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Distribution and dynamics of gibbsite and kaolinite in an oxisol of Serra do Mar, southeastern Brazil

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Abstract

In the Serra do Mar region, in southeastern Brazil, the soil mantle is mainly characterised by (i) a gibbsitic saprolite, (ii) various kaolinitic horizons within the gibbsitic material, (iii) kaolinito-gibbsitic topsoil horizons. This organisation does not match with the thermodynamic stability of gibbsite and kaolinite accompanying the solution percolation through soil profiles. A study of the micromorphological, mineralogical and chemical properties of the soil mantle reveals that this organisation arises from the in situ development of the soil from the crystalline bedrock. The bauxitic weathering of the bedrock, even if it is rich in quartz, can be explained by a fast renewal of the solutions and/or a high solubility of the kaolinite. Recycling of Si and Al by the forest can maintain a dynamic equilibrium of kaolinite in the topsoil horizons, as observed in Amazonia. The kaolinitic compact horizons evolve upslope at the expense of the gibbsitic material. At the contact between kaolinitic and gibbsitic material, dissolution patterns of quartz and gibbsite are observed, indicating that this evolution is in process. These observations and the organisation of the soil mantle set the problem of the apparent stability of gibbsite and kaolinite in this environment.

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Various assumptions that could explain this organisation of the soil mantle are discussed. Changes in the activity of water due to the pore size diminution and displacement of the gibbsite–kaolinite equilibrium appear insufficient to explain the stability of kaolinite. However, it could be allotted to the slow down of water flows in the soil mantle. Lastly, the eventual role of the complexing organic matter is presented. More investigations on the biogeochemical cycle of Si and Al and on the physico-chemical processes at the soil solution–mineral interface are necessary to explain the stability and dynamics of gibbsite and kaolinite in this environment. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Gibbsite; Kaolinite; Resilication; Mineral stability; Brazil

1. Introduction

The soils of the Serra do Mar and Serra da Mantiqueira region, in southeastern Brazil, are composed of residual, poorly weatherable primary material as quartz, and secondary newly generated minerals as gibbsite, kaolinite, goethite and hematite. These secondary minerals are located at the end of a climatic and geochemical sequence and are classically observed in oxisols (Pedro, 1968). The presence and spatial distribution of these minerals are generally interpreted as a function of their thermodynamic stability in aqueous solutions accompanying the water percolation through soil profiles and landscape (Lucas et al., 1993). With regards to the distribution of gibbsite and kaolinite, the normal sequence (Tardy, 1993) is: gibbsite at the top of the profiles and upslope, in conditions of better drainage (Millot, 1964), and kaolinite at the base of the profiles and downslope, in conditions of worse drainage. “Abnormal sequences” were frequently reported (Leneuf, 1959; Delvigne, 1965, 1967; Bourgeat, 1972; Sieffermann, 1973; Novikoff, 1974; Tardy and Novikoff, 1988; Dennen and Norton, 1977; Kronberg et al., 1982; Lucas et al., 1989; Lecomte, 1988; Butt, 1981; Boulet et al., 1993), but only few of these studies were accompanied by considerations about the conditions of stability of kaolinite and gibbsite. An abnormal sequence is described in the Serra do Mar region, where kaolinite predominates in the topsoil horizons and in compact clay loam horizons, respectively, located over and within a gibbsitic material. Therefore, authors differ significantly on the genetic interpretation of the soil profiles (De Ploey and Cruz, 1979; Grocke et al., 1983; Furian, 1994; Modenesi and Motta de Toledo, 1996). This anomaly has been classically attributed to the frequent mass movements in this area, and the presence of kaolinite allotted to an allochthonous materials through mass movements or colluvionment.

The purpose of this paper is to describe the organisation of the soil, the weathering mineral sequences and to show that this vertical succession corresponds to an in situ soil development. Therefore, the study of the soil organisation reveals an unusual dynamics of gibbsite and kaolinite in the soil mantle, and sets the problem of the stability of these minerals in the landscape.

2. Site

The studied area is located at 23°S in the Brazilian humid tropical zone, between the Serra do Mar and the Atlantic Plateau in the eastern part of São Paulo State. The fieldwork was concentrated on a small (56 ha) catchment of the River Paraibuna in the district of Cunha, known as the “D” catchment in the Serra do Mar State Park (Fig. 1). Cunha is part of the granite–gneiss high plateaux of the Serra do Mar. Uplifted since the Oligocene (Almeida, 1976), these plateaux belong, with the Serra da Mantiqueira, to the uppermost surface of the block mountains of southeastern Brazil’s Atlantic margin. The chemical weathering of the crystalline Precambrian basement has resulted in sandy loamy regoliths with a maximum thickness of 15 m (Bigarella et al., 1965).

Recent evolution of slopes in the Serra do Mar has been mainly controlled by mass movements, including slumping and planar slides in the regolith, rockfalls and rockslides according to Varnes (1958) classification (De Ploey and Cruz, 1979).

The wet tropical climate belongs to type “Cwa” of Köppen (Furian, 1994) with altitude and orographic influences. Annual precipitation ranges from 2000 to 2500 mm, with a rainy season from September to March giving 71% of the annual rainfall. The vegetation is rain forest of the “Atlantic forest” domain.

