

Dedicated to Prof. Dr U. Schwertmann on the occasion of his 75th birthday

Mineralogy of soils with unusually high exchangeable Al from the western Amazon Region

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ABSTRACT: Some soils from the western Amazon region contain KCl-extractable Al contents 5 to 10 times greater than is typical for highly weathered soils containing predominantly kaolinite and gibbsite. We studied a soil sequence from the Brazilian western Amazon consisting of two Typic Udifluvents on the levee of the Javari River, one Aeric Endoaquent in the backswamp, and two Typic Hapludults on an adjacent terrace. We used wet chemical and X-ray diffraction (XRD) analysis to characterize several size fractions of the 0 to 0.2 m layer of the soils. The exchangeable Al content was very high in the Aquent and Udults (up to 180 mmol_c kg⁻¹), but the 'total' Fe content was low in all samples (<60 g kg⁻¹). Smectite, vermiculite, hydroxy-interlayered smectite and kaolinite dominate the fine silt and clay fractions of all soils. The Fluvents contain illite in all size fractions and chlorite in the coarse clay and fine silt fractions. The Aquent and Udults have no chlorite, and small amounts of illite occur only in the coarse clay and fine silt fractions. Lepidocrocite was identified in the Aquent. Chlorite, which occurs in the sand, fine silt, and coarse clay fractions of the Fluvents, and pyrophyllite, which occurs in the fine silt fractions of all soils and in the coarse clay of the two Ultisols, appears to be inherited from the parent sediments. The hydroxy-interlayered 2:1 phyllosilicates that form as a result of weathering are the cause of the very high exchangeable Al contents.

KEYWORDS: soil mineralogy, Amazon region, Al, smectite, kaolinite.

Shifting cultivation is the dominant agricultural activity in the western Amazon region. After clearing an area, farmers crop it for just three or four years, then abandon it and move to new areas (Teixeira & Bueno, 1995). Aluminium toxicity is the major soil-limiting factor for agriculture in the Amazon as a whole, and soils that contain toxic levels of exchangeable Al cover 73% of the Amazon basin (Rodrigues, 1996). Recently, however, Gama & Kiehl (1999) found that crops grown in some western Amazon soils did not show

serious Al toxicity symptoms, even though the exchangeable Al was very high (145 mmol_c kg⁻¹). They suggested that Ca in the soil solution may be mitigating Al toxicity and that the standard method to extract exchangeable Al, 1 M KCl, may not be suitable for such soils. In another situation, the lack of toxicity symptoms in plants was attributed to very low Al contents in the soil solution, ~0.1 mmol_c l⁻¹, even when exchangeable Al in the soil was ~30 mmol_c kg⁻¹ and occupied ~90% of the CEC (Schroth *et al.*, 2000). A better understanding of the processes taking place in these soils may help farmers to switch from shifting cultivation to more sustainable land uses.

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Kaolinite is the most abundant mineral in the clay fraction of many soils in the Amazon region, with gibbsite, goethite and hematite being common accessory minerals (Kitagawa & Möller, 1979; Chauvel, 1981). Exchangeable Al in the surface horizons of most of these kaolinitic soils is $<20 \text{ mmol}_c \text{ kg}^{-1}$. In the eastern Amazon region, weathering has acted long enough so that the mineral controlling the solution Al concentration was assumed to be gibbsite by Ludwig *et al.* (1997). Soils from the western Amazon region, however, are often reported to have exchangeable Al contents $>200 \text{ mmol}_c \text{ kg}^{-1}$ (RADAMBRASIL, 1977; Teixeira & Bueno, 1995; Rodrigues, 1996) and, from the few data available, western Amazon soils with very high exchangeable Al are richer in 2:1 clays than soils with low exchangeable Al (Kitagawa & Möller, 1979; Volkoff *et al.*, 1989). The objective of this study was to determine whether soil mineralogy can explain the abnormally high exchangeable Al contents present in some western Amazon soils.

