0 ± 0.2b	182 ± 8b
Cr	Initial	0.03 ± 0.02a	0.04 ± 0.02a	0.61 ± 0.11d	110 ± 26a	2 805 ± 447a	314 ± 145b	6 320 ± 430ab
	SOM	0.59 ± 0.10a	0.42 ± 0.25b	0.17 ± 0.04a	123 ± 5a	2 750 ± 277a	205 ± 38a	7 276 ± 239c
	GLU	0.76 ± 0.14a	0.33 ± 0.16b	0.42 ± 0.11c	350 ± 45c	3 113 ± 466a	190 ± 31a	5 884 ± 153a
	CEL	0.14 ± 0.03a	0.20 ± 0.05ab	0.29 ± 0.07b	173 ± 13b	2 967 ± 439a	222 ± 25a	6 373 ± 458ab

† Solid-phase compartments are defined in the text.
‡ Soil organic matter treatment.
§ Glucose treatment.
¶ Shredded cellulose treatment.
# Values for a metal followed by the same letter within a column are not significantly different ($p < 0.05$).

Fe associated with FEOX1 (9100 mg kg^{-1} soil, i.e., 2.7% of Fe_7, initially) increased in the GLU treatment (30 567 mg kg^{-1} soil) and to a lesser extent in CEL (15 590 mg kg^{-1} soil), where microbial activity was high. Although this compartment remained small compared with FEOX2 and RES, these results show that a part of Fe oxides is rendered amorphous during microbial weathering, especially when it is stimulated by the addition of a biodegradable organic matter such as glucose or cellulose. In these treatments, subsequent sorption and coprecipitation processes likely occurred and contributed to the increase of the FEOX1 compartment. Transmisssion electron microscope observations showed the formation of an amorphous gel of Fe-Si (less electron dense part of the picture, Fig. 3a) in the GLU treatment, where a strong bacterial activity occurred. Microanalysis revealed that this amorphous Fe-Si gel contained Mn, Ni and Cr (Fig. 3b). A significant increase of Fe content was also observed in the OM compartment regardless of treatments.

Manganese

In the initial sample, Mn was mainly associated with the MNOX fraction solubilized by hydroxylamine hydrochloride (2330 mg kg^{-1} soil, i.e., 52% of Mn_7, Table 4), with 12 and 18% of Mn associated with FEOX1 and FEOX2, respectively. After batch incubation, a major redistribution of Mn in the different fractions was observed. The quantity of Mn in MNOX decreased significantly irrespective of treatment from 52 to 19.5, 15, and 12.5% (of Mn_7) for SOM, CEL, and GLU, respectively. In contrast, the amount of Mn increased significantly during incubation in three other compartments: EXCH, FEOX1, and OM. Manganese associated with the exchangeable fraction increased in CEL and SOM treatments from 3% (146 mg kg^{-1} soil) to 15 and 14%, respectively. The increased quantity of Mn in FEOX1 was particularly high for both GLU (2073 mg kg^{-1} soil, i.e., 43%) and CEL (1154 mg kg^{-1} soil, i.e., 28%) treatments.

Nickel

In the initial sample, Ni was mainly recovered in the FEOX2 (3170 mg kg^{-1} soil, i.e., 40% Ni_7) and RES (4486 mg kg^{-1} soil, i.e., 57% Ni_7) compartments (Table 4). In general, we observed that the most labile fractions of Ni (water soluble, exchangeable, Mn oxide, and poorly crystallized Fe oxide bound) increased in all the biotic treatments by a factor of two (SOM treatment) to four (GLU treatment) at the end of incubation. A significant increase in the OM compartment was observed for the three treatments. Nevertheless, these fractions were quantitatively minor compared with FEOX2 and RES, except for the FEOX1 fraction that, for example, increased from 1.3 to 5.7% of Ni in the GLU treatment.

