

Pedogenesis and Mineralogy of a Halaquept in Niger (West Africa)*¹

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ABSTRACT

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In a fossil river valley of Niger known as the Dallol Bosso, an aquic soil environment has Fe-oxide segregation coupled with biological SO_4 -reduction and Na_2CO_3 formation by evaporative pull. Depth to the water table, pH and water-soluble salts fluctuate seasonally but, most of the year, the water table is within 1 m of the surface. The presence of Na_2CO_3 is inferred from salt efflorescences and a pH of 9 at the soil surface in the dry season. The zone of Fe-oxide accumulation occurs between 30 and 54 cm and a soil layer with greyish green color and reduced Fe is present at the top of the water table. On the basis of field and laboratory characteristics, the soil is classified as an Aeric Halaquept. Mineralogical analyses (XRD, IR and SEM) show that goethite is the dominant iron oxide mineral and suggest that silica translocation in an iron-rich soil environment is promoting neof ormation of iron-rich beidellite.

INTRODUCTION

Generally, Aquepts occur on lowlands with a high water table or poor drainage: river floodplains, coastal plains, estuaries and deltas, downslope members of hillslope catenas. These soils are strongly influenced by the reducing and anaerobic conditions induced by waterlogging. The duration of saturation and the composition of the ground water affect intensity of reduction processes, soil pH, mineral equilibria, translocation of mobile materials and accumulation of organic matter (Wilding and Rehage, 1985).

Under semi-arid climates, soils with aquic soil moisture regimes can exhibit

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biogeochemical accumulation of Ca- and Na-carbonates, Fe- and Mn-oxides, silica, and the formation of smectite (Kovda, 1973). This paper discusses the genesis and mineralogy of an Aquept, developed under a semi-arid climate in the Dallol Bosso of Niger, which shows all these characteristics.

THE STUDY AREA

The Dallol Bosso is the fossil valley of the section of the ancient Azaouak River which runs north-south in western Niger from 15° to 12° N latitude along 3° E longitude (Fig. 1). In Niger, the word "dallol" refers to a wide, dry valley that is drained by intermittent streams during the rainy season only (Donaint, 1975).

The Dallol Bosso covers an area of about 3400 km² and falls within the Sahelian climatic zone. This is the semi-arid belt south of the Sahara characterized by a long dry season lasting from October through April and a short rainy season between May and September. The mean annual precipitation ranges from 200 to 600 mm going from north to south in the Dallol Bosso. The average annual temperature is 30°C although highs between 40° and 45°C are recorded during the dry season.

The Dallol Bosso is a relict braided river, with anastomosing channels and a low annual discharge, and is typical of rivers developed under semi-arid cli-

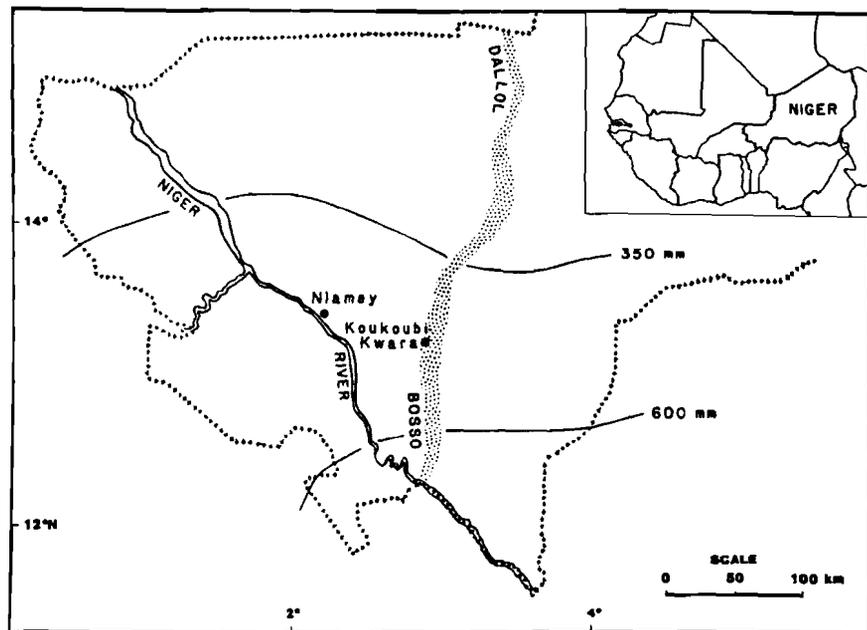


Fig. 1. Location of the study area.

One soil that showed evidence of Fe-oxide segregation, surface salt accumulation and whose pH suggested presence of Na_2CO_3 was described in detail and bulk sampled from a pit, by genetic horizons, in November 1984, during the dry season, and again in August 1986, during the wet season. Groundwater from this site was also collected on both dates.

