

Impact of andosolization on pedogenic Fe oxides in ferrallitic soils

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ABSTRACT

The accumulation of soil organic matter (SOM), poorly crystalline Fe oxides and metal-humus complexes is a trait of non-allophanic Andosols. The process of andosolization, which may occur in ferrallitic soils with high organic matter content, can involve transformation from well crystallized Fe oxides to poorly crystallized Fe oxides and Fe-humus complexes. This study investigates such changes in pedogenic Fe mineral associations for a soil topequence between 1500 and 2260 m altitude along the southern flank of the volcanic Bambouto Mountains, Western Cameroon. The soils consist of highly weathered material, dominated by kaolinite, gibbsite and Fe oxides, grading to Protoandic Umbrisols at high altitude, recording an increase in SOM content with increasing altitude. As revealed by selective extraction analysis, the relative amount of poorly crystalline Fe oxides is low in the Bt and Bo horizons of low-altitude pedons, as well as in deep subsurface horizons of the high-altitude pedons. In contrast, it is significantly higher in the A and Bw horizons of the high-altitude pedons, with a clear increase with increasing altitude. Mössbauer spectroscopy analysis of B horizon samples identifies goethite as the dominant Fe oxide phase in nearly all pedons, with higher hematite contents in a mid-altitude zone marked by lower annual rainfall than in other parts of the topequence. The Mössbauer spectra also reveal the presence of dissolved organic matter (DOM)-ferrhydrite, whose abundance is greatest in the Bw horizon of the high-altitude pedons, with an increase in relative abundance with increasing altitude. The observed patterns are attributed to dissolution-reprecipitation of Fe oxides that initially formed through ferrallitic weathering of volcanic parent materials that were roughly uniform along the topequence. At high altitude, coupled hematite dissolution and DOM-ferrhydrite formation are favoured by high organic matter contents and low pH, related to cool humid environmental conditions and their effect on the vegetation and organic matter cycling.

1. Introduction

Pedogenic Fe oxides can differ greatly with respect to abundance, mineralogical and crystallographic properties, depending on soil conditions. The resulting vertical and lateral distribution patterns of Fe oxides in soil profiles are highly diverse, providing relevant information about soil evolution (Schwertmann and Taylor, 1989; Bigham et al., 2002).

Ferrallitic soil development involves the accumulation of Fe oxides, as well as gibbsite and kaolinite. The resulting soils are widespread in the humid tropics (Herbillon, 1980) and are generally considered to be stable endpoints of soil formation in these environments. In some specific environmental conditions, however, ferrallitic soils can transform into Podzols (Chauvel et al., 1987; do Nascimento et al., 2004, 2008;

Fritsch et al., 2009, 2011) or Andosols (Caner et al., 2000, 2011). These transformations are linked to the accumulation of organic matter, promoting the formation of (Al,Fe)-humus complexes. Depending on the metal/carbon ratio of the organo-metallic complexes, two different pathways exist. High ratios prevent the mobility of those complexes, inducing the formation of non-allophanic (Aluandic) Andosols (Caner et al., 2011). In contrast, low metal/carbon ratios promote metal-humus complex mobility, inducing the formation of Podzols (do Nascimento et al., 2008; Fritsch et al., 2011). The common driver of both transformation processes is soil organic matter (SOM), which can accumulate following a period of ferrallitic soil development in response to climate change (Caner and Bourgeon, 2001; Caner et al., 2003) or to non-climate controlled changes in soil water regime (Bardy et al., 2008; do Nascimento et al., 2008; Fritsch et al., 2011). In these soil

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transformations, SOM contributes to the dissolution of Al oxides, Fe oxides and kaolinite through complexation of Al and/or Fe and through inhibition of Al and Fe oxide crystallization (Bigham et al., 2002; Huang and Keller, 1971; Huang et al., 2002; Wieland and Stumm, 1992). However, the magnitude in the supply of Fe and Al from oxides and kaolinite (Balan et al., 2005; Fritsch et al., 2005, 2009) may be determinant to orientate the process of soil deferrallitization towards andosolization or podzolization (Caner et al., 2011).

The present study deals with ferrallitic soils affected by andosolization, which involves organic matter accumulation and the formation of poorly crystalline compounds (see Duchaufour, 1977). The studied soils are part of a toposequence in the Bambouto Mountains of West Cameroon that was recently re-investigated by Van Ranst et al. (2019), who demonstrated the importance of Fe and Al derived from the dissolution of Fe oxides and gibbsite in the stabilization of organo-metallic complexes, which are abundant at high altitude. This complementary paper focusses entirely on the detailed characterization of the Fe oxide phases along the toposequence. This is done in part by selective dissolution analysis, documenting changes in the ratio between poorly crystalline and crystalline Fe oxides, but the emphasis is mainly on quantification of pedogenic Fe oxide species by Mössbauer spectroscopy analysis. Overall the study aims to assess how Fe oxides are affected during increasing transformation of ferrallitic soils with changes in altitude-related climatic conditions, exploring the hypothesis of preferential dissolution and precipitation of specific Fe oxide minerals. Variations in environmental conditions can be significant along the toposequence, as the southern flank of the Bambouto volcano exhibits substantial temperature and rainfall variability over short distances.

2. Environmental setting

The Bambouto Mountains in West Cameroon (9°57' to 10°15'E, 5°27' to 5°48'N) constitute an elongated shield and conical complex with a diameter of 25 km (E-W) to 50 km (SW-NE). The massif culminates in a large caldera at 2680 m and its base is at about 1500 m a.s.l., on a metamorphic Precambrian basement complex of gneiss, migmatites and anatexites (Tchoua, 1974). The Bambouto volcanic cone (Mount Méléta, 2740 m) was built up during the Upper Miocene (Morin, 1989). The study area is south of the Bambouto caldera, extending between altitude 2500 and 1450 m along the side of the volcanic cone (Fig. 1). The landscape consists of two parts: (i) the Bamilike plateau (1400–1640 m), where an Oligocene volcanic sheet (trachytic tuff and basalt) overlies the Precambrian basement complex (Hieronymus, 1972; Regnault, 1986), and (ii) the Miocene Bambouto volcanic cone (trachyte and basaltic flows).