MATERIALS AND METHODS

The sampling area is located at latitude $4^{\circ}22'S$, longitude $70^{\circ}10'W$, 150 m above sea level, $\sim 10 \text{ km}$ northwest of the town of Benjamin Constant in the

State of Amazonas, Brazil (Fig. 1). The sampling sites are located on the flood plain and an adjacent terrace of the Javari River, a tributary of the Amazon River. The climate is Af \bar{i} (rainy tropical without dry season) according to the Köppen classification, with an average annual rainfall of $\sim 3000 \text{ mm}$ and a temperature of $\sim 26^{\circ}\text{C}$ throughout the year (Saleti & Marques, 1984). The natural vegetation is tropical rainforest. The parent materials for soils in the western Amazon region are mixed-textured Tertiary and Quaternary fluvial sediments of Andean origin (Rodrigues, 1996). The average depositional rate along the major rivers has been estimated at 1.9 mm per year over the last 44,000 years (Kronberg *et al.*, 1998).

We sampled the 0 to 0.20 m surface horizons of five pedons, two Typic Hapludults, one Aeric Endoaquent and two Typic Udifluvents according to Soil Taxonomy (Soil Survey Staff, 1999). These classifications are based on information from the soil survey of the area (RADAMBRASIL, 1977). All pedons are in the isohyperthermic soil temperature regime. Land use at sampling time was pasture (*Brachiaria* sp.), peach palm (*Bactris gasipaes* H.B.K.) and cupuazu tree (*Theobroma grandiflorum* Willd. ex Sprang.) plantations on the Udults, cassava (*Manihot esculenta* Crantz) on the Aquents, and maize (*Zea mays* L.) on the Fluvents.



FIG. 1. Map of Brazil showing the state boundaries and the location of the study area.

Figure 2 shows the positions of the pedons in the landscape. The lagoon in the backswamp may be an old meander channel. A stream connects the lagoon to the Javari River during the annual flood.

The samples were air dried, sieved through a 2 mm sieve, and stored in plastic bags prior to analysis. Soil fertility analyses were made according to Brazilian standard methods (Embrapa, 1997). In brief, they were: pH in H₂O (1:2.5); available P and K extracted by Mehlich-1 solution; Al, Ca and Mg extracted by 1 M KCl (1:20); and organic C determined by wet oxidation with K₂Cr₂O₇. The effective CEC was calculated as the sum of Al, Ca, Mg and K. The base saturation at the soil's natural pH was defined as (Ca+Mg+K)/effective CEC × 100. The particle-size distribution was determined by the method of Jackson (1973). We determined Si, Al, Fe, Ti and P after digestion with 9.4 M H₂SO₄ (Embrapa, 1997). This method is a standard procedure in Brazilian soil surveys and is assumed to reflect the composition of the clay fraction. We extracted Fe from the clay fraction separately with sodium dithionite-citrate-bicarbonate (Fe_d) (Mehra & Jackson, 1960) and pH 3 ammonium oxalate in the dark (Fe_o) (Schwertmann, 1964).

We fractionated the samples for mineralogical analysis using the procedures described by Jackson (1973), with the exception that the Fe-oxides were not removed. We prepared oriented slides of the 5 to 2 (fine silt), 2 to 0.2 (coarse clay), and <0.2 µm (fine clay) fractions. One set of slides was Mg saturated and glycerol solvated, the other was K saturated. Diffractograms were obtained using Co-Kα radiation and a Philips 3100 vertical diffractometer equipped with a fixed 1° divergence slit, 0.2 mm receiving slit, incident and diffracted beam Soller slits, and a graphite, diffracted-beam monochromator. The slides were scanned from 2 to 35°2θ using 0.02°2θ steps and 1 s counting times per step. The K-saturated slides were scanned at room temperature, and after successive heating to

100, 300 and 550°C. The 2000 to 53 µm (total sand) fraction was ground to <105 µm in an agate mortar, and random powder mounts were prepared and scanned from 2 to 50°2θ using 0.05°2θ steps.

RESULTS

One Hapludult is a silty clay at the surface and the other is a sandy clay loam, while the Udifluvents are silt loams, reflecting the variability that one expects in floodplains and low terraces (Table 1). The Endoaquent in the backswamp is a clay, consistent with deposition of clay from very slowly moving or stagnant water.