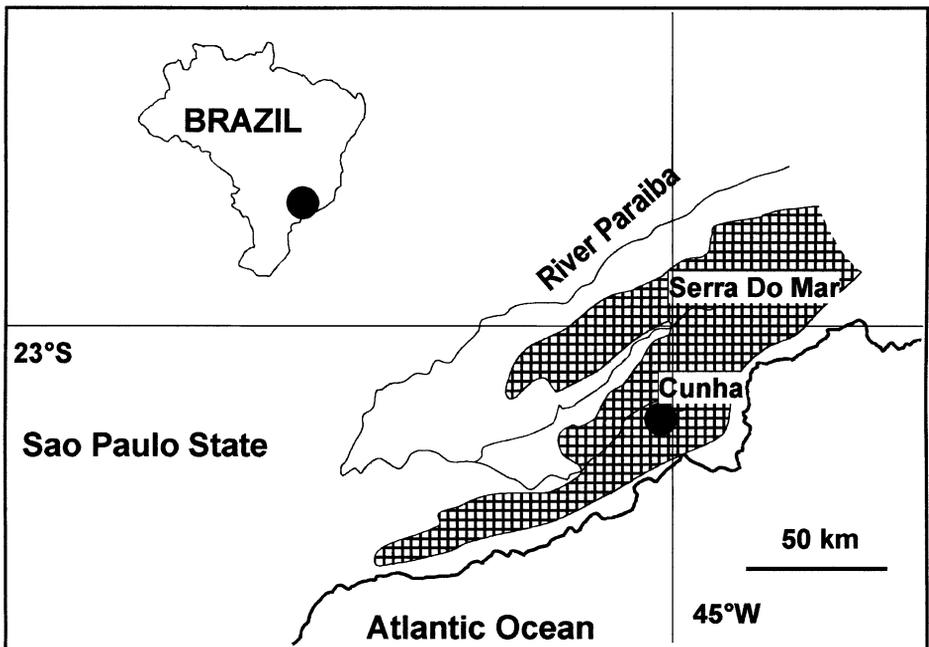


Fig. 1. Location of the studied site in southeastern Brazil.

3. Methods

The soil mantle organisation was reconstructed along four sequences located on the crest line and on the slope. The mineralogy was studied by X-ray diffraction (XRD) analysis on randomly oriented powder and oriented deposit of the $< 2\text{-}\mu\text{m}$ fraction, which was studied in five conditions: K saturation, Mg saturation, Mg saturation and treatment with glycol ethylene, heating at 450 and 550 °C.

Undisturbed blocks were collected and impregnated with an acetone-diluted polyester resin (Scott–Bader Crystic) after dehydration by acetone exchange, and vertical thin sections (70×110 mm) were made and described according to Brewer (1976) and Bullock et al. (1985). Some samples were collected for S.E.M. (XL 20 Philips at 15 kV) observations and analyses on aggregate (LINK Analytical eXL energy dispersive X-ray system).

Total analyses have been performed after alkaline fusion using lithium tetraborate. Fe, Al and Ti were quantified by colorimetry; Ca, Mg and Mn by atomic adsorption; Na and K by emission. Si was quantified by gravimetry. Total chemical analyses of the secondary minerals produced by weathering have been performed using a three-acid digestion method (Harrassowitz, 1926). Semi-quantitative estimations of the abundance of secondary mineral phases of gibbsite and kaolinite were calculated from the K_i index ($K_i = \text{SiO}_2/\text{Al}_2\text{O}_3$) according to Pedro (1966). The pore size distribution, between 0.0037 and 100 μm equivalent radii, was studied with a Carlo Elba 2000 mercury porosimeter using air-dried centimetric aggregates outgassed at room temperature.

4. Organisation and composition of the soil mantle

The soil mantle is not continuous and preliminary observations (Furian et al., 1999) allow us to distinguish the in situ material from the material arising from landslide processes, which are frequent in the region. The following description concerns the non-colluvial material. The soil mantle consists of a 5/12-m-thick ferrallitic soil. The horizons distinguished are: (1) the parent rock, (2) a sandy gibbsitic saprolite locally microaggregated and locally with gibbsitic pebbles and blocks, (3) kaolinitic compact clay loam horizons, (4) a kaolinito-gibbsitic microaggregated horizon and burrowed topsoil horizons. The main features of this soil system are presented on cross-section (Fig. 2) and on the map of the studied slope (Fig. 3). The mineralogical characteristics and relative composition of the secondary minerals are presented in Tables 1 and 2.