Mean annual rainfall along the southern flank of the Bambouto volcano is 1918 mm, with a large standard deviation (255 mm). Rainfall and elevation show no significant correlation. Spatial variability of rainfall is due to the effects of relief, distance from the sea, and wind exposure (Kengni et al., 2009). Two distinct seasons exist, with negligible rainfall from December to February/March when the powerful continental harmattan wind predominates and the marine monsoon is inexistent. Based on rainfall variability, three zones are recognized along the southern slope: (i) a low-altitude zone (1400–1600 m), with high mean annual rainfall (2030 mm at Dschang, 1400 m altitude); (ii) a mid-altitude zone (1600–2000 m), along the Melang-Loung-Djuttitsa axis, with somewhat drier conditions (about 1760 mm at both Loung and Djuttitsa, 1838 and 1890 m altitude); and (iii) a high-altitude zone (≥ 2000 m), with the highest mean annual rainfall (2507 mm at Méléta, 2608 m altitude). The latter zone has a tropical climate with altitude-related temperate characteristics (Morin, 1988, 1989), and frequent tornadoes that compensate the long dry season (December to February/March).

The original vegetation in the Bambouto highlands was open grassland savanna, in the form of *Sporobolus* prairies typical of temperate environments (e.g., Morin, 1988; Tsozué et al., 2009). This natural

vegetation is progressively being destroyed by intensification of agriculture, driven by increasing human population (e.g., Kuété, 1999; Bitondo et al., 2013). The soils are increasingly used for growing Irish potatoes and carrots (> 70% of the produce), while cattle rearing is disappearing. Scarce fallow lands are dominated by *Pteridium aquilinum*, *Rafia vinifera*, *Eucalyptus grandis*, *Imperata cylindrica*, and *Pennisetum purpureum*.

The studied soils are derived from volcanic parent materials along the southern slope of the Bambouto Mountains, between 1500 and 2260 m altitude. They have been extensively studied for their physico-chemical and mineralogical properties, focused on pedogenesis and classification (Doube and Van Ranst, 1984; Van Ranst et al., 1987; Doube, 1989; Tematio et al., 2004, 2011; Tematio, 2005). The high-altitude pedons (≥ 2000 m) were originally classified as Andosols. However, all requirements for andic properties are not fulfilled (Van Ranst et al., 2019) because P-retention was below 85% (see Table S1). Yet they exhibit a thick surface layer with high SOM content in both A and Bw horizons. This humus-rich layer was previously interpreted as an altered volcanic ash layer developed under cool and humid climatic conditions that promote a low turnover rate of accumulated SOM. Besides, the high-altitude pedons are characterized by an abundance of residually accumulated gibbsite and Fe oxides, presenting a source of Al and Fe that play a crucial role in the formation of organo-metallic complexes. The formation of non-crystalline materials and accumulation of organic matter as dominant processes in soils derived from volcanic materials are typical for the process of 'andosolization' (Duchaufour, 1977; Ugolini and Dahlgren, 2002). The increasing degree of andosolization with altitude in the Bambouto Mountains is well reflected by soil classification names, especially by the humic qualifier for the low-altitude Lixisols, Acrisols and Ferralsols, and the protoandic subqualifier for the high-altitude Umbrisols (Van Ranst et al., 2019). It is also reflected by a decrease in gibbsite content with increasing altitude, especially in the high-altitude pedons, due to acid soil conditions and high organic matter content, and an increase in oxalate extractable contents of Al and Fe (Van Ranst et al., 2019).

3. Materials and methods

3.1. Soil materials

For this study, six pedons between 1500 and 2260 m altitude along the southern slope of the Bambouto volcano (Fig. 1) were selected. All these pedons have been studied earlier (Doube and Van Ranst, 1984; Doube, 1989), but new information concerning physico-chemical, mineralogical and micromorphological properties, as well as their classification, has recently been obtained (Van Ranst et al., 2019; see also Table S1).

All studied pedons formed on pediments derived from trachytic and basaltic parent materials (Van Ranst et al., 2019). All soil horizons were analyzed by selective chemical extraction to assess the crystallinity status of pedogenic Fe oxides, and samples of B horizons (Bt, Bo, Bw) taken at a depth of around 50 cm were analyzed by Mössbauer spectroscopy to quantify Fe-bearing phases.

At low and mid altitude (< 2000 m), the pedons comprise Bt and Bo horizons that are dark red (2.5 YR 3/6, moist) and red (2.5 YR 4/8, dry) (Van Ranst et al., 2019). In contrast, the pedons at high altitude (≥ 2000 m) are characterized by Bw horizons with (dark) reddish brown (5 YR 3/3–4/4, moist) to dark brown (7.5 YR 3/4, dry) colours and with a fluffy consistency ($BD < 0.9 \text{ Mg m}^{-3}$) (Van Ranst et al., 2019). These Bw horizons have a much higher OC content (> 4%) than the Bt and Bo horizons of the low-altitude pedons (< 3%). All B horizons have a clayey texture. P-retention is < 85%, also in the high-altitude pedons, so not all requirements for andic soil properties (Soil Survey Staff, 2014; IUSS Working Group WRB, 2015) are fulfilled (Table S1).