Cobalt

Initially, Co was mainly extracted by hydroxylamine (337 mg kg^{-1} soil, i.e., 47% Co_7) and thus appeared to be associated with Mn oxides. Furthermore, 32% of the

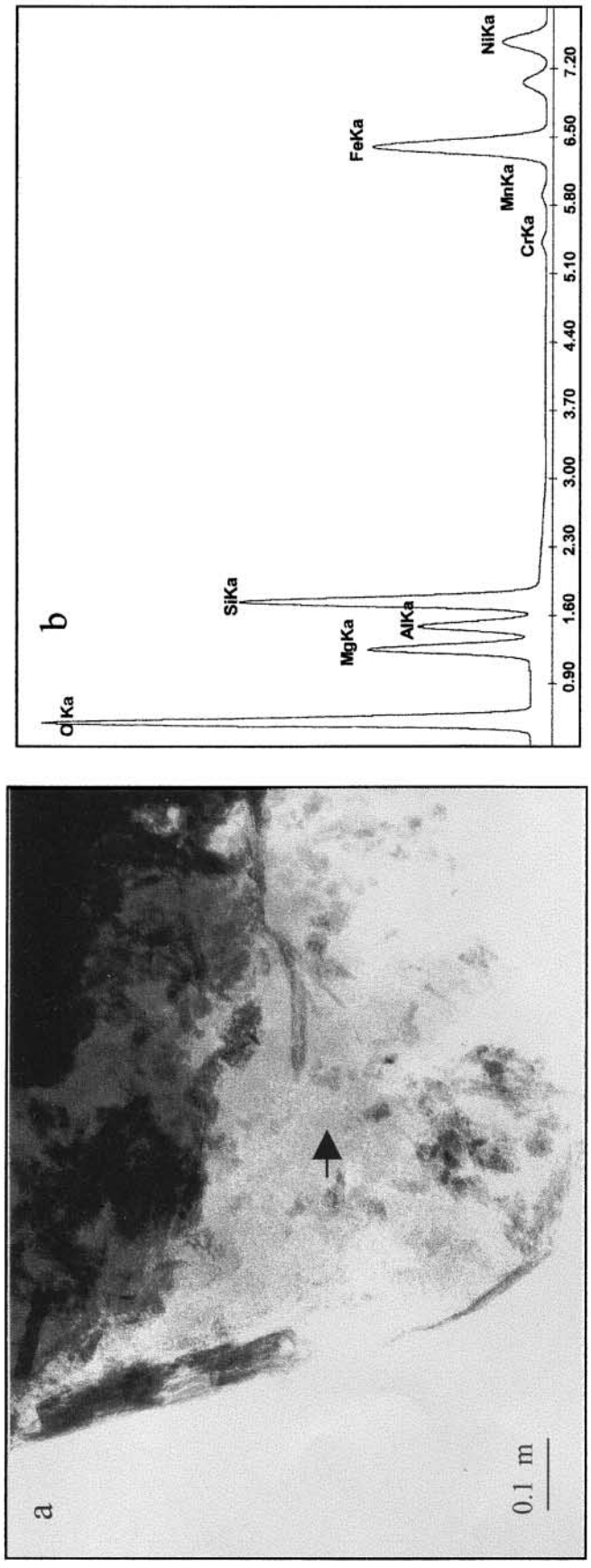

Fig. 3. Transmission electron microscopy (TEM) micrograph of amorphous Fe-Si gel in GLU treatment (a) and EDX spectrum of the gel (b).

Co was associated with FEOX1 and FEOX2, and 20.3% with RES, and <1% was exchangeable by KCl.

After incubation, a major redistribution of Co occurred in the solid phase, as observed for Mn. The quantity of Co associated to the Mn oxides decreased significantly in all treatments, whereas Co increased in EXCH, FEOX1, and FEOX2. Exchangeable Co was particularly high for the GLU and CEL treatments, where microbial activity was high.

Chromium

For Cr, 85 to 95% of Cr_t were recovered by the SSE procedure. Initially, 6320 mg kg^{-1} soil, that is 67% of Cr_7 were present in the RES fraction. Becquer et al. (2001a) showed that Cr can be incorporated partly in spinel minerals such as chromite. Given the resistance of this mineral, we can consider that the black residue observed on filters even after diacid attack was mainly composed by chromite. Thirty percent of Cr_7 were recovered as FEOX2 and only 2 and 1.2% were associated with OM and FEOX1, respectively. Nevertheless, Becquer et al. (2001a) showed that after long time DCB extraction Cr appeared preferably associated with crystallized Fe oxides (substituted goethite). The relatively lower content extracted here may be because of an incomplete oxide solubilization during the extraction. Besides Cr is known to stabilize the oxide structure (Schwertmann, 1991; Bousserrhine et al., 1999), which may explain the incomplete solubilization of Fe oxide during DCB extraction.