The material of the sandy saprolite derived from an in situ weathering of the parent rock. The gibbsite and kaolinite weight contents in the secondary minerals range from 85% to 90% and from 10% to 15%, respectively. According to Claisse (1968), the triacid method may dissolve a part of the quartz,

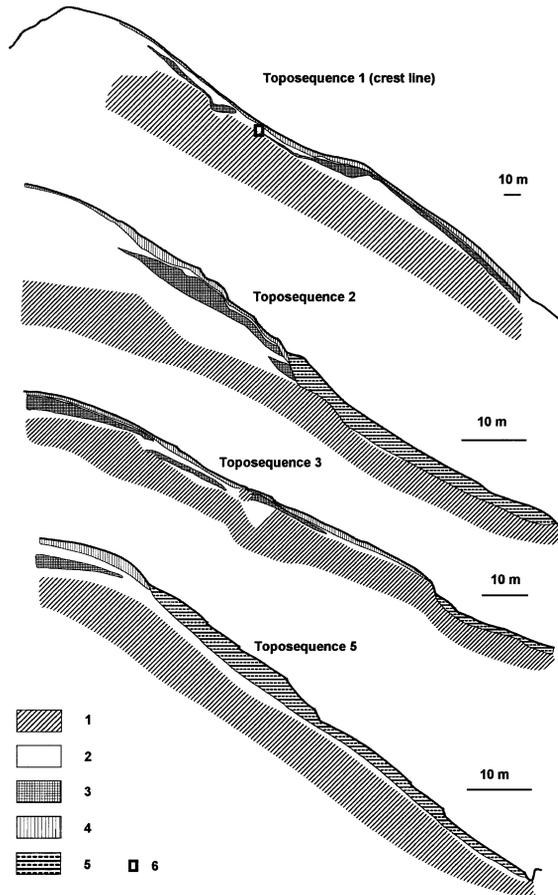


Fig. 2. The main features of the soil system. (1) Parent rock, (2) sandy gibbsitic saprolite locally microaggregated with gibbsitic pebbles and blocks, (3) kaolinitic clay loam compact horizons, (4) kaolinito-gibbsitic-microaggregated horizon and burrowed topsoil horizons, (5) colluvium, (6) sampling point of the block presented in Fig. 7.

leading to super-estimate the kaolinite proportion with regard to gibbsite. This super-estimate, if it occurs, would not change the “gibbsite-rich” classification of this material. On thin sections, we can observe that the original mineral structures and that of the rock itself are preserved in gibbsite pseudomorphs. This results in a gibbsitic horizon with a box-work structure (Fig. 4). The polysynthetic twinning of plagioclases and the cleavage of amphiboles are also preserved in the gibbsite, indicating that the formation of gibbsite was the first stage in weathering of the parent rock. Only quartz and muscovite were unaltered at this stage. Biotite transformation into gibbsite accompanies the opening of the layers. Millimetric veins of porcelanous gibbsite are observed. They probably infilled fissures in the parent rock (Fig. 5).

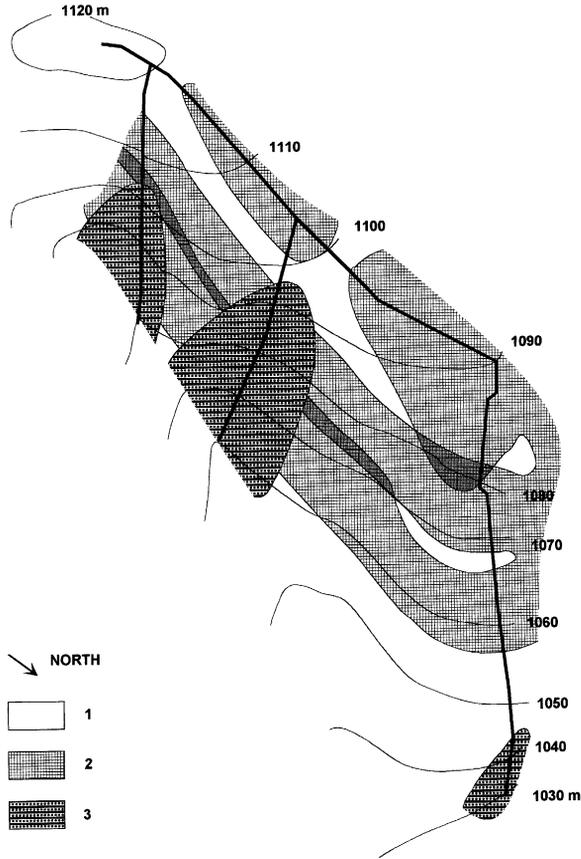


Fig. 3. Limits of the kaolinitic compact horizons and of the colluvium on the studied slope. (1) Gibbsitic weathering material without kaolinitic compact horizons, (2) kaolinitic compact horizon within the gibbsitic material, (3) colluvium.

Pebbly and blocky horizons, composed of ferruginised gibbsitic material, are observed at the top of the thick gibbsitic saprolite. The structure and orientation of the parent rock is still preserved in the blocks. Gibbsite also predominates in pebbles and blocks, and its weight content is around 85% of the secondary minerals.