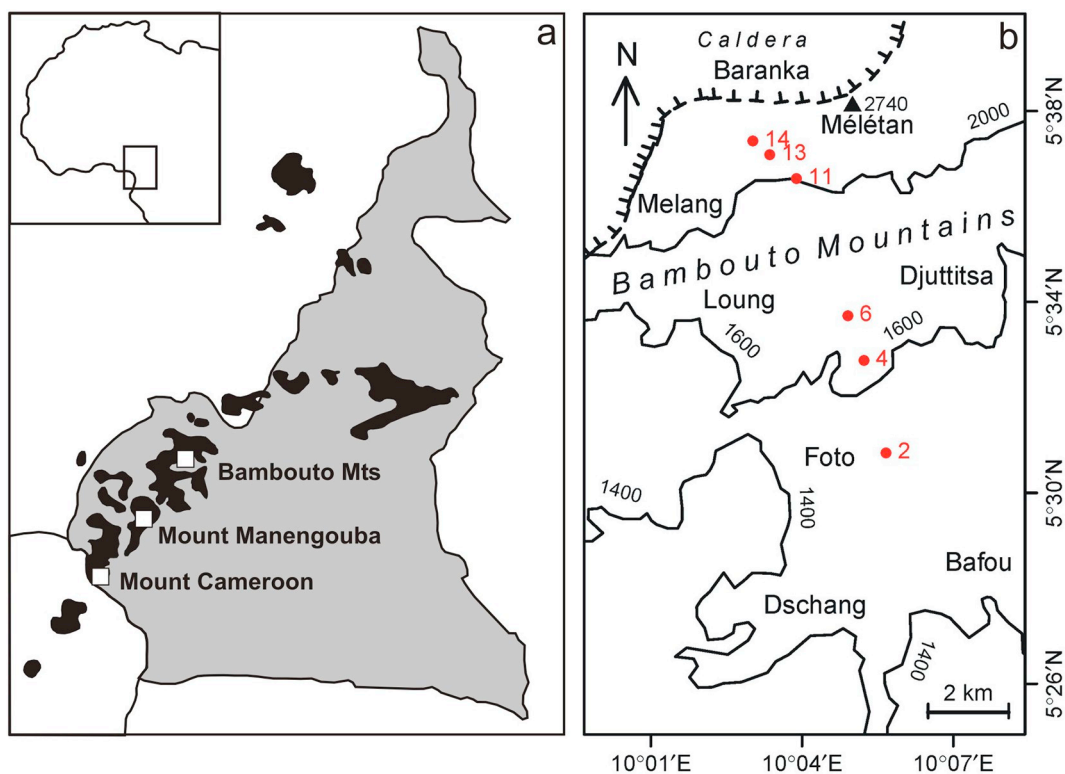


Fig. 1. Profile location. (a) Location of Cameroon Volcanic Line Deposits (black), including the Bambouto Mountains, within Cameroon; (b) the southern slope of the Bambouto Mountains, with location of six representative pedons selected for this study.

3.2. Chemical analyses

Samples were air-dried and passed through a 2 mm-sieve before analysis (NF ISO 11464; AFNOR, 2006). The total elemental composition of the fine-earth fraction (< 2 mm) was determined after fusion with tetraborate and metaborate at 950 °C, followed by dissolution in 4% HNO₃. Si, Al, Fe concentrations were measured using ICP-OES (only Fe concentrations are reported).

Secondary Fe and Al-bearing phases were studied by selective chemical extraction of the fine-earth fraction, using dithionite-citrate-bicarbonate (DCB, d) (Mehra and Jackson, 1960), acid-ammonium oxalate (o) (Blakemore et al., 1981), and sodium pyrophosphate (p) (Bascomb, 1968), whereby Fe and Al concentrations of the extracts were measured by ICP-OES. The DCB method extracts Fe by reductive dissolution, and as such DCB-extractable Fe (Fe_d) provides an upper limit for the total abundance of Fe oxides (Biggam et al., 2002). Acid-oxalate extraction, involving acid treatment (pH 3) in darkness with oxalate as chelating agent, targets poorly crystalline phases or short-range-order (SRO) Fe oxides, including ferrihydrite, fine-grained lepidocrocite (Poulton and Canfield, 2005), and organo-metallic compounds, complicated by a contribution from mixed-valence Fe oxides such as magnetite (Gamble and Daniels, 1972; Rhoton et al., 1981; Biggam et al., 2002). Pyrophosphate-extractable iron (Fe_p) is largely attributed to Fe in organo-metallic complexes.

3.3. Mössbauer spectroscopy analysis

The Mössbauer spectra (MS) of the selected B horizons were collected at room temperature (RT), at ~80 K, and at ~10 K (8 to 16 K), using a time-mode transducer and a triangular drive signal. The source was ⁵⁷Co in a rhodium matrix. All isomer shift values (δ) quoted hereafter are with reference to α-Fe at RT. Counts were accumulated in 1024 channels until an off-resonance (background) rate of typically 2.10⁻⁶ was reached. The velocity scale was regularly calibrated against

the spectrum obtained for a standard hematite powder. The velocity increment per channel was approximately 0.04 mm/s. Low temperatures were applied to the respective absorbers using standard cryogenic equipment. The spectra were fitted with model-independent distributions of hyperfine-parameter values, according to the method described by Vandenberghe et al. (1994). Specific details about the fitting models used are provided in the Results section.

4. Results

4.1. Selective extraction analysis

The total Fe (Fe_t) content of bulk samples (Table 1) ranges between 8 and 14%. These relatively high Fe_t values, with high Al total contents (13 to 21% Al_t) and Si/(Al + Fe) values between 0.67 and 0.29, reflect the typical ferrallitic mineralogical assemblage dominated by gibbsite, Fe oxides and kaolinite. The high Fe_d/Fe_t ratio (Table 1) indicates that most iron is present as Fe oxide (72 to 95%).