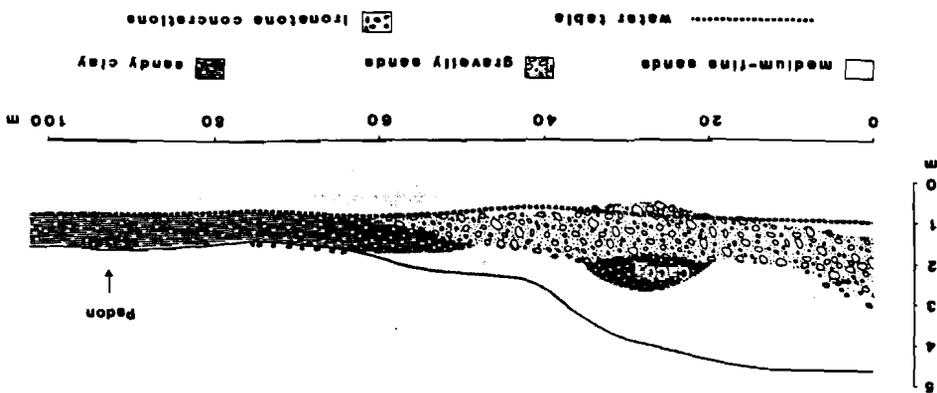
MATERIALS AND METHODS

This paper discusses the mineralogy and genesis of a Halaquept in the Koukoubi Kwara depression of the Dallol Bossa.

The ancient channels are plugged by sand and form closed depressions that are often alkaline. These depressions cover an estimated 20% of the valley. Clay horizons (Anonymous, 1978) are common where the water table is shallow. In many instances, examples of what have been called hydromorphic or groundwater laterites (Maignien, 1966) have formed along the edges of these depressions. Near the village of Koukoubi Kwara, an alkaline depression showed evidence of Fe-oxide segregation as well as sodicity (Fig. 2). Villagers indicated that this had been a permanent pond but had dried up about 20 years before.

The dominant clay mineral of these soils is kaolinite. Base saturation is variable but generally higher than 35% throughout the upper surface horizon. Aluminum comprises up to 50% of the exchangeable cations. Their reaction is acid, with pH ranging from 5.2 to 6.5 in the meq./100 g soil. Their fertility is low: organic C is less than 1% and CEC is less than 3. Most are classified as Psammic (Doeglas, 1962). Its sediments are dominated by sands although lenses of clays do occur. These fluvial sediments have been reworked by wind to varying degrees throughout the valley (Bui, 1986). Today, the valley floor looks like a vast undulating sand plain, with dunal micro-relief of 1-6 m. The sandy soils of dunes generally show only incipient pedogenic development (organic matter accumulation and color Bw horizons). Most are classified as Psammic. Their fertility is low: organic C is less than 1% and CEC is less than 3 meq./100 g soil. Their reaction is acid, with pH ranging from 5.2 to 6.5 in the surface horizon. Aluminum comprises up to 50% of the exchangeable cations. Base saturation is variable but generally higher than 35% throughout the upper 50 cm of the soil. The dominant clay mineral of these soils is kaolinite.

Fig. 2. Landscape cross-section at the study site.



Bulk samples were shipped to the U.S.A. in cotton cloth bags. They were dried at 35°C in a forced-draft oven, weighed, hand-crushed with a wooden rolling pin and sieved through a 2-mm sieve. The > 2-mm fraction was weighed and expressed as a percentage of the total weight. The < 2-mm or fine earth fraction was used in subsequent soil characterization analyses conducted at the Soil Characterization Laboratory of the Texas Agricultural Experiment Station.

Particle-size distribution was determined by the pipette method, after Kilmer and Alexander (1949).

Soil pH was measured on a 1:1 by volume soil:water suspension (Soil Survey Staff, 1972, 8C1a).

Extractable bases, cation exchange capacity and exchangeable Al were determined using a mechanical extractor (Holmgren et al., 1977). Bases were extracted by leaching with 1 N NH₄OAc at pH 7 (Soil Survey Staff, 1972, 5A6). Cation exchange capacity was determined by replacement of soil cations at pH 8.2 with 1 N NaOAc, washing with ethanol and subsequent displacement of Na with NH₄ at pH 7 (Soil Survey Staff, 1972, 5A2). Exchangeable Al was measured in samples with pH < 5.5 by extraction with 1 N KCl (Soil Survey Staff, 1972, 6G2).

Electrical conductivity and water-soluble cations and anions were determined on saturated paste extracts (Soil Survey Staff, 1972, 8A). The filtered water samples were also analyzed for cations (Ca, Mg, K, Na) and anions.

Calcium, Mg and Al were measured by atomic absorption spectrometry, and Na and K by flame emission spectrometry. Bicarbonate, carbonate and chloride anions were determined by titration (Soil Survey Staff, 1972, methods 6I, 6J and 6K, respectively). Sulfate was measured by turbidimetry (Jackson, 1958). Chloride and sulfate were also measured by ion chromatography (Tabatabai and Dick, 1983).

Iron was determined by Na-citrate-Na-dithionite (CD) extraction and reported on a weight percent basis (Soil Survey Staff, 1972, 6C2).

Powder-mounts of iron oxide concretions (pedotubules) and mineral residue filtered from the groundwater were analyzed by X-ray diffraction on a Philips-Norelco X-ray diffractometer equipped with a Cu tube, a θ -compensating slit and curved crystal monochromator and operated at 35 kV and 15 mA. Oriented mounts on ceramic tile of the < 2- μ m fraction were analyzed by XRD after the following treatments: Mg-saturation (air-dry and glycerated); K-saturation (air-dry at 25°C, heated to 300°C and 550°C).