On the crest line and on the slope, some compact clay loam horizons occur within the gibbsitic saprolite. They are tongue-shaped, generally thick in their low part (downslope) and thin upslope. The parent rock structure appears locally preserved in these compact horizons. The quartz exhibit dissolution patterns (Fig. 6) and muscovites are strongly kaolinised. The gibbsite and kaolinite weight contents range from 15% to 20% and from 80% to 85%, respectively, of the secondary minerals. XRD analyses confirm that kaolinite predominates in these horizons. However, if the main picks of kaolinite are well defined and of

Table 1
Mineralogical composition of the soil horizons

	Gibbsite	Kaolinite	Al. vermiculite	Quartz	Hematite	Goethite
Gibbsitic saprolite and gibbsitic blocky horizon	+++	t to +	t	+++	+ to ++	+ to ++
Kaolinitic clay loam horizon	+	+++		++	+	+
Topsoil horizon and microaggregated horizon	++	++	t	+ to ++	t to +	+

+ indicate relative abundance as judged from the XRD peak intensities and from the thin section examination; t = traces.

strong intensity, a low discrimination of the picks at 4.46, 4.36 and 4.18 Å is noted.

A microaggregated horizon is made up of gibbsitic microaggregates from dismantling of the box-work structure at the contact with the clay loam kaolinitic horizon. Its gibbsite and kaolinite proportions are 60% and 40%. As gibbsite predominates in this horizon, it was therefore included in the gibbsitic saprolite (2) in Fig. 2. Another microaggregated horizon composed of biofabrics, whose gibbsite and kaolinite proportions are 40% and 60%, respectively, was gathered among kaolinite dominant topsoil horizon (4) in Fig. 2.

Although the soil fauna has burrowed into the topsoil horizons, it is still possible to identify relicts of the millimetric porcelanous gibbsitic veins. In spite of the bioturbation, they are not randomly oriented and globally still preserve the orientation of the parental material. These topsoil horizons exhibit a gibbsite–kaolinite ratio of 35:65 in the secondary minerals.

On a block sampled on the contact between the kaolinitic clay loam horizon and the gibbsitic saprolite (6 in Fig. 2), we can observe that the structure of the kaolinitic material truncates that of the gibbsitic one (Fig. 7). At this contact, under petrographic microscope, the gibbsite has lost its optical properties

Table 2
Relative proportions of gibbsite and kaolinite produced by weathering, calculated from the Ki index

	Gibbsite (%)	Kaolinite (%)	Ki = SiO ₂ / Al ₂ O ₃
Gibbsitic sandy saprolite	85–90	10–15	0.12–0.22
Kaolinitic clay loam horizon	15–20	80–85	1.5–1.65
Microaggregated and topsoil horizon	35–60	40–65	0.65–1.05

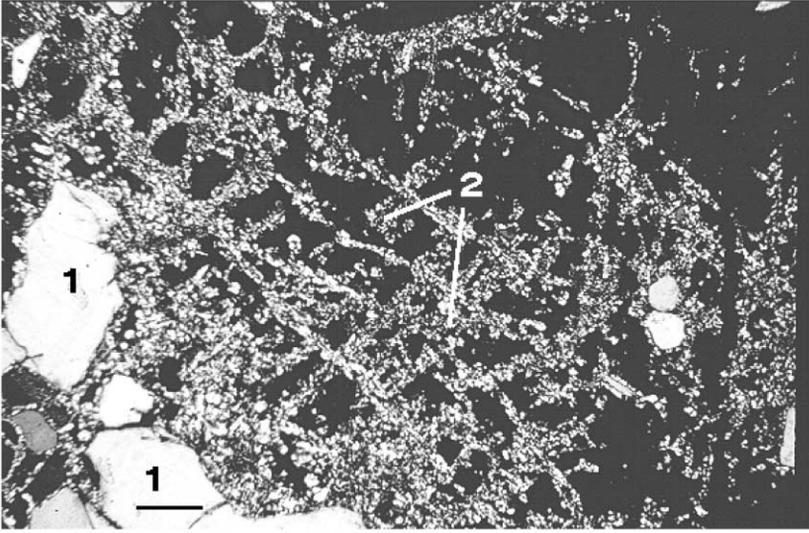


Fig. 4. The parent rock structure is preserved as gibbsitic box-work. (1) Quartz; (2) gibbsite; bar = 100 μm .

becoming isotropic, acquiring a pale yellow colour, decreasing in crystal size and losing its box-work structure (Fig. 8). Dissolution patterns of quartz and gibbsite are observed using S.E.M. (Figs. 9 and 10), in the gibbsitic saprolite, just upslope the kaolinitic clay loam horizon. Different morphological types of gibbsite are observed, from euhedral crystals to those showing extensive surface etching by dissolution.

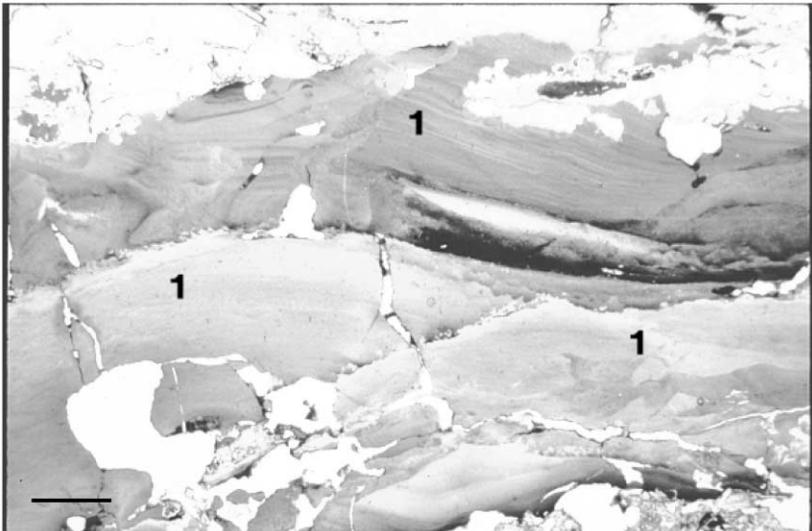


Fig. 5. Millimetric veins of porcelanous gibbsite. (1) Gibbsite; bar = 100 μm .