Selective extraction results (Table 1; Table S1) show that the Bw horizons of the high-altitude pedons (P11, P13, P14) all have higher extractable Al (Al_d, Al_o, Al_p) and Fe (Fe_o, Fe_p) contents than the Bt and Bo horizons of the low-altitude pedons (P2, P4, P6). In contrast, Fe_d content does not differ in the same manner between low- and high-altitude pedons. The Al_o + 1/2Fe_o content exceeds the minimum required for andic soil properties (2%) for the A and Bw horizons of pedons P11, P13 and P14. The fraction of poorly crystalline Fe oxides, as indicated by the Fe_o/Fe_d ratio, is between 0.03 and 0.18 (Table 1). This fraction is much more important in most A horizons and especially in the Bw horizons of the high-altitude pedons (0.07–0.18), compared to the Bt and Bo horizons of the low-altitude pedons (0.03–0.05) and the lower subsoil horizons of the high-altitude pedons (0.04–0.08). In the low-altitude Bt and Bo horizons and the high-altitude deeper subsoil, the fraction of poorly crystalline Fe oxides is fairly constant (Fe_o/Fe_d ratio between 0.03 and 0.06), with only slightly higher values for

Table 1

Total Fe (t), extracted Fe and Al with dithionite-citrate-bicarbonate (d), acid oxalate (o) and pyrophosphate (p), and Fe_d/Fe_t and Fe_o/Fe_d ratios of the soil horizons of the selected pedons.

Pedon (altitude)	Hor. ^a	Depth (cm)	Fe _t (%)	Fe _d (%)	Al _d (%)	Fe _o (%)	Al _o (%)	Fe _p (%)	Al _p (%)	Fe _d /Fe _t	Fe _o /Fe _d
P2: Rhodic Lixisol (Clayic, Humic) ^b											
(1500 m)	Ap1	0–6	13.03	9.37	1.86	0.46	0.82	0.19	0.44	0.72	0.05
	Ap2	6–18/24	12.68	9.30	1.78	0.44	0.73	0.22	0.44	0.73	0.05
	Bt1	18/24–32/34	12.91	9.51	1.71	0.43	0.60	0.22	0.41	0.74	0.05
	Bt2	32/34–67	13.64	9.79	1.63	0.40	0.38	0.03	0.10	0.72	0.04
	Bt3	67–103	14.27	10.98	1.51	0.46	0.36	0.01	0.07	0.77	0.04
	Bt4	103–150	14.18	11.19	1.26	0.45	0.33	0.01	0.07	0.79	0.04
P4: Rhodic Acrisol (Clayic, Humic)											
(1700 m)	Ap	0–22	9.09	7.13	1.67	0.50	1.30	0.22	0.74	0.78	0.07
	AB	22–40/47	10.16	7.55	1.43	0.40	0.67	0.64	0.70	0.74	0.05
	Bo1	40/47–70	11.11	8.53	1.22	0.33	0.43	0.07	0.14	0.77	0.04
	Bo2	70–108	11.41	9.09	1.08	0.38	0.41	0.01	0.08	0.80	0.04
	Bo3	108–136	11.61	9.30	1.05	0.42	0.39	0.01	0.07	0.80	0.05
	Bo4	136–190	11.31	9.37	0.95	0.42	0.36	0.01	0.06	0.83	0.04
P6: Humic Rhodic Ferralsol (Dystric, Clayic)											
(1780 m)	Ap	0–12/18	9.91	7.52	1.88	0.57	1.23	0.37	0.83	0.76	0.08
	BA	12/18–32/39	11.07	8.55	1.37	0.40	0.54	0.44	0.40	0.77	0.05
	Bt1	32/39–52/67	11.92	8.68	1.32	0.29	0.37	0.02	0.09	0.73	0.03
	Btcs2	52/67–88/100	n.d.	9.04	1.05	0.34	0.32	0.01	0.07	n.d.	0.04
	2Bo1	88/100–110/128	12.19	9.31	0.96	0.35	0.35	0.01	0.06	0.76	0.04
	2Bo2	110/128–178	11.75	9.27	0.93	0.29	0.27	0.01	0.05	0.79	0.03
P11: Dystric Protoandic Cambisol (Clayic, Hyperhumic)											
(2000 m)	Ap	0–25/28	8.65	7.41	1.72	0.66	2.02	0.33	1.16	0.86	0.09
	Bw1	25/28–44/52	9.16	7.41	1.99	0.71	1.96	0.31	0.85	0.81	0.10
	Bw2	44/52–63/72	9.61	7.55	2.14	0.70	1.75	0.38	0.89	0.79	0.09
	Bw3	63/72–77/84	9.86	8.18	2.07	0.58	1.21	0.91	1.43	0.83	0.07
	2Bo	77/84–190	10.64	9.51	1.84	0.61	0.83	0.21	0.21	0.89	0.06
P13: Cambic Umbrisol (Protoandic, Clayic, Chromic)											
(2120 m)	A1	0–15/25	7.83	6.22	2.53	0.90	2.40	0.70	1.81	0.79	0.14
	A2	15/25–42/43	8.45	8.05	2.32	0.97	2.77	0.73	1.44	0.95	0.12
	Bw1	42/43–52/54	10.41	8.87	2.23	0.87	1.57	1.06	1.31	0.85	0.10
	Bw2	52/54–101	10.99	9.45	1.86	1.15	1.10	1.20	1.07	0.86	0.12
	2Bo1	101–131	11.13	9.79	0.98	0.43	0.43	0.07	0.13	0.88	0.04
	2Bo2	131–190	11.57	10.66	0.88	0.42	0.26	0.01	0.06	0.92	0.04
P14: Cambic Umbrisol (Protoandic, Clayic, Chromic, Pachic)											
(2260 m)	Ap	0–54/59	9.07	7.29	2.50	1.29	2.64	0.71	1.53	0.80	0.18
	Bw1	54/59–82/90	12.60	10.82	2.93	1.99	2.04	2.33	2.58	0.86	0.18
	Bw2	82/90–120/128	13.07	11.71	2.22	1.84	1.51	1.45	1.42	0.90	0.16
	2Bo	120/128–140/150	14.28	11.10	1.37	0.91	0.64	0.90	0.54	0.78	0.08
	2Bcs	140/150–190	14.49	11.26	0.93	0.48	0.22	0.71	0.05	0.78	0.04

n.d.: not determined.