The effective CEC is >100 mmol_c kg⁻¹ in all five soils (Table 1) and is high relative to an effective CEC of ~20 mmol_c kg⁻¹ that is typical for the surface horizons of many Oxisols in the Amazon region (Rodrigues, 1996). The high CEC is not due to organic matter because the organic C contents are not much different from other Oxisols with much lower CEC. The pH for the two Hapludults and the Endoaquent is ≤4.7. The base saturation at natural pH for one of the Hapludults and for the Endoaquent is very low (<30%), and consequently the Al saturation is very high. Total exchangeable Al for the clayey Endoaquent is 181 mmol_c kg⁻¹, but it is about half that for the less clayey Hapludults. The two Udifluvents, however, have pHs ≥6.0, 100% base saturation, and no exchangeable Al. Soils from other areas within the Amazon basin generally have considerably lower exchangeable Al, <40 mmol kg⁻¹ (Embrapa, 1975; Botschek *et al.*, 1996; Rodrigues, 1996; Ludwig *et al.*, 1997). The lower organic C content of the Fluvents probably reflects the average organic C content of the fresh sediments that are deposited regularly every year.

The Brazilian Soil Classification System emphasizes the Ki index (SiO₂/Al₂O₃ molar ratio) as an effective means to assess the degree of soil weathering and to obtain general information about the mineralogy of the clay fraction. An ideal kaolinite with the formula Al₂Si₂O₅(OH)₄ has a Ki = 2.0. One of the Ultisols (soil S2) has Ki = 1.11 (Table 2) and thus should have an appreciable content of minerals in the clay fraction less siliceous than kaolinite, probably gibbsite and Al-substituted Fe oxides, while the Aquent (Ki = 2.62) should have an appreciable content of minerals more siliceous than kaolinite, probably smectites. Although we expected that the Ultisols would have



FIG. 2. Schematic distribution of the soils in the western Amazon landscape. Numbers indicate the sampling sites.

TABLE 1. Soil fertility and particle-size distribution results of the western Amazon soils.

Soil no.	Classification	pH H ₂ O	Effective CEC -mmol _c kg ⁻¹	Exch. Al kg ⁻¹	Base saturation %	Mehlich P mg kg ⁻¹	Org. C	Sand	Coarse silt	Medium silt g kg ⁻¹	Fine silt	Coarse clay	Fine clay	Particle-size class
S1	Typic Hapludult	4.7	150	74	51	3	16	106	177	173	93	179	228	Silty clay
S2	Typic Hapludult	4.7	125	91	27	3	21	545	83	66	36	82	146	Sandy clay loam
S3	Aeric Endoaquent	4.4	222	181	18	3	20	7	32	83	107	292	470	Clay
S4	Typic Udifluent	6.0	171	0	100	200	6	219	362	171	67	87	60	Silt loam
S5	Typic Udifluent	6.3	183	0	100	180	5	147	320	217	95	105	69	Silt loam

TABLE 2. Chemical analysis of soils from the western Amazon.

Soil no. [†]	9.4 M H ₂ SO ₄ attack				Ki [‡]	Fe _o [§]	Fe _d [¶]	Fe _o /Fe _d
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅				
	— g kg ⁻¹ —							
S1	196	152	46	0.20	2.19	7	23	0.31
S2	65	99	21	0.07	1.11	6	28	0.23
S3	336	218	58	0.32	2.62	10	21	0.46
S4	151	114	55	0.66	2.25	15	33	0.47
S5	168	131	58	0.64	2.18	15	33	0.47

[†] Numbers correspond to soil classification in Table 1.

[‡] SiO₂/Al₂O₃ molar ratio

[§] Fe extracted by pH 3 ammonium oxalate in the dark (Schwertmann, 1964)

[¶] Fe extracted by sodium dithionite-citrate-bicarbonate (Mehra & Jackson, 1960)

the lowest Ki indices, only soil S2 is appreciably lower, while soil S1 has a Ki index similar to that of the Udifluvents.