Infrared analysis was performed on a double beam Perkin-Elmer 283 IR spectrophotometer. The very fine clay (< 0.05 μ m) fraction from the Bg horizon was fractionated by centrifugation. KBr pellets (1 mg clay/300 mg KBr) were prepared from this sample and from the Clay Minerals Society KGa-2 source clay, a poorly crystallized kaolinite which best approximates soil kaolinite. An infrared spectrum was obtained for each pellet and computer-stored.

The IR spectrum of the fine clay of the Bg horizon indicated kaolinite was present. Consequently, by trial and error, a small percentage of the KGa-2 spectrum was subtracted from the clay spectrum of the Bg horizon until a maximum of the kaolinite bands were removed without generating any false negative peaks.

For scanning electron microscopy, samples were cleaned of Fe-oxide and clay coatings by boiling 15 min in 50% HCl. The fine sand fraction (125–250 μm) was sieved, mounted on Al-stubs using double sticky tape, sputter-coated with 200 Å of Au-Pd and examined using a JEOL-SM-25 II.

RESULTS AND DISCUSSION

Physical and chemical properties

The field description and laboratory analyses are presented in Tables I and II, respectively. The upper 67 cm are sandy clay loam to sandy loam in texture with an abrupt contact with sedimentary sand. The CEC/100 g clay ranges

TABLE I

Description of pedon under study (November, 1984)

Horizon	Depth (cm)	Soil description (colors for moist soil material unless stated)
A	0–10	Dark yellowish brown (10YR 4/6) sandy clay loam, yellowish brown (10YR 5/6) dry; common coarse distinct brownish yellow (10YR 6/8) mottles; weak medium subangular blocky structure; very hard, very sticky; common fine and medium roots; alkaline; gradual wavy boundary.
Bwc1	10–30	Dark yellowish brown (10YR 4/6) sandy clay loam, yellowish brown (10YR 5/6) dry; common coarse distinct brownish yellow (10YR 6/8) mottles; strong coarse subangular blocky parting to angular structure; very hard, very sticky; common fine and medium roots; common yellowish brown concretions; moderately alkaline; gradual wavy boundary.
Bwc2	30–54	Dark yellowish brown (10YR 4/6) sandy loam; common medium distinct yellowish red (5YR 5/8) mottles; strong coarse subangular blocky parting to angular blocky structure; friable; plastic; few fine and medium roots; common Fe-Mn stains along root channels; common yellowish brown concretions; moderately alkaline; clear wavy boundary.
Bg	54–67	Very dark gray (N 3/) sandy loam; strong medium subangular blocky parting to angular blocky structure; friable; plastic; few medium roots; moderately alkaline; abrupt smooth boundary.
2Cg	67–90	Dark olive gray (5YR 3/2) sand; structureless; nonsticky; few medium roots; moderately alkaline.

Remarks. Textures are field-, not laboratory-determinations. 20% by volume indurated Fe-pipetern concretions 3–5 mm in diameter along root channels between 10–54 cm. Water table at 90 cm.

TABLE II

Selected physical and chemical properties

Horizon	Depth (cm)	% Sand (50 μ m- 2 mm)	% Clay ($<2 \mu$ m)	CEC (meq./100 g clay)	% O.C.	pH		ESP		% CD-Fe
						11/84	8/86	11/84	8/86	
A	0-10	74	12	66	1.52	<9	7.4	N.A.	5	N.A.
Bwc1	10-30	68	20	55	0.45	9.0	7.6	71	8	16
Bwc2	30-54	69	18	73	0.24	8.8	6.5	47	15	19
Bg	54-67	79	18	45	0.27	5.1	6.1	19	33	7
Cg	67-90	93	3	7	0.05	5.2	6.0	50	20	2

Water table at 90 cm in 11/84, at 70 cm in 3/85, at 150 cm in 8/86. N.A. = not analyzed.

from 45 to 73 and indicates a mixed, borderline smectitic, clay mineralogy in the upper 67 cm. In the Cg, the CEC/100 g clay is 7 and is suggestive of kaolinitic alluvium. Organic C is less than 1.6% and decreases with depth. Depending on the season, pH, exchangeable sodium percentage (ESP) and water-soluble salts exhibit different distributions through the profile. The pH gradient is steep during the dry season with an abrupt change in the Bg horizon. During the dry season, the surface pH is above 9. Water-soluble salt data attest to the presence of Na-(bi)carbonates in the upper solum. Salts decrease with depth to the Bg horizon where the pH obtains a minimum of 5.1. During the wet season, the zone of maximum Na-(bi)carbonate accumulation migrates further down the profile.

While the clay distribution with depth is suggestive of an argillic horizon, field and micromorphological observations do not indicate the presence of oriented clay. Moreover, the probable mechanism of origin of much of the clay (discussed below) is neof ormation and not illuviation. The B horizon is therefore felt to be a cambic horizon.