^a Horizon symbols of the original profile descriptions based on field morphological properties.

^b WRB classification (IUSS Working Group WRB, 2015).

the high-altitude pedons.

A single-factor regression analysis was conducted to test and reveal the covariation between the fraction of poorly crystalline Fe oxides (Fe_o/Fe_d) and the altitude of the pedon along the toposequence, using the R statistical package (R Core Team, 2018). A linear regression equation was identified as the best fit for the subgroup of Bt and Bo horizons, and a quadratic regression equation was the best fit for the A and Bw horizons (Fig. 2). The covariation of Fe_o/Fe_d ratio against altitude is statistically confirmed at the most significant level for A and Bw horizons, with variations in altitude alone explaining 91% of the variation in Fe_o/Fe_d ratio. For the Bt and Bo horizons, covariation of Fe_o/Fe_d ratio against altitude is statistically insignificant, showing that the Fe_o/Fe_d ratio does not vary with altitude for those intervals (Fig. 2). The fraction of poorly crystalline Fe oxides clearly increases upwards in most pedons, and this increase becomes much more pronounced with increasing altitude (Fig. 2).

4.2. Mössbauer spectroscopy analysis

All RT spectra consist of a superposition of a doublet and a broad

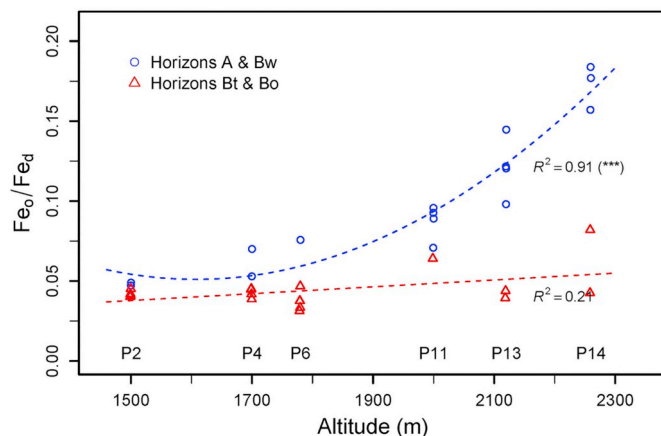


Fig. 2. Covariation between the fraction of poorly crystalline Fe oxides, represented by the Fe_o/Fe_d ratio, and the altitude of the pedons along the toposequence. A quadratic trend is evident in A and Bw horizons, while a linear trend exists in Bt and Bo horizons. *** $p < 0.001$.

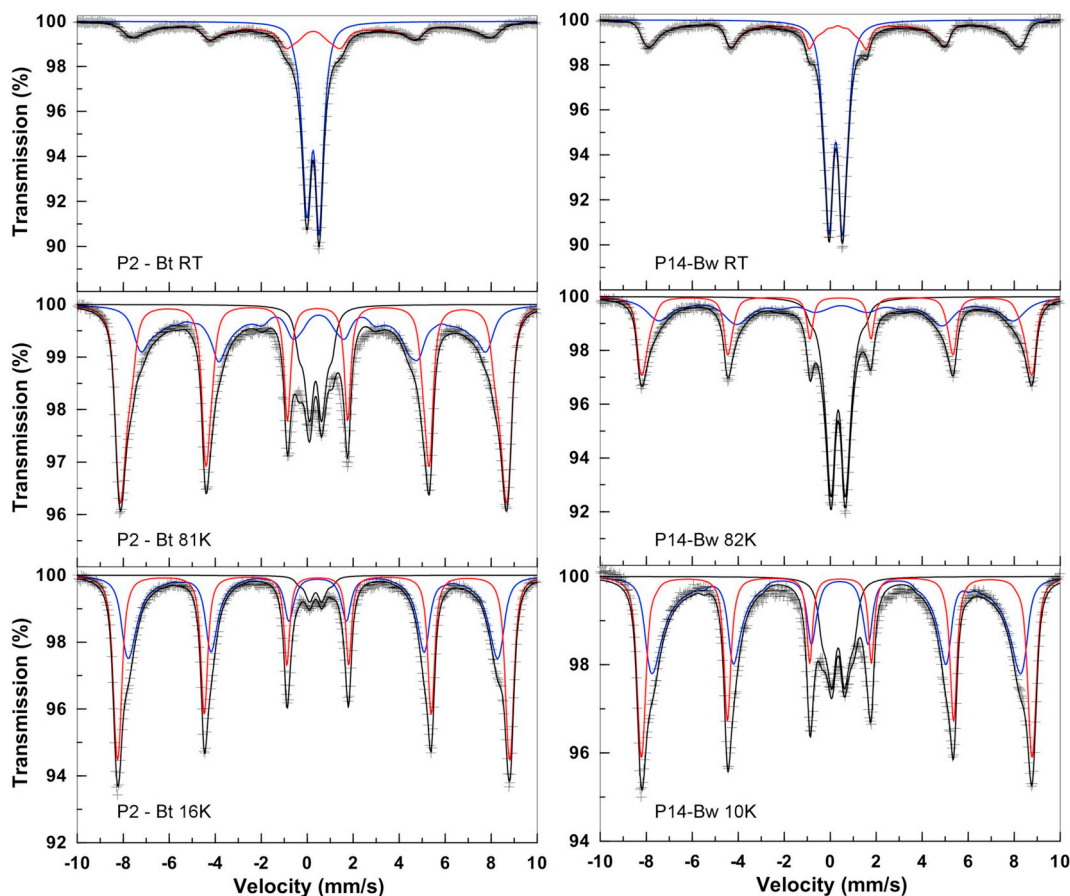


Fig. 3. Fitted Mössbauer spectra for the Bt horizon of pedon 2 (P2) and the Bw horizon of pedon 14 (P14) at room temperature (RT), and at low temperature, 81 and 82 K, and 16 and 10 K, respectively. All spectra consist of a superposition of a broad sextet and a central quadrupole doublet; the sextet components are much more prominent in the low-temperature spectra.