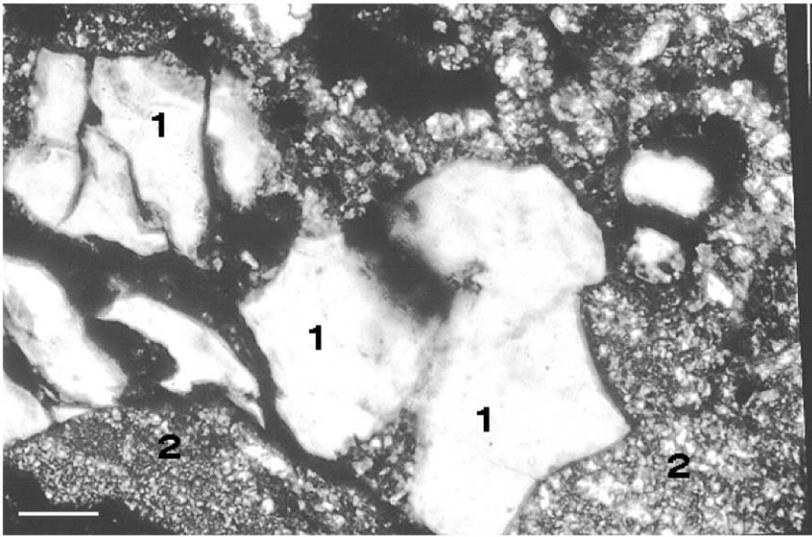


Fig. 6. Dissolution patterns of the quartz. (1) Quartz; (2) gibbsite; bar = 50 μm .



Fig. 7. Detail of the contact between kaolinitic clay loam horizons and gibbsitic saprolite on an impregnated block. Bar = 1 cm.

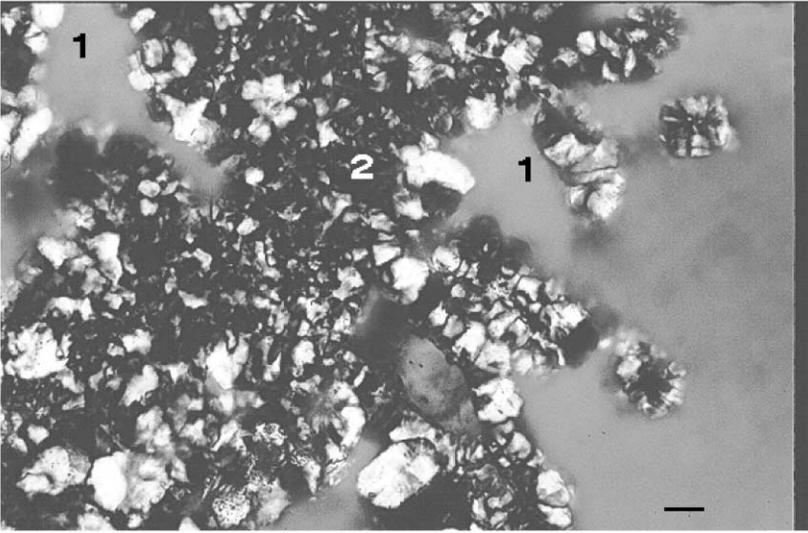


Fig. 8. Decrease in crystal size and lost of the box-work structure accompanying the gibbsite dissolution. (1) Voids; (2) gibbsite; bar = 10 μm .

Both topsoil, microaggregated and gibbsitic saprolite exhibit a bimodal distribution of pore sizes, corresponding to intra- and inter-aggregate pores as classically observed in oxisols (Cambier and Prost, 1981; Curmi et al., 1994). In

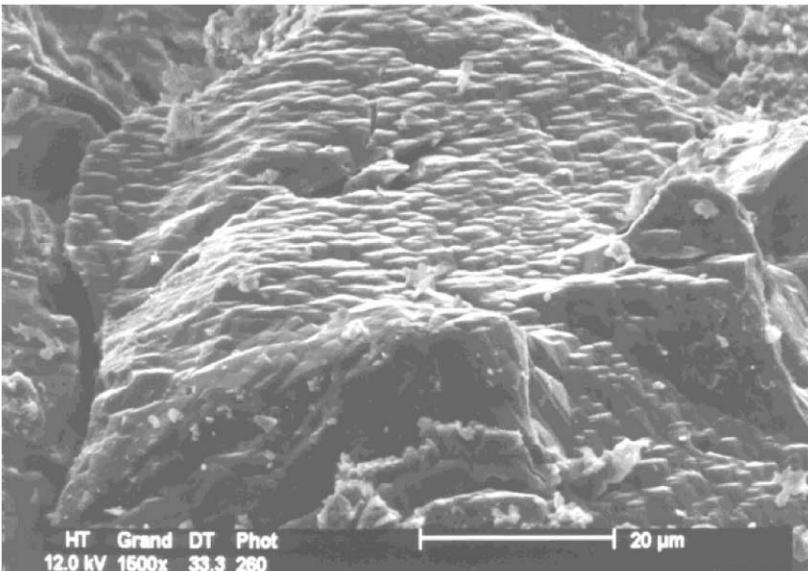


Fig. 9. Dissolution patterns of the quartz at the contact between gibbsitic and kaolinitic horizons.