The water table is within 150 cm of the surface throughout the year and reducing conditions exist at a depth of 54 cm as evidenced by the very dark grey (N 3/) Bg layer and the olive gray (5Y 3/2) Cg layer. The Cg horizon gives a strong positive field test for Fe(II) with α,α -dipyridyl. In the upper 54 cm, oxidizing conditions prevail as evidenced by the brown to red colors. The zone between 10 and 54 cm is rich in Fe-oxide pedotubule concretions precipitated along old root channels; this is reflected in the high percentage of CD-extractable Fe in this section of the profile.

The diagnostic characteristics of this soil are an ochric epipedon, aquic soil moisture regime, high chroma and ESP > 15, therefore, the soil is classified in Soil Taxonomy (Soil Survey Staff, 1975) as an Aeric Halaquept, fine-loamy over sandy, oxidic, non-acid, isohyperthermic.

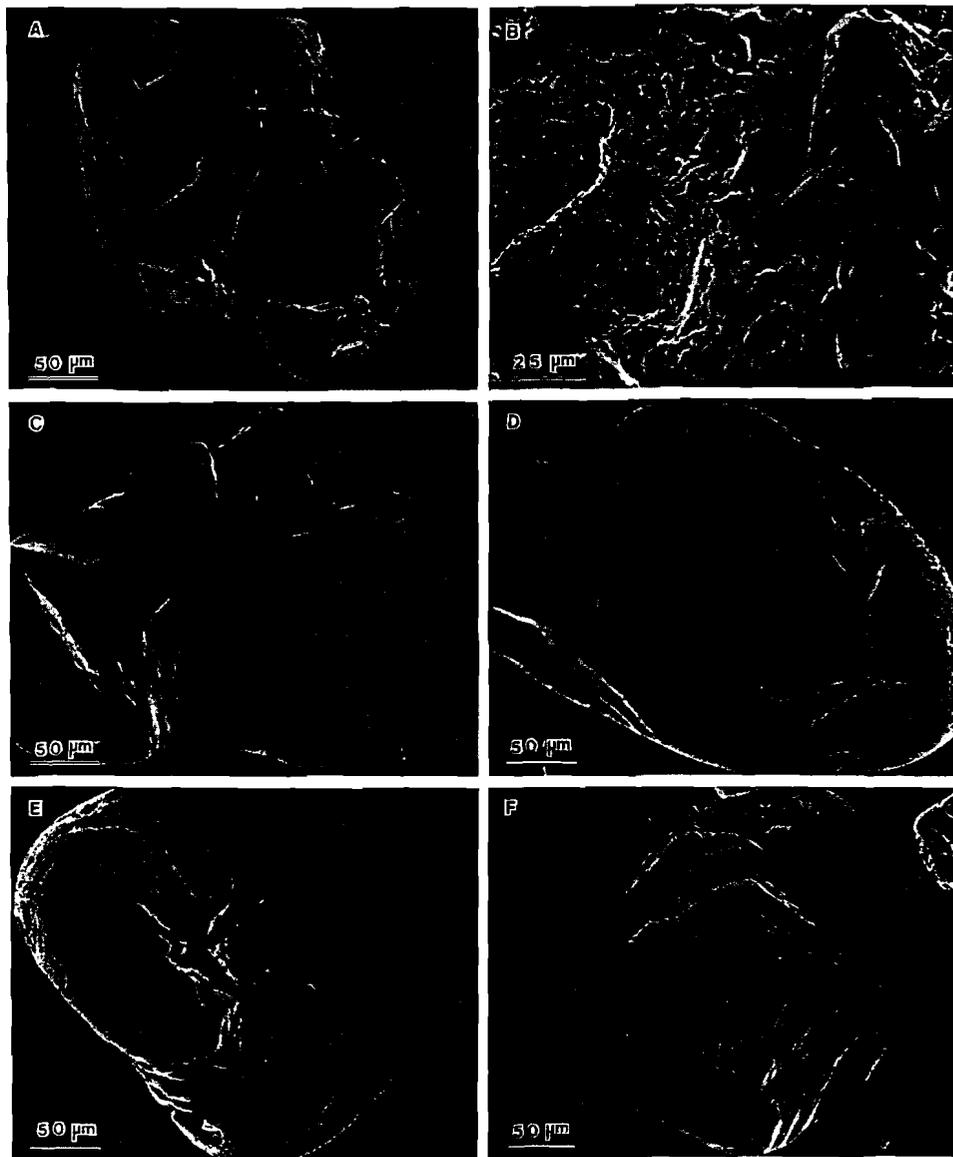


Fig. 3. Scanning electron micrograph of fine quartz sand showing: (A) incipient quartz overgrowths on grain from Bwc1 horizon; (B) close-up of (A); (C and D) non-oriented silica covering entire grains in Bg horizon; (E and F) euhedral overgrowths on grains from the Cg horizon.