Table 2

Adjusted values of the relevant parameters characterizing the model-independent hyperfine-parameter distributions fitted to the Mössbauer spectra of the investigated soil samples recorded at room temperature. B_{hf} is the maximum-probability hyperfine field, σ the square-root of the second-order moment of the HFD, $2\epsilon_Q$ the average quadrupole shift of the magnetic component, $\Delta E_{Q,m}$ the maximum-probability quadrupole splitting of the Fe^{3+} doublet component and RA the fractional area of the doublet contribution to the total spectrum. δ_{Fe} is the average isomer shift.

Pedon - Hor.	Sextet component				Fe^{3+} doublet		
	$B_{\text{hf,m}}$ (T)	σ (T)	δ_{Fe} (mm/s)	$2\epsilon_Q$ (mm/s)	$\Delta E_{Q,m}$ (mm/s)	δ_{Fe} (mm/s)	RA
P2 - Bt2	48.4	16.1	0.34	-0.17	0.52	0.36	0.52
P4 - Bo1	48.7	16.5	0.36	-0.15	0.54	0.36	0.54
P6 - Bt1	48.9	16.6	0.34	-0.15	0.52	0.36	0.55
P11 - Bw1 ^a	49.2	15.1	0.34	-0.13	0.52	0.35	0.55
P13 - Bw1	49.5	16.3	0.36	-0.17	0.54	0.35	0.59
P14 - Bw1	50.0	13.6	0.36	-0.17	0.56	0.35	0.55

^a Spectrum contains a weak Fe^{2+} doublet (RA = 0.02); indicated RA value refers to sum of Fe^{3+} and Fe^{2+} doublet.

sextet (Fig. 3). They were fitted with a model-independent hyperfine-field (Bhf) distribution (HFD) in the range of 5 to 53 T, and with a model-independent quadrupole-splitting (ΔEQ) distribution (QSD) in the range of 0.2 to 1.6 mm/s. The adjusted values of relevant parameters that characterize the distribution are listed in Table 2. From the adjusted values of the isomer shift (δ), which is 0.35 ± 0.01 mm/s for all samples, it is obvious that both the magnetic (sextet) component and the non-magnetic (doublet) component are due to Fe^{3+} -bearing

species. One exception is sample P11-Bw, whose spectrum shows the presence of a weak Fe^{2+} doublet with a fractional area of ~ 0.02 . For the magnetic component, the average value of the quadrupole shift ($2\epsilon_Q$) is -0.17 mm/s, and its maximum-probability hyperfine field ($B_{\text{hf,m}}$) is in the range of 48.4 to 50.0 T. These results indicate that this component is likely due to a hematite phase, with poor crystallinity and possibly with structural substitution of Fe^{3+} by other cations (most likely Al^{3+}), based on its low field values (Vandenberghe and De Grave, 2013). The adjusted value of the maximum-probability quadrupole splitting ($\Delta E_{Q,m}$) of the QSD is 0.54 ± 0.02 mm/s for all samples, and it is as such not diagnostic for any specific Fe phase that commonly occurs in soils.

All low-temperature spectra also consist of a superposition of a broad sextet and a central quadrupole doublet, but in these conditions, the sextet components are much more prominent (Fig. 3). They were numerically decomposed into two HFD components (HFD1, HFD2) and one QSD component. For the spectra recorded at ~ 80 K, the hyperfine fields were allowed to vary in the range of 48 to 54 T for HFD1 and 25 to 50 T for HFD2, whereas for the spectra recorded at ~ 12 K these field ranges were chosen to be 48 to 55 T (HFD1) and 35 to 52 T (HFD2). In both temperature conditions, the QSD component had a quadrupole splitting (ΔEQ) range of 0.3 to 1.6 mm/s. The adjusted parameters values for the two HFD components at the lowest applied temperature (~ 12 K) are listed in Table 3. Based on the hyperfine parameters (B_{hf} , δ_{Fe} , $2\epsilon_Q$), the HFD1 component is attributed to a hematite phase, and HFD2 to a goethite phase. The negative values of the quadrupole shift ($2\epsilon_Q$) of the hematite sextet imply that the hematite phase remains weakly ferromagnetic down to the lowest applied temperature, which means that no Morin transition has occurred. This feature is likely the

Table 3

Adjusted values of the relevant parameters characterizing the model-independent magnetic hyperfine-field distributions, HFD1 and HFD2, and average quadrupole splitting of the ferric doublet component fitted to the Mössbauer spectra of the investigated soil samples recorded at the lowest applied temperatures. See caption of Table 2 for meaning of listed quantities.

Pedon - Hor.	HFD1 – hematite phase						HFD2 – goethite phase					Fe ³⁺ doublet	
	T (K)	B _{hf,m} (T)	σ (T)	δ _{Fe} (mm/s)	2ε _Q (mm/s)	RA	B _{hf,m} (T)	σ (T)	δ _{Fe} (mm/s)	2ε _Q (mm/s)	RA	ΔE _{Q,m} (mm/s)	RA
P2 - Bt2	16	52.9	0.6	0.48	-0.20	0.50	50.0	3.0	0.46	-0.21	0.45	0.74	0.05
P4 - Bo1	12	52.8	0.8	0.47	-0.18	0.61	50.1	3.4	0.45	-0.21	0.33	0.74	0.06
P6 - Bt1	13	52.7	0.8	0.48	-0.18	0.69	49.8	2.8	0.45	-0.20	0.28	0.73	0.03
P11 - Bw1	13	52.9	0.7	0.47	-0.16	0.56	49.9	3.8	0.44	-0.15	0.32	0.86	0.12
P13 - Bw1	8	52.7	0.7	0.47	-0.18	0.48	50.1	3.5	0.45	-0.18	0.42	0.85	0.10
P14 - Bw1	10	52.7	0.8	0.47	-0.17	0.39	50.0	3.9	0.45	-0.15	0.46	0.84	0.15