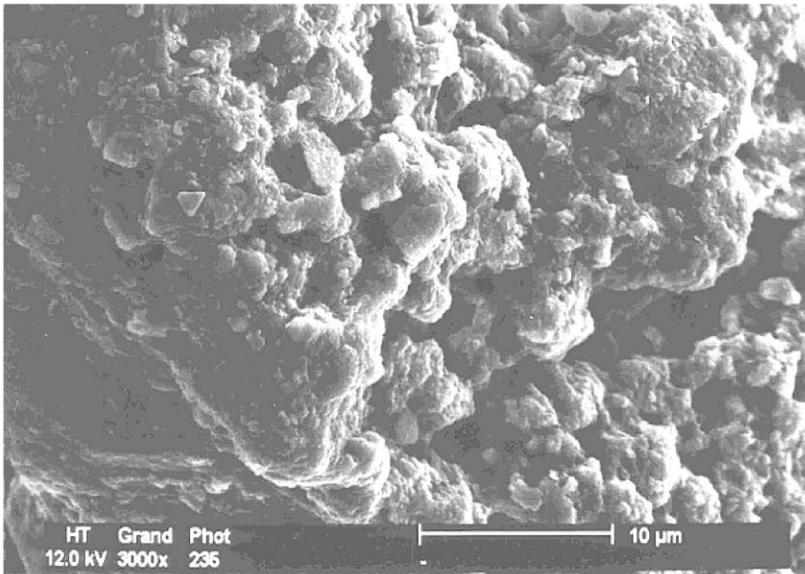


Fig. 10. Dissolution patterns of the gibbsite at the contact between gibbsitic and kaolinitic horizons.

compensation, the kaolinitic clay loam horizon has a unimodal distribution. About 90% of the pores intruded by mercury belong to the microporosity (equivalent radius $< 1.5 \mu\text{m}$; Fig. 11) (Grimaldi and Boulet, 1989).

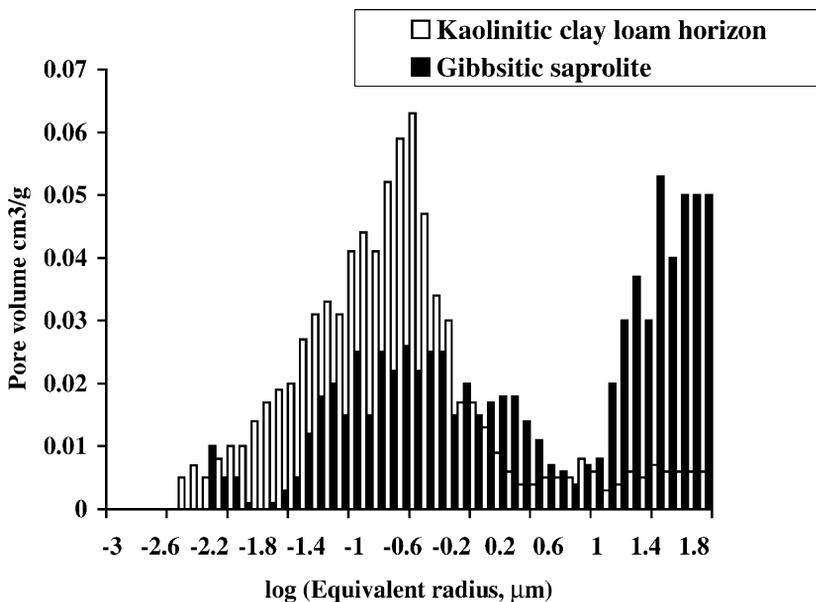


Fig. 11. Pore size distribution of gibbsitic and kaolinitic horizon.

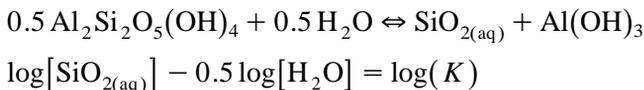
5. Discussion

The soil cover is derived from the in situ gibbsitic weathering of the bedrock, the structure of which is preserved in the soil, even up to the surface horizons where gibbsitic veins occur. Therefore, three characteristics of this soil cover do not match with the normal distribution of gibbsite and kaolinite in lateritic profiles. They are:

1. a bauxitic weathering of the parent rock, without kaolinite intermediate formation;
2. the presence of kaolinite in the topsoil horizons; and
3. the presence of kaolinitic compact clay loam horizons into the gibbsitic saprolite.