Mineralogy

Silica

The high pH generated by the presence of Na-(bi)carbonates is favorable for the dissolution of silica. Evidence of silica translocation through the profile

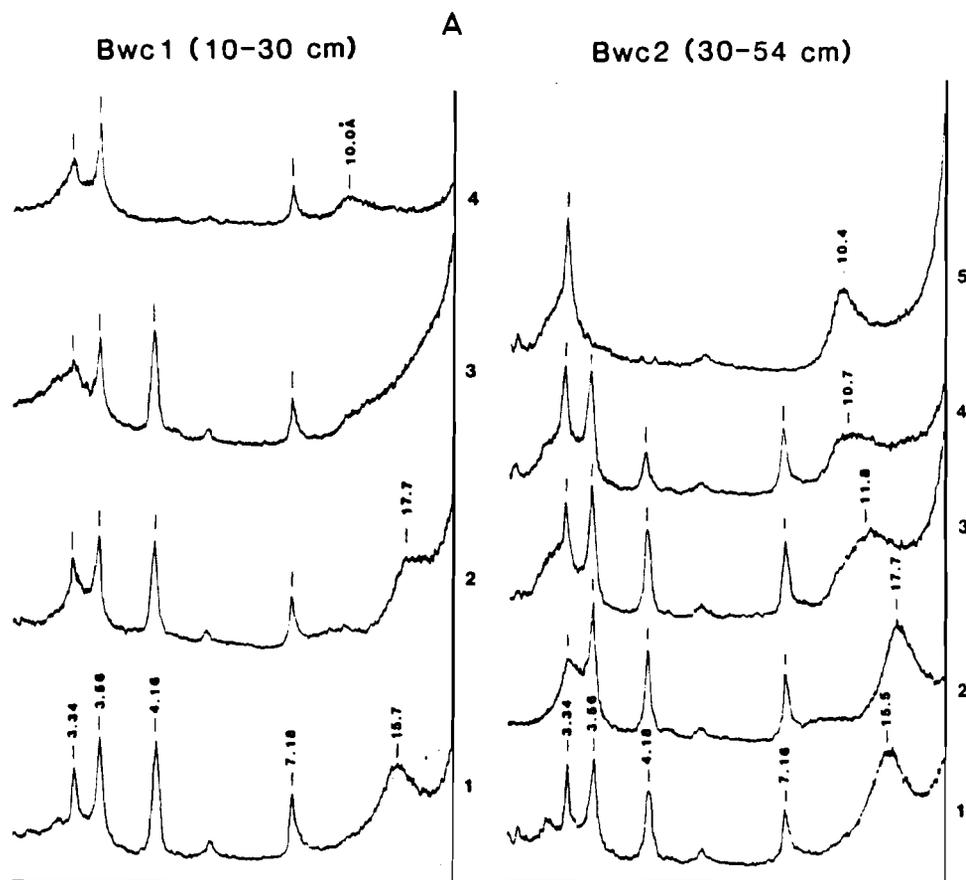


Fig. 4. (A) XRD pattern of $<2\text{-}\mu\text{m}$ fraction of Bwc1 horizon and Bwc2 horizon. Treatments: 1 = Mg-saturated, air dry; 2 = Mg-saturated, glycerated; 3 = K-saturated, air dry; 4 = K-saturated, 300°C ; 5 = K-saturated, 550°C .

is visible in the form of incipient silica overgrowths on quartz sands in the Bwc1 and Bwc2 horizons (Fig. 3, A and B). Massive and rapid silica precipitation occurs in the Bg horizon where the pH suddenly drops to 5, as evidenced by the non-oriented, continuous cover of silica on quartz (Fig. 3, C and D). In the Cg horizon, where silica precipitation is slower, euhedral quartz overgrowths are observed (Fig. 3, E and F). No comparable overgrowths are found in other fluvial sands.

The source of soluble silica is probably finer-textured quartz particles. Very little quartz is present in the clay ($<2\ \mu\text{m}$) fraction (Fig. 4). The dominant minerals in the clay fraction of this soil are goethite, kaolinite and smectite (Fig. 4); note the peaks at $4.18\ \text{\AA}$, $2.70\ \text{\AA}$, and $2.45\ \text{\AA}$ for goethite, and at $7.18\ \text{\AA}$ and $3.56\ \text{\AA}$ for kaolinite. Smectite is identified by peaks at $15\ \text{\AA}$ under Mg-