Most soils from the Amazon region have 'total' P contents of ~0.5 g P₂O₅ kg⁻¹ (Embrapa, 1975) and, thus, the 'total' P content of these soils (0.2 to 0.66 g P₂O₅ kg⁻¹) is reasonable, with the exception of soil S2 (Table 2). Most of this P, however, is not plant available since the Mehlich-extracted P (Table 1) is very low, with the exception of the Fluvents. The Fe oxide content (Fe_d) is similar to other soils in the Amazon region (Botschek *et al.*, 1996). The Fe_o/Fe_d ratio is high in all samples and

is highest in the soils that are periodically flooded (Aquent and Fluvents). The high Fe_o/Fe_d ratio suggests that much of the Fe occurs as ferrihydrite or as complexes with organic matter. The higher ratio for the Aquent could also be an artifact because if the samples contain some Fe²⁺, the Fe²⁺ can catalyse the dissolution of more crystalline Fe oxide minerals (Cornell & Schwertmann, 1996).

Sand fraction mineralogy

The sand fraction of the Udults consists almost entirely of quartz (Fig. 3). The Fluvents, on the

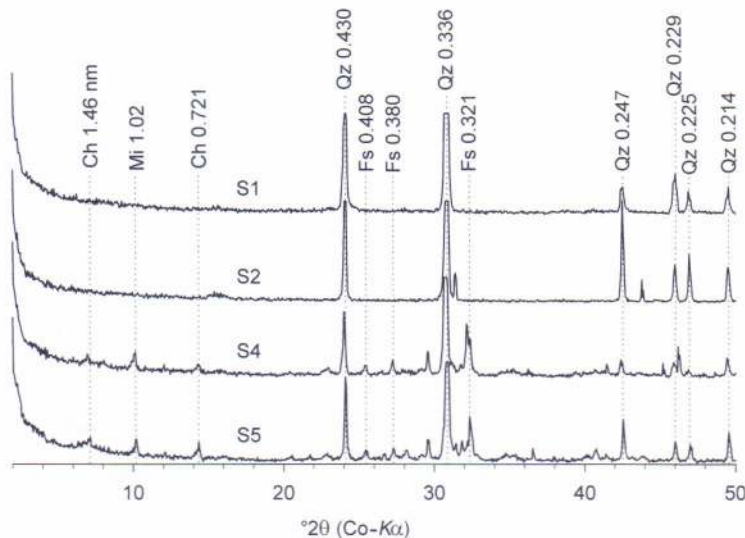


FIG. 3. XRD patterns (randomly-oriented powder) of the sand fraction (2000 to 53 μm) of western Amazon soils. Mineral codes: Ch = chlorite, Mi = mica, Qz = quartz, Fs = feldspars.

other hand, contain appreciable quantities of primary minerals such as feldspars, mica and chlorite. The Aquent did not have enough sand to obtain a diffraction pattern. The release of plant-essential nutrients from weathering feldspar, mica and chlorite makes the Fluvents more suitable for agriculture from a fertility standpoint than the adjacent Aquents and Udults. The diffractogram of soil S2 showed peaks at 0.331 and 0.240 nm which could not be assigned to any mineral.

Silt fraction mineralogy

The fine silt fraction of all five soils contains quartz, kaolinite, illite and pyrophyllite (Fig. 4). The occurrence of kaolinite in the fine silt fraction is not abnormal, especially in kaolinitic soils. The peaks at 0.92 and 0.31 nm indicate pyrophyllite. Lepidocrocite in the Aquent is indicated by the peak at 0.631 nm. Lepidocrocite is consistent with the aqic moisture regime of this acid soil. Both Fluvents contain smectite and vermiculite because after K saturation at 25°C, the 1.8 nm peak disappears completely and the 1.4 nm peak becomes much weaker, while the 1.0 nm peak becomes stronger (Figs 4 and 5). The charge on these smectite and vermiculite layers is quite high and there is little hydroxy-interlayering because collapse is complete at 25°C. The Fluvents also contain some chlorite because the 1.44 nm peak does not disappear completely after heating to 550°C.