5.1. The gibbsitic saprolite

Although the parent rock is rich in quartz, a gibbsitic weathering is observed where we could expect kaolinite. This gibbsitic weathering of the parent rock was described on various sites under similar climatic conditions in Africa, but more frequently in South America, generally on alkaline rocks (Delvigne, 1965; Grocke et al., 1983) but even in the case of parent rocks rich in quartz. Most of the models of soil formation are based on thermodynamic equilibrium of mineral assemblages (Fritz, 1975; Lasaga, 1984; Ambrosi, 1990). The equilibrium between gibbsite and kaolinite depends on the H_2O activity according to the reaction:



where [] denotes the activity and K the equilibrium constant of the reaction.

Kobilseck (1990) supposed that within the water table with an activity of water close to 1, the equilibria with respect to gibbsite-quartz can be reached together without kaolinite intermediary. According to Tardy (1993), the kaolinite–gibbsite equilibrium value of $\log (K) = -4.5$ (Fritz and Tardy, 1973) was selected so that kaolinite appears more stable than the association gibbsite quartz (kaolinite 1, Fig. 12). This value corresponds to a relatively well-crystallised kaolinite and without impurities. In the kaolinitic clay loam horizon, the low discrimination of the secondary picks of kaolinite by XRD analysis indicates a low crystallinity (Brindley and Brown, 1980), i.e. a kaolinite with higher solubility (kaolinite 2, Fig. 12). A value slightly higher than -4 , which is the product of solubility of quartz, can be chosen and then the gibbsite–quartz association (D in Fig. 12) is possible when the activity of water is close to 1. When the water activity decreases, the kaolinite becomes in its turn more stable than the gibbsite–quartz association.

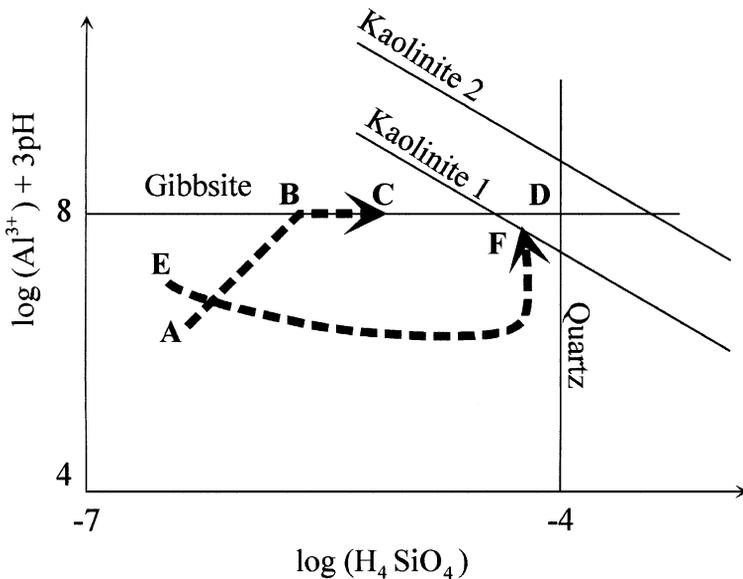


Fig. 12. Advance of the soil solution in a gibbsite–quartz–kaolinite equilibrium diagram. (A, B, C) The soil solution leaves the system before the equilibrium with respect to kaolinite being reached; (E, F) advance considering the role of the complexing organic matter (modified from Lucas et al., 1996).

These authors supposed that the equilibrium between minerals and solution is reached in the soil. The gibbsite–quartz association can be obtained by considering a fast renewal of the soil solution, under conditions of humid climate and good drainage. This is particularly possible, as the kinetic of dissolution of the quartz is very slow. The solutions reached the equilibrium with respect to the gibbsite (B in Fig. 12) but leave the system before the reaction of dissolution is finished, and before the double point of the equilibrium with respect to gibbsite–kaolinite is reached. In this case, the profiles are, to some extent, truncated by the bottom, the depth horizons classically expected in a water percolating model are not formed (Fritz, 1975), and gibbsite–quartz association is observed in the soil. According to Bourrié (1990), the soil solution could be at the equilibrium with respect to gibbsite and over-saturated with respect to kaolinite. This mineral forms slowly and the proportions of the different minerals are kinetically controlled. Therefore, a fast renewal of the solutions, even if they are temporarily over-saturated with respect to kaolinite, could explain the gibbsite–quartz association.

5.2. The kaolinitic topsoil horizons

The proportion of kaolinite is higher in the topsoil horizon than at depth, in the sandy gibbsitic material. This phenomenon, which today could appear classical, has been particularly studied in Amazonian forest environment of

Brazil (Lucas et al., 1993; Cornu, 1995; Cornu et al., 1998). These authors have shown that the forest recycles significant quantities of chemical elements, particularly Si and Al, maintaining a dynamic equilibrium and causing the stability of kaolinite in the topsoil horizons. Microscopic investigations allow Callot et al. (1992) to identify the precipitation of kaolinite in the vegetal tissues in decomposition. A similar recycling is probable under the coastal Atlantic rain forest, which still covers a large area of the Serra do Mar.