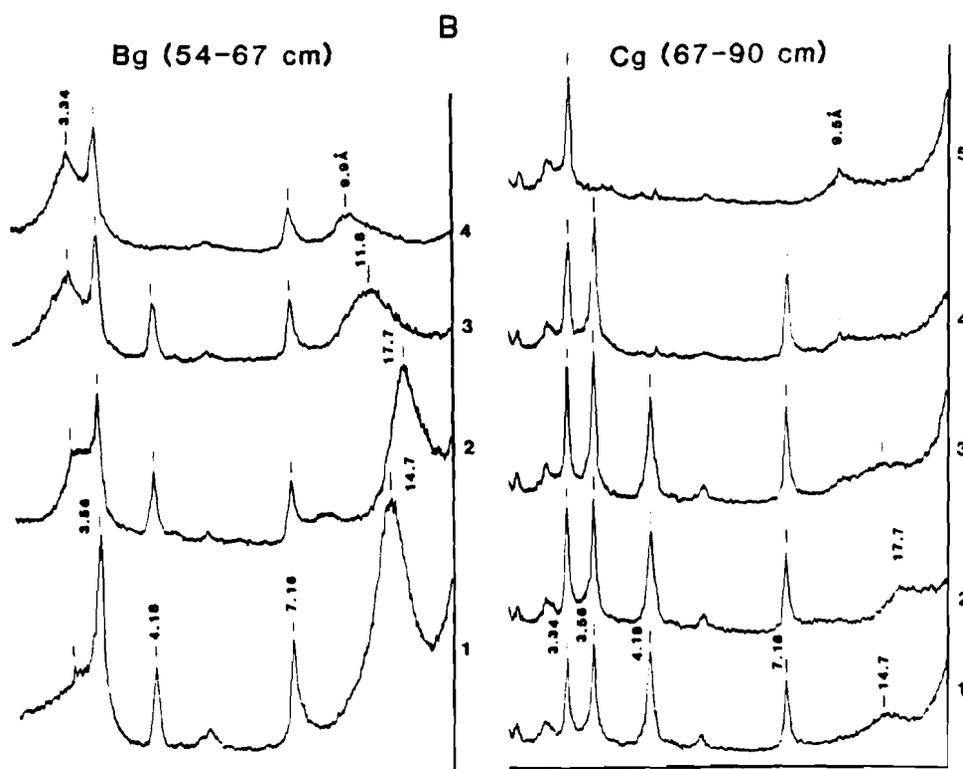


Fig. 4. (B) XRD pattern of $<2\text{-}\mu\text{m}$ fraction of Bg horizon and Cg horizon. Treatments: 1 = Mg-saturated, air dry; 2 = Mg-saturated, glycerated; 3 = K-saturated, air dry; 4 = K-saturated, 300°C ; 5 = K-saturated, 550°C .

saturated treatment which shift to 17.7 \AA upon glyceration and collapse to 10 \AA under a combination of K-saturation and heat to 300°C . Smectite is present throughout, although dominantly in the Bwc2 and Bg horizons. Hydroxy-interlayering of smectite is suggested by the resistance to collapse under K-saturation and heat treatment to 300°C in the Bwc2 horizon.

Neof ormation of smectite

According to infrared data, the smectite of the Bg horizon, which is concentrated in the very fine clay fraction, is Fe-rich (Fig. 5): $\text{Fe}_2^{+3}\text{-OH}$ at 818 cm^{-1} , Fe-Al-OH at 875 cm^{-1} , (Fe,Mg)-OH at 3570 cm^{-1} and Si-O-Fe vibrations at 675 cm^{-1} are identified based on data presented by Farmer (1974) and Van der Marel and Beutelspacher (1976). A trace of kaolinite is detectable from small OH vibrations at 3695 , 3660 , 3650 and 3620 cm^{-1} and from Si-O vibrations at 790 and 755 cm^{-1} . The peaks at 3620 and 910 cm^{-1} represent Al-OH and $\text{Al}_2\text{-OH}$ vibrations, respectively, of both smectite and kaolinite. The vibration at 840 cm^{-1} is attributed to Mg-Al-OH in smectite. By differential IR

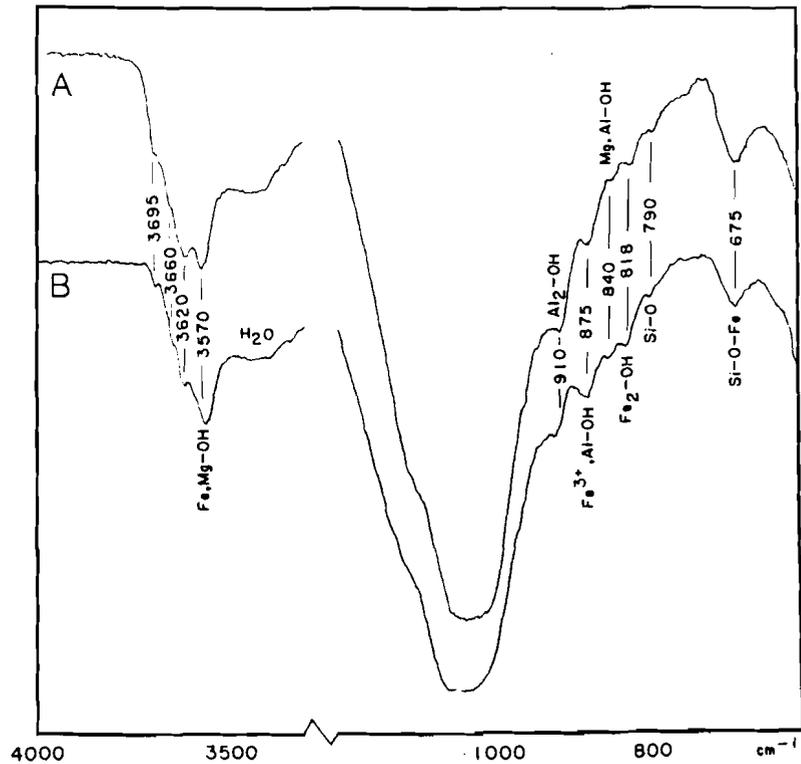
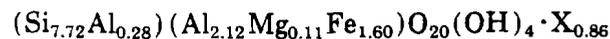


Fig. 5. Infrared spectrum of smectite ($<0.05 \mu\text{m}$) fraction of Bg horizon. (A) Initial spectrum; (B) after subtracting 16% kaolinite. Subtracting this amount of kaolinite from the initial sample spectrum enhances the Fe,Mg-OH and Fe-Al-OH vibrations at 3570 and 875 cm^{-1} , respectively, but does not affect the $\text{Fe}_2\text{-OH}$ vibration at 818 cm^{-1} .

analysis, after trial and error, the amount of kaolinite was estimated to be about 16%.