result of poor crystallinity (particle size smaller than ~20 nm) and/or of Al-for-Fe substitution, two characteristics that were already suggested for the hematite phase by the RT spectra. The ferric doublet component, remaining in the low-temperature spectra, may be due to the presence of so-called DOM-ferrihydrate, with DOM standing for dissolved organic matter, which is a ferrihydrate type that does not order magnetically at the lowest temperatures applied in the present study (Schwertmann and Murad, 1988; Schwertmann et al., 2005). The fractional areas (RA) of the doublet subspectra and their average quadrupole splitting (ΔE_{Q,av}), as determined at the lowest applied temperatures, are listed in Table 3. These RA values are much more reliable than those for the relative proportions of the hematite (HFD1) and goethite (HFD2) components, which are generally ill defined due to the strong overlap of the respective distribution profiles.

The RA data (Table 3) suggest that the analyzed B horizons can be subdivided into two groups. One group (P2-Bt, P4-Bo, P6-Bt), representing the Bt and Bo horizons of the lower part of the toposequence, shows a fractional doublet RA of ~0.05 and an average quadrupole splitting (ΔE_{Q,av}) of ~0.74 mm/s. The other group, representing the Bw horizons of the high-altitude pedons, is characterized by doublet RA values ≥ 0.10 and ΔE_{Q,av} ≈ 0.85 mm/s. This indicates that the Bw horizons contain a larger amount of so-called DOM-ferrihydrate particles and that the Fe³⁺ co-ordinations in these particles are significantly more distorted.

When variations in relative abundance of the hematite, goethite and DOM-ferrihydrate components with altitude are considered together (Table 3; Fig. 4), goethite is clearly the dominant Fe oxide in all B horizons (except in pedon P6), with high relative concentration (between 42 and 64%). Pedons P4 and P6, at mid-altitude, stand out as profiles in which the proportional percentage of hematite is relatively high (44 to 53%). In the Bw horizons of the high-altitude pedons, the hematite content clearly decreases with increasing altitude, from 39 to 25%. The proportional percentage of the DOM-ferrihydrate phase is clearly much higher (13 to 18%) in the Bw horizons of the high-altitude pedons (P11 to P14) than in the Bt and Bo horizons (5 to 9%) of the low-altitude pedons (P2 to P6).

5. Discussion

The Fe_o/Fe_d ratios of < 0.2, and in most horizons < 0.1, indicate that most of the Fe oxides are in crystalline state, corresponding to goethite-hematite associations characteristic for highly mature ferrallitic soil materials (Schwertmann and Taylor, 1989). In a *catena*, decreasing Fe_o/Fe_d values may record a gradual disappearance of metastable ferrihydrate in favour of goethite and/or hematite as the soils become older (Malucelli et al., 1999). The implied advanced stage of weathering is an additional argument against a young age of the parent material, which would characterize the Late Pleistocene (ca. 15,000 yr BP) volcanic ash deposit that has previously been assumed to be present (see Van Ranst et al., 2019). The highest Fe_o/Fe_d values were recorded

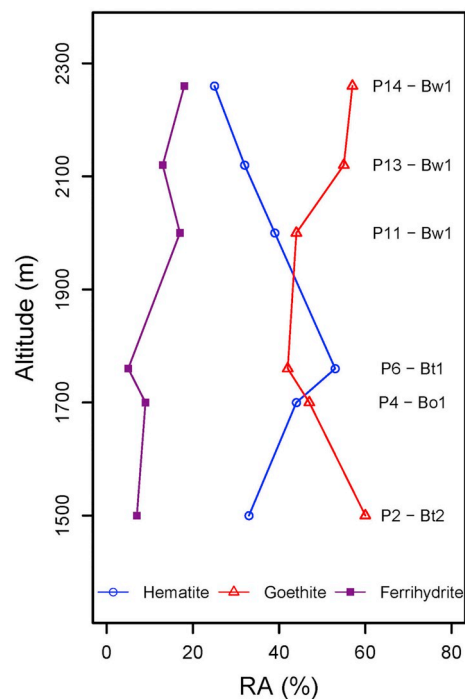


Fig. 4. Relative spectral areas of the various Fe-bearing components in the B horizons of pedons P2 to P14 versus altitude.

for the upper part of all pedons, particularly in the A and Bw horizons. For the B horizons at around 50 cm depth, the ratios are up to two to three times higher for the Bw horizons of the high-altitude pedons than for the Bt and Bo horizons of the low-altitude pedons. This reflects the retarding effect of humic acids on the crystallization of Fe oxides (Schwertmann, 1966), whereby the presence of organic matter inhibits crystal growth of more stable Fe oxide phases (Childs, 1992), which also applies to Fe oxide formation by dissolution-reprecipitation reactions.

The development of the humus-rich A and Bw horizons of the high-altitude ferrallitic pedons is related to the grass vegetation and to the cool and humid climatic conditions, restricting bio-mineralization and causing low SOM turnover rates (Van Ranst et al., 2019). Variation in the relative abundance of the various types of extractable Fe suggests an overall decrease in crystallinity, with DOM-ferrihydrate formation at the expense of more crystalline Fe oxides, such as hematite, during development of these OM-rich surface horizons. In such horizons, dissolution of crystalline Fe oxides (e.g., hematite, goethite) is strong (do Nascimento et al., 2004, 2008; Peretyashko and Sposito, 2006) depending on the nature of SOM (Bardy et al., 2008). Metal cations (Fe, Al) released during weathering of pedogenic oxyhydroxides (Fe oxides, gibbsite) are trapped by organic ligands to form organo-metallic

complexes, which are immobilized due to the high metal-to-OC ratios. The process of formation of non-crystalline materials with strong accumulation of OM in soils derived from volcanic materials has been named 'andosolization' (Duchaufour, 1977; Ugolini and Dahlgren, 2002).