After 140 d of incubation, Cr associated with FEOX1 increased significantly in CEL and GLU treatments from 1.2 to 3.7 and 1.8% of extracted Cr, respectively. Exchangeable Cr which initially represented 0.035 mg kg^{-1} soil increased significantly in all treatments.

DISCUSSION

The present experimental approach simulated the interactions between minerals, organics and microbes occurring in soil. The results underline that, under anaerobic conditions, bacterial degradation of organic matter and bacterial Fe and Mn reduction can drastically influence the mobility of metals and their partitioning into different compartments of the solid phase.

Soil organic matter as a C source supported bacterial activity that increased with the addition of easily biodegradable compounds (glucose or cellulose). Thus C mineralization increased, and the kinetics of CO_2 production varied with the nature of the organic substrate and the involvement of different types of microbial communities, as described by Quantin et al. (2001).

The oxidation of organic matter leads to the production of electrons, and is as a consequence associated to the reduction processes of electron acceptors. Manganese and Fe oxides are among the main electron acceptors that allow bacterial activity in soils under anaerobic conditions, and Mn and Fe solubilization is a direct result of anaerobic bacterial activity (Quantin et al., 2001). Solubilization is greatly stimulated by organic matter inputs, as observed in the experiments where Mn and Fe release reached quite high levels. The bacterial reduction of Mn and Fe also resulted in the solubilization of Co and Ni associated to oxides. Fe and Mn oxides are known to be the main scavengers of these trace metals in this type of soil (Schwertmann and Latham, 1986; Becquer et al., 2001b), and the association of Co and Ni with Fe and Mn oxides was verified by selective SSE.

A reduced content of Mn, Ni, and Co in solution and, to a lesser extent, Fe was observed at the end of experiment. This probably corresponded to sorption and coprecipitation processes. Selective sequential extractions are commonly used to determine element partitioning in soils (Shuman, 1985; Schramel et al., 2000; Han et al., 2001), in lakes, river, or synthetic sediments (Tessier et al., 1979; Kheboian and Bauer, 1987; Chartier et al., 2001), as well as in sewage sludges and urban wastes (McGrath and Cegarra, 1992; Prudent et al., 1996). Such extractions were used in this study to describe the evolution of the metal distribution among soil compartments. Chemical reagents are expected to remove elements from well-defined geochemical compartments, and each extraction refers to the target fraction (e.g., Mn oxides for hydroxylamine hydrochloride). The characterization of metals through SSE has been criticized for the lack of specificity of certain reagents, for the risk of element redistribution during the procedure, and for the change in redox status of released elements (Sheppard and Stephenson, 1995; Cornu and Clozel, 2000; Han et al., 2001). Some authors reported a redistribution of metals (particularly Mn and Fe) and a change in redox status after drying and rewetting (Bartlett and James, 1980; Bartlett and James, 1993; Sparks, 1996). These modifications seem to affect the most labile fractions (i.e., water soluble and exchangeable ones). Either an increase (Bartlett and James, 1980) or a decrease (Gambrell, 1996; Loeppert and Inskeep, 1996) in metal content of these fractions have been reported. In our experimental conditions, drying may lead to underestimate the water soluble and also to a lesser extent the exchangeable elements, particularly Mn and Fe. Still such SSE have been used to describe the partitioning of trace metals in paddy soils in relation to Zn nutrition (Mandal and Mandal, 1986), in arid soils after repeated wetting-drying cycles (Han et al., 2001) and in sediments after apatite addition (Arey et al., 1999) or oxygenation (La Force et al., 1999).