After dithionite-citrate-bicarbonate and $\text{NH}_4\text{-oxalate}$ treatments to remove Fe-oxides and a correction for 16% kaolinite, total chemical analysis by the method of Bernas (1968) yields the following structural formula:



where X is a univalent cation. The smectite therefore appears to be an Fe-rich beidellite.

The dominant clay mineral in the Continental Terminal sandstones and in soils of the dunes is kaolinite and there is no nearby source of smectite outside other channel clays. The smectite is therefore thought to be pedogenic, an interpretation which is consistent with the prevailing geochemical conditions. At the high pH prevailing in the upper 54 cm of this soil (8.8–9), silica becomes most soluble (Morey et al., 1962) and is free to recombine with soil cations

such as Mg, Fe and Al to form secondary clay minerals. In this poorly drained environment rich in Fe, a neoformed Fe-rich smectite is reasonable. In other channel soils, where the Fe concentration is less, other smectites may be expected to form.

The occurrence of pedogenic Fe-rich smectites is well documented in vertic soils of semi-arid West Africa (Trauth et al., 1967; Paquet, 1970; Millot, 1970) and polders of Lake Chad (Tardy et al., 1974; Droubi et al., 1976; Carmouze et al., 1977; Pedro et al., 1978; Carmouze, 1983). The neoformation of smectite in this region is intimately related to the geochemical evolution of solutions under a semi-arid climate with seasonal contrast (Paquet, 1970; Tardy et al., 1974; Droubi et al., 1976). The Fe-content of the smectite is a function of the chemical composition of the circulating water: nontronite is favored by "dilute" neutral systems and Mg-montmorillonite by concentrated, alkaline systems (Tardy et al., 1974; Carmouze et al., 1977); Fe-rich beidellite forms under intermediate conditions.

Fe-oxide mineralogy

Goethite was the only Fe-oxide mineral identified in the pedotubule concretions (Fig. 6A) whereas maghemite and hematite were also present in the suspended residue (Fig. 6B) from a water sample collected from the base of the profile. The very dark grey color of the Bg-horizon may be imparted by finely divided, poorly crystallized FeS or hydromagnetite (Ponnamperuma, 1972) or, possibly, by organic matter.

The strong contrast with depth in this profile undoubtedly plays an impor-

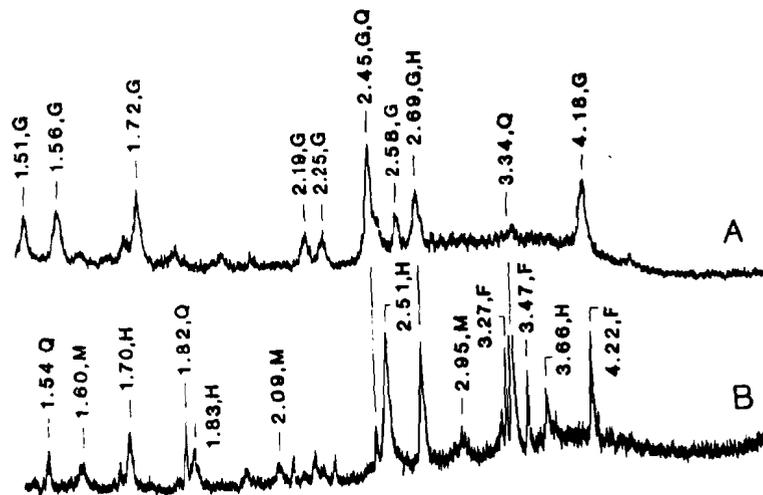


Fig. 6. (A) X-ray diffraction pattern of pedotubule concretions. (B) X-ray diffraction pattern of colloidal water residue.

tant role in the Fe-oxide mineralogy and the occurrence of maghemite, hematite and goethite in the same soil. The goethite pedotubules may be relict features having precipitated around the roots of aquatic plants in the pond. Similar Fe-segregation phenomena are observed in waterlogged rice soils (Ponnamperuma, 1972; Chen et al., 1980; Kumazawa, 1984). By actively transporting O_2 to their roots, paddy rice plants protect themselves from injury by H_2S , Fe(II) and other reduced substances which are common in paddy fields (Kumazawa, 1984). In this soil, maghemite probably forms by the oxidation, at pH above 7, of a "green-rust" Fe(II,III)-hydroxy salt precursor whose presence is suggested by the color of the gleyed horizon. The occurrence of maghemite and hematite in the groundwater residue reflect fluctuations in the micro-aeration of the soil environment and presence of Fe(II) and Fe(III) at the capillary fringe of the water table (Taylor and Schwertmann, 1974; Coventry et al., 1983). The moist pedoenvironment favors goethite over hematite in the upper profile. Although the soil is hydromorphic, goethite (α -FeOOH) rather than lepidocrocite (γ -FeOOH) forms because of the high pCO_2 near the surface (Schwertmann and Taylor, 1977). Apparently, the high level of soluble silica is not inhibiting goethite crystallization as it reportedly can (Schwertmann and Taylor, 1977).