Clay fraction mineralogy

Smectite and kaolinite are the main minerals in the coarse clay fraction (Fig. 6). The smectite probably has appreciable hydroxy-interlayering because it does not collapse completely to 1.0 nm upon K-saturation and heating (Fig. 7). The sandiest soil, soil S2, is the only one that does not have significant amounts of smectite and it is the soil with the lowest Ki index (Table 2). Additionally, the smectite in soil S2 seems to be quite disordered because it did not swell completely to 1.8 nm. Perhaps the hydroxy-interlayering is so complete in parts of the stacks that those areas did not swell with glycerol, while adjacent areas where interlayering is less complete swelled. The result is very chaotic swelling where the spacing between two adjacent sheets is not 1.8 nm all the way across, but 1.4 nm in some places and 1.8 nm in others. This

would give an extremely broad, almost non-existent diffraction peak as shown for S2 in Fig. 6. The Fluvents also contain vermiculite and chlorite because a 1.43 nm peak in the Mg glycerol XRD pattern collapses only partially after K-saturation (Fig. 7). The two Udults clearly contain pyrophyllite in the coarse clay fraction, but the other soils also appear to contain traces of pyrophyllite as indicated by weak peaks at 0.92 nm.

The fine clay fraction of all five soils (Fig. 8) consists mainly of hydroxy-interlayered smectite and kaolinite. Pyrophyllite does not occur in the fine clay fractions of any of the soils. Lepidocrocite occurs in the fine clay of soil S3.

DISCUSSION

The sediment load of the Amazon tributaries that drain the Andes Mountains consists predominantly of primary minerals such as mica and Fe-rich chlorite (Irion, 1984a). These sediments are initially deposited on extensive floodplains in the Andean foreland. The sediment load of the rivers that drain these floodplains consists predominantly of low-charge montmorillonite, with lesser amounts of kaolinite, minerals which probably formed by weathering of primary minerals in the wet floodplains of the Andean foreland (Irion, 1984a).

Since the mineralogy of Fluvents predominantly reflects recent sediment additions, the mineralogy of the Fluvents in our study area (mica, chlorite, smectite, pyrophyllite and kaolinite) is consistent with deposition of sediments containing these minerals. Pyrophyllite, however, was apparently not found in the sediments that Irion (1984a) analysed from a number of Amazonian rivers, and he considered the pyrophyllite that he found in a soil collected near the Branco River to be the result of leaching of cations from smectite (Irion, 1984b).

Pedogenic formation of pyrophyllite is not likely and is not consistent with the occurrence of pyrophyllite either geologically or pedologically. Geologically, pyrophyllite is often found in rocks and saprolites in the Andes (Wilke & Zech, 1987; Brattli, 1997) and is often reported in soils that are likely to have received sediments from the Andes range (Irion 1984b; Zelazny & White, 1989; Lips & Duivenvoorden, 1996). The pedologic occurrence of pyrophyllite in the soils from our study area points to a sedimentary origin of the pyrophyllite as well. Pyrophyllite occurs only in the coarse clay (>0.2 µm) and coarser fractions, but not in the