5.3. *The compact kaolinitic clay loam horizons*

The presence of the compact kaolinitic horizons within a gibbsitic weathering material sets more problems. It cannot indeed be attributed to a recycling of solution enriched in Si and Al by the top of the profile because of the geometry of this horizon being intercalated between two gibbsitic horizons. The examination of the contact between the gibbsitic saprolite and the kaolinitic clay loam horizon can inform us about the dynamics of this organisation. At the block scale, the structure of the kaolinitic material truncates that of the gibbsitic one, indicating that the latter developed first from the bedrock and subsequently changed into a kaolinitic material (Fig. 7). The silica and aluminum necessary for kaolinite formation could have been supplied by dissolution of gibbsite and quartz observed just upslope. This evolution is today in process. Destruction of gibbsite in oxisols was originally proposed by Delvigne (1965) in an Ivory Coast catena, and has been observed by Eswaran and Daud (1980) in gibbsitic nodules in the surface horizon of the Malacca series in Malaysia. More recently, Dedecker and Stoops (1999) presented the gibbsite dissolution in saprolite of Malaysia and Mulyanto et al. (1999) in the outer layer of an andesite core stone in Indonesia. Goldman and Tracey (1946) and later, Keller and Clark (1984) observed resilication of bauxite producing kaolin in Arkansas. Lucas et al. (1989) also described resilication in Amazonian bauxites, as Boulangé and Carvalho (1997) in the upper kaolinitic layer of Brazilian soils in Pará.

The hypothesis of climatic changes during the quaternary, with a diminution of the wet season, has been frequently used for the interpretation of abnormal sequences (Novikoff, 1974). In this case, it could explain the presence of some ferruginised blocks in topsoil. However, it cannot be responsible for the formation of the compact kaolinitic horizons, which evolution appears today in process.

The matricial effects due to the pore size can be a determinant for the stability of kaolinite in the kaolinitic clay loam horizon. The transition from the gibbsitic saprolite to the kaolinitic clay loam horizon corresponds to a high increase of the volume of fine pores, with an equivalent diameter around 0.3 μm (Fig. 11). The decrease in the water activity associated to this change in the pore size, which would be from 1 to 0.993 (Bourrié and Pedro, 1979), is not sufficient to displace significantly the gibbsite–kaolinite equilibrium.

The gibbsitic horizon exhibits a strong well-connected macroporosity, permitting a quick percolation of fresh solutions, undersaturated with respect to quartz and gibbsite and able to dissolve these minerals. In the compact kaolinitic horizon, the solutions are slowed down and/or concentrated under the effect of evaporation by the forest, and kaolinite can precipitate. This assumption can explain the self-upslope development of kaolinitic clay loam horizon. The phenomenon can be initiated by the numerous micaceous layers, which were observed in the gneiss saprolite, the micas being transformed into kaolinite, contrary to the feldspars, which are transformed directly into gibbsite. On the other hand, this assumption does not make it possible to explain why the dissolution patterns of quartz and gibbsite is observed just upslope of the kaolinitic clay loam horizon.

According to the studies carried out in Amazonian oxisols, the role of organic matter is also determinant in the solution–kaolinite equilibrium conditions. The complexing organic matter formed by the biological activity in the topsoil horizons subtracts a large proportion of Al from the solution (Cornu, 1995; Eyrolle et al., 1996). However, these complexes are retained onto material of high surface exchange and cannot migrate out of the system. Between the rainy events and at depth, due to the mineralisation of the organic matter and the increase in Al contents and pH value, the solution reached the equilibrium with respect to kaolinite (E and F in Fig. 12) (Lucas et al., 1996). This process could explain the intermediate kaolinitic clay loam horizon within the gibbsitic saprolite.

6. Conclusion

In the Serra do Mar region, the bedrock is subjected to a weathering that leads to a thick gibbsitic saprolite. The gibbsite–quartz association is observed without intermediary of kaolinite. This phenomenon has been frequently described in South America. It could be explained by high solubility of the kaolinite, due to low crystallinity and/or impurities in the crystalline net, or the high rainfall and intense leaching process, the solution being at the equilibrium with respect to gibbsite but leaving the system before the equilibrium with respect to kaolinite being reached.

In spite of the gibbsite weathering of the crystalline bedrock, the proportion of kaolinite increases in the topsoil horizons. As observed in Amazonian oxisols, the biological recycling of Si and Al could maintain a dynamic equilibrium causing the stability of kaolinite.

Some compact kaolinitic horizons are observed within the gibbsitic material. The organisation of the contact, the presence of dissolution patterns of quartz and gibbsite, indicates that the kaolinitic horizon evolves currently at the expense of the gibbsitic material.

Changes in the water activity due to the diminution of pore size can hardly displace significantly the kaolinite–gibbsite equilibrium. However, the pore size distribution in the soil conditioning of the water flows is proposed to explain the self-upslope development of these kaolinitic horizons.

The subtraction of Al from the soil solution by the complexing organic matter, and the mineralisation of this organic matter at depth, could explain the kaolinite formation within the gibbsitic saprolite.

The biogeochemical cycle of Si and Al in this environment and the physico-chemical processes at the soil solution–mineral interface have to be investigated to verify these assumptions.

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