Formation of sodium carbonates

The very high pH (>9) of the white efflorescences at the soil surface indicates that they are Na_2CO_3 . The anion composition of the groundwater at the base of this pedon is dominated by bicarbonate and sulfate (Table III). The water composition together with the landscape position (Fig. 2), profile morphology (Table I) and release of H_2S at the freshly dug pit site suggests that this soil fits the genetic pattern for alkaline soils put forth by Tyurin et al. (1967) in the U.S.S.R. and by Whittig and Janitzky (1963) in the Sacramento Valley in California. As outlined by these authors, a biochemical mechanism is active in the formation of Na_2CO_3 in soils when the following conditions occur concurrently: (1) anaerobic soil environment; (2) presence of fresh organic matter; (3) source of SO_4^{2-} in the groundwater; (4) presence of SO_4^{2-} -reducing bacteria (e.g., *Desulfovibrio*); and (5) climate with wet and dry seasons and high evapotranspiration. The actual genetic mechanism is discussed below.

MECHANISMS FOR ACCUMULATION

An overall genetic mechanism for the accumulation of Na_2CO_3 , Fe-oxides and smectite in channel soils can be summarized as follows (Fig. 7). Anaerobic SO_4^{2-} -reducing bacteria reduce SO_4^{2-} to S^{2-} and generate CO_2 during respiration. Sulfide hydrolyzes to produce H_2S and OH^- and can also react with Fe(II) to form FeS. Microbial and plant activity generate more CO_2 near the soil surface. Hydroxyl and CO_2 react to produce HCO_3^- . The bicarbonate com-

TABLE III

Water-soluble cations and anions (in meq./l) for saturated paste extracts and groundwater

Depth (cm)	EC (mmhos/ cm)		Ca		Mg		Na		K		HCO ₃ ⁻¹		Cl		SO ₄	
	11/84	8/86	11/84	8/86	11/ 84	8/86	11/84	8/86	11/84	8/86	11/ 84	8/86	11/ 84	8/86	11/84	8/86
0-10	N.A.* ²	0.70	N.A.	1.9	N.A.	0.6	N.A.	4.7	N.A.	0.2	N.A.	4.8	N.A.	0.8	N.A.	0.8
10-30	1.1	0.68	0.3	1.4	0.1	0.8	14.3	5.2	0.3	0.5	13.7	4.6	0.5	1.2	0.7	0.6
30-54	0.6	0.64	0.2	0.5	0.2	0.3	7.6	0.7	0.2	0.3	7.1	1.0	0.6	0.4	0.6	0.9
54-67	N.A.	0.35	N.A.	0.2	N.A.	0.2	N.A.	1.1	N.A.	0.1	N.A.	1.0	N.A.	0.3	N.A.	0.2
67-90	N.A.	0.17	N.A.	0.4	N.A.	0.3	N.A.	0.8	N.A.	0.3	N.A.	0.0	N.A.	0.2	N.A.	0.1
Water	0.10	N.A.	0.9	N.A.	0.0	N.A.	0.4	N.A.	0.1	N.A.	0.8	N.A.	0.0	N.A.	0.6	N.A.

*¹CO₃ was not detected in any of the samples

*²N.A. = not analyzed.

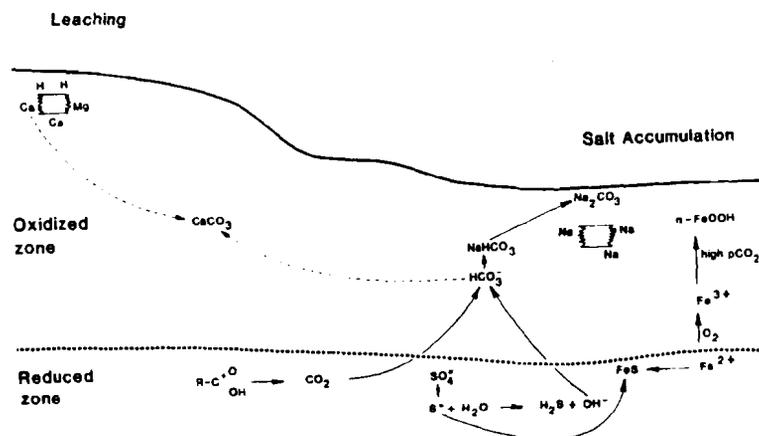


Fig. 7. Schematic diagram of overall genetic mechanism for Na_2CO_3 and $\alpha\text{-FeOOH}$ formation.

bins with exchangeable cations such as Ca and Na to form $\text{Ca}(\text{HCO}_3)_2$ and NaHCO_3 . As these compounds are brought to the surface by capillary rise and evaporative pull, they form CaCO_3 and Na_2CO_3 as the solubility product of these carbonates is exceeded. The high pH generated by Na_2CO_3 leads to increased solubilization of silica which recombines with Mg, Al (and Fe) to form smectite. At the same time, although the soil is hydromorphic, goethite rather than lepidocrocite forms because of the high p_{CO_2} near the surface.

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