Mössbauer spectroscopy analysis identifies ferrihydrite as a relatively important Fe oxide phase, especially in the Bw horizons of the high-altitude pedons. Its occurrence as poorly crystallized DOM-ferrihydrite is clearly related to high SOM contents, as documented by other studies (Schwertmann et al., 2005), in soil horizons that are also characterized by high Fe_p concentrations, indicating the presence of Fe-humus complexes. The fraction of poorly crystalline Fe oxides increases upwards in the pedons, particularly those of the high-altitude zone. This vertical trend is much more pronounced at the higher altitudes, reflecting a higher degree of andosolization. The higher hematite content of the B horizons of pedons P4 and P6 compared to those of the other pedons can be explained by the relative drier climatic conditions in the middle part of the toposequence, between 2000 and 1600 m. In soils, hematite is usually associated with other Fe oxides, but mostly goethite rather than ferrihydrite (Cornell and Schwertmann, 2003). Ferrihydrite-hematite associations have been reported for Andisols formed on basalt in the warm and moist climate of Hawaii, with an increase in relative ferrihydrite content with increasing mean annual precipitation, whereby ferrihydrite formation was interpreted to be induced by high rates of Si release from the parent rock (Parfitt et al., 1988). Drier and warmer soil environments are expected to promote hematite formation, with ferrihydrite as a possible precursor. In altitudinal sequences, the cooler and wetter high-altitude part of the sequence typically has hematite-poor soils, whereas hematite-rich soils prevail in the drier and warmer zone at lower altitude, so that the hematite-to-goethite ratio decreases with decreasing temperature and increasing rainfall (Curi and Franzmeier, 1984; da Motta and Kämpf, 1992; Cornell and Schwertmann, 2003; Fritsch et al., 2005). In the present study, the well-expressed decrease in relative hematite content with increasing altitude suggests dissolution-reprecipitation, with selective hematite dissolution and the formation of DOM-ferrihydrite and Al-rich Fe oxides in conditions with high Al availability (Fritsch et al., 2005; Van Ranst et al., 2019). The degree of Al-for-Fe substitution is determined by Al activity in solution, which is governed by the nature of the Al compounds that the soils contain, mainly gibbsite and Al-silicate clays. Aluminum goes preferentially into goethite, which becomes more resistant against weathering with increasing degree of Al-for-Fe substitution (Fontes and Weed, 1991; Fontes et al., 1991; Prasetyo and Gilkes, 1994; Fritsch et al., 2005), ensuring the persistence of goethite in the studied soils. The progressive replacement of hematite and Al-poor Fe oxides by Al-rich Fe compounds, nanometre-sized Fe oxides and DOM-ferrihydrite attests to high water and aluminum activities and low silica activity, which can be related to longer periods of wetting at advanced stages of weathering. This would be similar to water regime control of the transformation of hematite and Al-poor goethite to Al-rich goethite, with associated yellowing, in ferrallitic soils of the middle Amazon Basin (Fritsch et al., 2005).

In line with earlier reports (Chauvel et al., 1987; Balan et al., 2005; Fritsch et al., 2005, 2011; Bardy et al., 2008; do Nascimento et al., 2008; Caner et al., 2011), the present study shows that ferrallitic soils may not be the endpoints of soil development in the humid tropics. As argued by Fritsch et al. (2005), kaolinite, hematite and Al-poor goethite form during early stages of ferrallitic soil development, and these compounds are next replaced by gibbsite, nanometre-sized Al-rich Fe oxides, driven by a decrease in silica activity. The transformation of ferrallitic soils is driven by the accumulation of SOM. Humic acids dissolve Al and Fe oxides and form complexes with those metals. This process is promoted by the small grain size of the secondary oxides and by environmental factors that enhance SOM preservation. The pathway from ferrallitic soils towards Andosols or Podzols then depends on the relative amounts of available Al and Fe, and the resulting metal:carbon ratio (Bardy

et al., 2008; Caner et al., 2011; Fritsch et al., 2011). The relative abundance of Al and Fe could be determined by the nature of the parent rock, whereby evolution of highly weathered soils derived from felsic rocks are likely to evolve into Podzols and those derived from mafic rocks can be expected to be transformed into non-allophanic Andosols.

6. Conclusions

This study uses a combination of selective extraction and Mössbauer spectroscopy to characterize and understand variations in Fe oxide composition along a toposequence on highly weathered volcanic materials. It identifies a greater abundance of poorly crystalline Fe oxides in the upper part of the high-altitude pedons than in other horizons and soils of the toposequence. This is compatible with elevation-dependent variations in environmental conditions that also resulted in a transition from ferrallitic soils at low altitude to soils that qualify as protoandic at high altitude. A key factor in the development of the high-altitude pedons is the combined high concentration of organic matter, Al oxides and Fe oxides, in cool humid conditions, favouring the formation and persistence of organo-metal complexes, and, as shown by the present study, promoting the formation of DOM-ferrihydrite and nanometre-sized Fe oxides at the expense of more crystalline Fe oxides.

The observed variations in relative abundance of Fe oxide minerals along the toposequence are in agreement with current gradients in environmental conditions, which are not likely to be identical with those that existed during initial saprolite and soil development on the volcanic rock substrate. Instead, the current Fe oxide associations are assumed to derive from the one that now characterizes the low-altitude pedons, developed from parent materials that were similar throughout the toposequence. At mid-altitude, relatively low rainfall resulted in development or persistence of high hematite contents, whereas at high altitude the Fe oxide fraction of the precursor ferrallitic soil was modified towards an association marked by a greater relative amount of poorly crystalline Fe oxides.

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