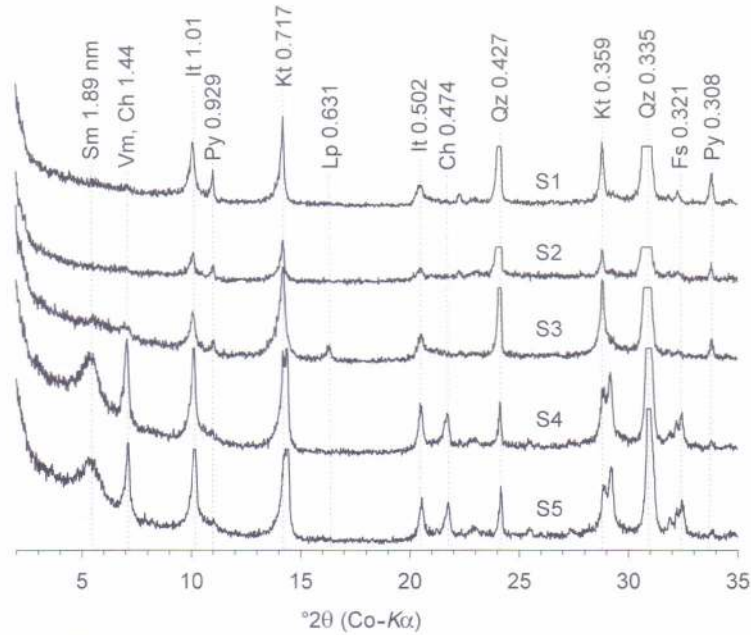


FIG. 4. XRD patterns (Mg-glycerol-saturated oriented samples at 25°C) of the fine silt fraction (5 to 2 μm) of western Amazon soils. Codes S1 to S5 indicate the sample number. Mineral codes: Sm = smectite, Vm = vermiculite, Ch = chlorite, It = Illite, Py = pyrophyllite, Kt = kaolinite, Lp = lepidocrocite, Qz = quartz, Fs = feldspars.

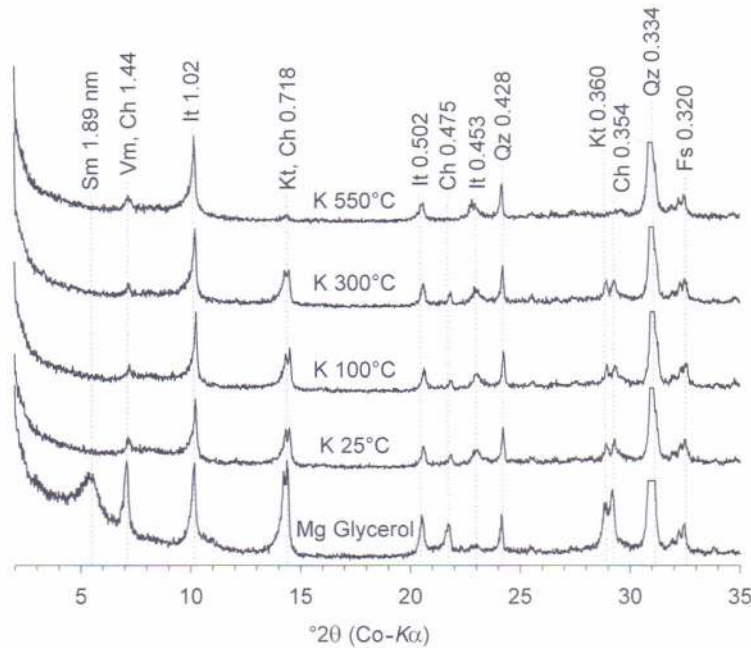


FIG. 5. XRD patterns (oriented samples) of the fine silt fraction (5 to 2 μm) of a Typic Udifluent (S4) from the western Amazon. Mineral codes: Sm = smectite, Vm = vermiculite, Ch = chlorite, It = Illite, Py = pyrophyllite, Kt = kaolinite, Lp = lepidocrocite, Qz = quartz, Fs = feldspars.