The partitioning of metals described by SSE showed two types of behaviors corresponding to the association of two distinct groups of metals with the main mineral phases of the soil. Firstly, Mn and Co, associated in Mn oxides at the start of the experiment, behaved similarly and disappeared to a large extent in this mineral compartment, whereas their concentration in the amorphous and poorly crystallized Fe oxide compartment increased correspondingly, as well as in the exchangeable fraction. A similar increase in FEOX2 (reducible Fe oxide compartment) was also noted for Co. Secondly, Fe, Ni, and Cr, that were mainly associated with FEOX2 at the beginning, increased in the amorphous and poorly crystallized Fe oxide compartment and, to a lesser extent,

in the exchangeable compartment. The bacterial reduction of Mn and Fe oxides leads to a major transformation of mineral phases and a redistribution of metals through the solid phase. Soil incubation yields a strong decrease of the Mn oxides and an increase of amorphous and poorly ordered Fe oxides, as well as exchangeable compartments. The increase in the amorphous and poorly ordered Fe oxide compartment was greater than the decrease of the Fe content in solution, showing that a real amorphization of Fe oxides occurred. Transmission electron microscope observations and EDXS analysis also confirmed the formation of an amorphous Fe oxide phase associated with the metals.

Amorphous Fe oxides are strong sorbents because of their high specific surface area (Cornell and Schwertmann, 1996) and the formation of substituted metal Fe oxides. During microbial weathering, amorphous Fe oxides can also act as a sink for metals released in solution. After microbial weathering, a large proportion of Mn, Ni, and Co occurs in the amorphous Fe oxide fraction. The net increase with time of this freshly formed mineral phase with a high sorbing capacity, simultaneously with the decrease of the reduction process and metal solubilization, resulted in increased quantities of metals bound to this fraction. Formation of this mineral phase explains the decrease of metal concentrations in solution as suggested by Soon (1994), who observed that Zn released during soil weathering became preferentially associated with amorphous Fe oxides, whereas the crystalline oxides were stable. Thus different Fe compounds appear to control the behavior of other metals under experimental conditions as Hazra et al. (1987) observed for Zn availability to rice. Mandal and Mandal (1986) also reported that hydrous Fe oxides controlled Zn availability to plant under flooded conditions. Other reports have attributed a smaller or negligible role of Fe oxides in plant mineral nutrition under aerobic conditions (Soon, 1994) because of the diffusion of metals like Zn into oxide lattices which renders them unavailable (Brümmer et al., 1988). Further, during the bacterial reduction processes, pH increases (Quantin et al., 2001) because of the Fe^{3+} to Fe^{2+} reduction and leads to a decrease in metal solubility that also favored precipitation of metal hydroxides and their adsorption on the surfaces of freshly formed amorphous and poorly crystallized Fe oxides. During the drought periods, the crystallization of amorphous Fe oxides and the subsequent stabilization and incorporation of the metals into the mineral lattices (Han et al., 2001) could lower the availability of metals. Microbial weathering led to the increase of some easily available phases. Despite some bias discussed above, the water soluble and the exchangeable fractions of metals increased significantly. Organic matter also appears to play an important role in the dynamics of Fe, Mn, and Ni as the fraction of metals associated with organic matter, either specifically adsorbed or complexed, also increased. Moreover, this fraction is probably underestimated because a part of metals associated to this fraction can be removed before the organic matter step of the SSE procedure. These different compartments (water soluble, exchangeable and organic) are the sources of easily bioavailable metals and these elements could also be leached out and then removed from the soil profile.

CONCLUSION

Bacterial weathering processes under anaerobic conditions, involving reduction and dissolution of major (Fe, Mn) and trace elements (Co, Ni) from oxides, brings about a significant modification of metal distribution into the geochemical compartments of soil. An increase in the concentration of metals in the most labile compartments is readily observed during anoxic incubation. An increase may be observed in amorphous or poorly crystallized Fe oxides that are highly dependent on soil properties and environmental factors such as pH, E_H, and microbial activity. The well-crystallized Fe oxides as well as the residual fraction are quite stable metal compartments. Metals in these two latter compartments may be considered as the least labile or least bioavailable metals.

Soil moisture and available organic C both control bacterial activity including bacterial reduction directly affecting metal redistribution. Soils experiencing both saturation and wetting-drying regimes are very reactive, then the metals they contain can be redistributed into more or less labile fractions. The Ferralsol used in this study constitutes a major soil type in New Caledonia. Thus it is likely to experience major fluctuations in availability of metals. During drought periods, low availability will result from the crystallization of amorphous Fe oxides and the subsequent stabilization and incorporation of the metals into the mineral lattices. Upon water saturation, metal availability will again increase and be prone to plant uptake during the subsequent growth season.

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