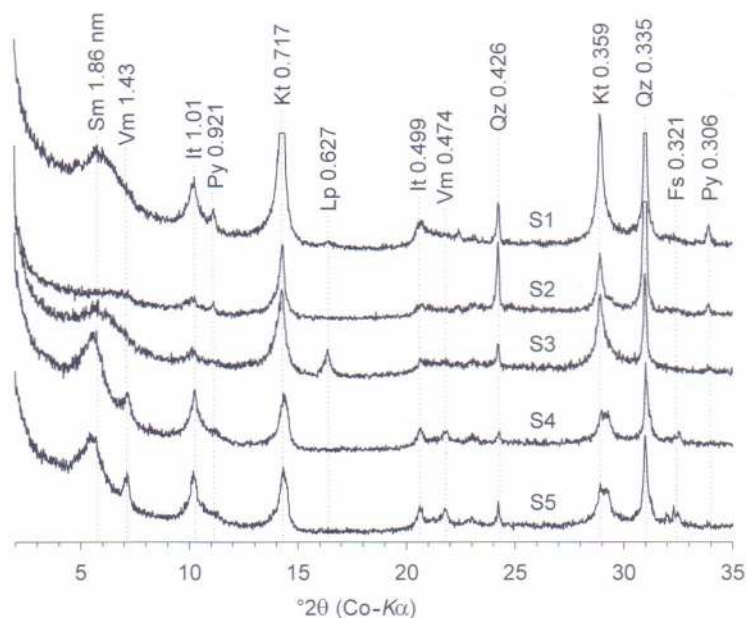


FIG. 6. XRD patterns (Mg-glycerol-saturated oriented samples at 25°C) of the coarse clay (2 to 0.2 μm) fraction of western Amazon soils. Codes S1 to S5 indicate the sample number. Mineral codes: Sm = smectite, Vm = vermiculite, It = Illite, Py = pyrophyllite, Kt = kaolinite, Lp = lepidocrocite, Qz = quartz, Fs = feldspars.

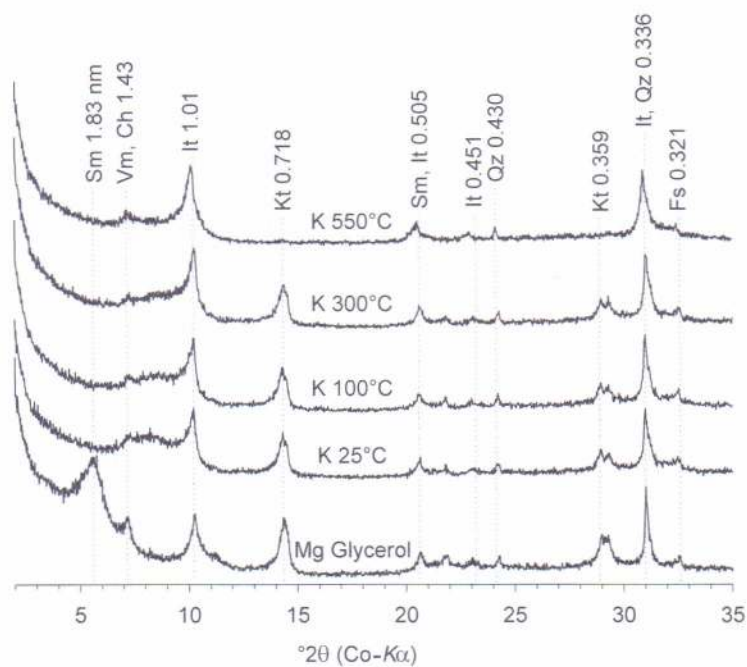


FIG. 7. XRD patterns (oriented samples) of the coarse clay fraction (2 to 0.2 μm) of a Typical Udifluent (S4) from the western Amazon. Mineral codes: Sm = smectite, Ch = chlorite, Vm = Vermiculite, It = Illite, Kt = kaolinite, Qz = quartz, Fs = feldspars.

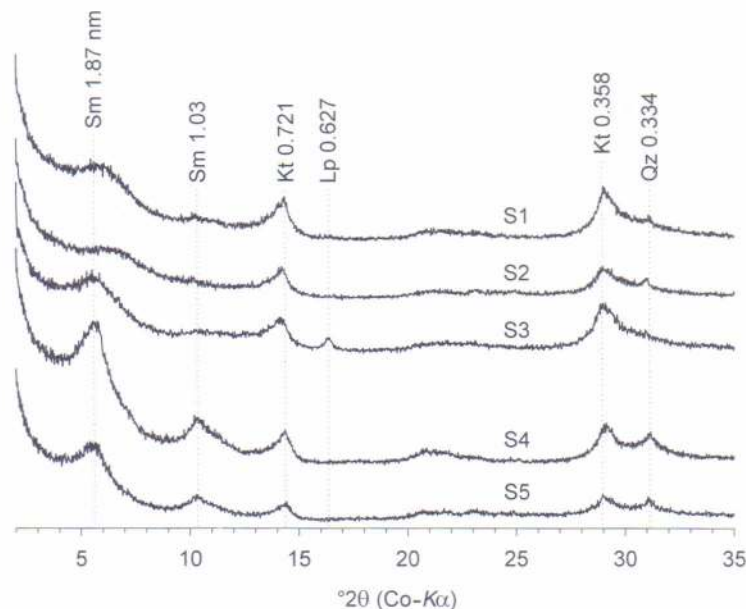


FIG. 8. XRD patterns (Mg-glycerol-saturated oriented samples at 25°C) of the fine clay (<math>< 0.2 \mu\text{m}</math>) fraction of western Amazon soils. Codes S1 to S5 indicate the sample number. Mineral codes: Sm = smectite, Kt = kaolinite, Lp = lepidocrocite, Qz = quartz.

fine clay (<math>< 0.2 \mu\text{m}</math>) fraction. If pyrophyllite had formed by leaching of exchangeable cations from smectite, as postulated by Irion (1984b), then we would expect pyrophyllite to be most abundant in the fine clay fraction, which contains most of the smectite. The fact that pyrophyllite occurs in the fine silt and coarse clay fractions of the surface horizons of all of the soils, even the considerably more weathered Udults, indicates that pyrophyllite can be quite resistant to weathering.

Like pyrophyllite, the chlorite in these soils is depositional. Chlorite weathers quickly, particularly at acid pH, by losing its interlayer hydroxide sheet and releasing Al. If the 2:1 sheet is trioctahedral, the whole structure is unstable and weathers to release Si, Al, Mg, Fe and other ions to the soil solution. Chlorite occurs in the Fluvents because of both recent sedimentary additions and a relatively slow weathering rate as a result of the slightly acid pH and high base status (Table 1). Removal of the interlayer hydroxide sheet from some of the chlorite probably accounts for some of the vermiculite identified in the fine silt and coarse clay fractions of the Fluvents. In the older, more acid Udults, any chlorite initially present has been completely removed by weathering.

Smectites occur in these soils for a number of reasons. Some of the smectite is depositional, as already mentioned above, while additional smectite is added by precipitation from solution, and some by transformation of precursor 2:1 minerals such as mica and chlorite. In addition to the transformation from chlorite mentioned above, vermiculite in the fine silt fraction can form by transformation of primary mica as well. The stability of both smectite and vermiculite in the Fluvents is favoured by the slightly acid pH and high base status. Although the Aquent receives regular sedimentary additions of smectite, the dominant process in the more acid Aquent and in the two Udults appears to be smectite dissolution and the formation of hydroxy-interlayered smectite.

Like smectite, kaolinite in these soils occurs from a combination of sedimentary additions and precipitation from solution. Gibbsite is absent, despite the high rainfall, because of the high solution Si concentration supported by feldspars and chlorite in the Fluvents, and smectite and hydroxy-interlayered smectite in all of the soils.

The presence of hydroxy-interlayered smectite in the Aquent and Udults results in the large amounts of exchangeable Al in these soils.

CONCLUSIONS

The soils from the western Amazon region examined in this study contain smectite, vermiculite and hydroxy-interlayered smectite as a result of sedimentary additions, precipitation from solution, and transformation from primary 2:1 minerals. Aluminium released by weathering at acid pH is adsorbed onto the exchange sites of the 2:1 phyllosilicates, resulting in KCl-extractable Al contents 5–10 times greater than soils containing predominantly kaolinite, gibbsite, goethite and hematite. The fact that crops grown on some western Amazon soils do not show serious Al toxicity symptoms, even though the exchangeable Al is very high, is explained by the fact that Al extracted from the hydroxy-interlayered smectite by 1 M KCl is not necessarily correlated with soil solution Al activity under field conditions. Soils from the Amazon basin are commonly thought to be highly weathered and have clay fractions that consist mainly of kaolinite and gibbsite, but soils along the major rivers can contain appreciable quantities of 2:1 phyllosilicates that strongly influence soil chemical properties.

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