SOLUTION OF SILICA AND FORMATION OF QUARTZ AND SMECTITE IN MANGROVE SWAMPS AND ADJACENT HYPERSALINE MARSH ENVIRONMENTS

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ABSTRACT

Under the dry tropical climate of New Caledonia, ferruginous sediments eroded from peridotites of the Dumbéa drainage basin were deposited in a Holocene deltaic structure. Mangroves grew in the deltaic marginal depressions. They were separated by a hypersaline marsh from the savanna on top of the levees. Diatom frustules enriched the sediments of the swamps with silica. The water table in mangrove soil was fed by the first water of the flood, which was brackish, and occasionally by rain at low tide. It formed a brackish-water lens in the soil of the central mangrove swamp and prevented further infiltration of salt water at high tide. That brackish-water lens permeated slowly toward the hypersaline marsh where it was concentrated by evaporation up to 2.5X the chlorinity of sea water. Infiltrated water, dissolved silica from diatom and other sources in the central mangrove swamp, with the help of organic matter, up to 200 ppm, and redeposited it on the way to the hypersaline area. In this process, quartz was synthesized everywhere and mostly under Eh conditions where iron was less soluble: i.e., a strongly reducing environment suitable to pyrites (mangrove soil) or oxidizing environments suitable to iron hydroxides (hypersaline marsh). Under intermediate Eh conditions such as the frontal area between swamp and hypersaline marsh environment, iron was soluble and combined with silica to form nontronite, and the pore water content in silica was then limited to 13 ppm.

INTRODUCTION

Mangrove remnants in Holocene and Pleistocene sediments from New Caledonia are often associated with smectitic clays (i.e., clays rich in silica) and with quartz deposits, even in drainage basins almost completely situated on outcrops of ultramafic rocks, or on their deeply weathered soils. The purpose of my work was to check if that coincidence is also found in very recent sediments.

New Caledonia lies between 20° and 22°S. Its climate alternates between seasons of subtropical anticyclones (from June to August) and intertropical low pressures (doldrums) from December to March. Mean temperature at sea level is 26 C in February and 20 C in August. Rainfall is approximately 1,000 mm at sea level and more than 3,000 mm in the mountains. Tropical hurricanes reach the island intermittently. They bring heavy rains of up to 500 mm a day, for instance. Evaporation rate is 1,000 mm/yr (Giovannelli 1953).

Approximately 80% of the drainage basin of our study lay on an ultramafic massif in which ultramafic rocks are found with some basic feldspathic rocks and a little granite (Guillon 1973). The remaining 20% of the basin is of low hills of sedimentary and old volcanic rocks. Because they are low, these hills receive little rainfall and do not account appreciably in the balance of sedimentation. Most sediments come from the ultramafic massif.

Trescases (1973) studied the weathering of ultramafic rocks of the southern ultramafic massif of New Caledonia. Weathering dissolves magnesium and silica of peridots and pyroxenes and these elements are found in runoff. Consequently, iron hydroxides concentrate on the field with Mn, Co, Cr and Al due to gabbro.

The elements of these soils are transported by mechanical erosion (Baltzer and Trescases 1971). A recent upheaval of the island (Baltzer 1970a), less than 5,000 years ago, increased the mechanical erosion rate and resulted in rapid filling of rias formed during the previous glacial low sea level. A series of small deltas, such as the Dumbea River Delta, is a consequence of this recent movement. The Holocene marine transgression is at present slow, but is recovering part of the land exposed during the building of the deltas. The Dumbea River Delta developed in a ria which lay perpendicular to the axis of the geological folds. Consequently, the ria is a succession of wide reaches separated by narrow passages at the crossing of hard rocks. The upstream part of the delta is an alluvial plain which fills the ria. The downstream part of the delta is made of one channel, except for a division by a small island. Natural levees on each side of the channel separate it from the marginal basins. On the left bank, the marginal basin has been almost completely filled with mangrove swamp and salt marsh deposits. A narrow channel drains the depression in the middle. On the right bank, the filling of the marginal basin is not complete and a small lagoon called "Baie Hoff" is a remnant of the former ria. Its water will be referred to as "sea water" in the following pages although the upper layer is brackish.

Between the Dumbea Channel and Baie Hoff are a levee, a hypersaline marsh, and a mangrove swamp over a width of 600 m (Fig. 1). On the levee, *Imperata* grass and various trees (*Casuarina equisetifolia* L.) develop on a nonhaline soil. The limit of the levee is shown by *Sporobolus virginicus* L. and *Lumnitzera racemosa* (L.) Gaertn. *Salicornia australis* Solander ex Forster. grows on the salt marsh. Patches of flat covered with algal mats or even bare patches are found in the middle of the *Salicornia* zone, in areas of extreme salinity. Mangrove swamps are populated with *Avicennia officinalis* L. on their salt marsh side, and by *Rhizophoraceae* in the other areas (*Rhizophora mucronata* Lamk. and *Bruguiera eryopetala* Wight and Arn.).

PRESENT SEDIMENTATION

Usually, sedimentation rate is very low. After an ordinary shower, river water becomes red, but no significant amount of sediment is carried in suspension by the river. On the contrary, during hurricanes, floods may be 1,000 m^3/sec, with 700 mg/ℓ of suspended mineral matter and the river overflows the levees and fills marginal basins. After a hurricane, a layer of newly-laid ferruginous sand of a few cm deep was found on the levee and a layer of silt a few mm deep and a clay fraction approximately one mm deep were found on the swamp. Therefore, mean grain size decreased from the levee to the swamp, as did thickness, and the deltaic morphology was built and maintained by hurricane floods.

The mangrove swamp is almost flat in the interior but slopes steeply for 50 m before reaching Baie Hoff. There, sediments are a very soft mud from present accretion. It is very similar to the mud on the bottom of Baie Hoff, which also is very flat. The steep slope of the 50 m of the outer mangrove suggests that particles set in suspension by small waves in Baie Hoff settle where wave agitation is damped by *Rhizophora* roots. Also, abundant organic production is partly responsible for that local sedimentation.

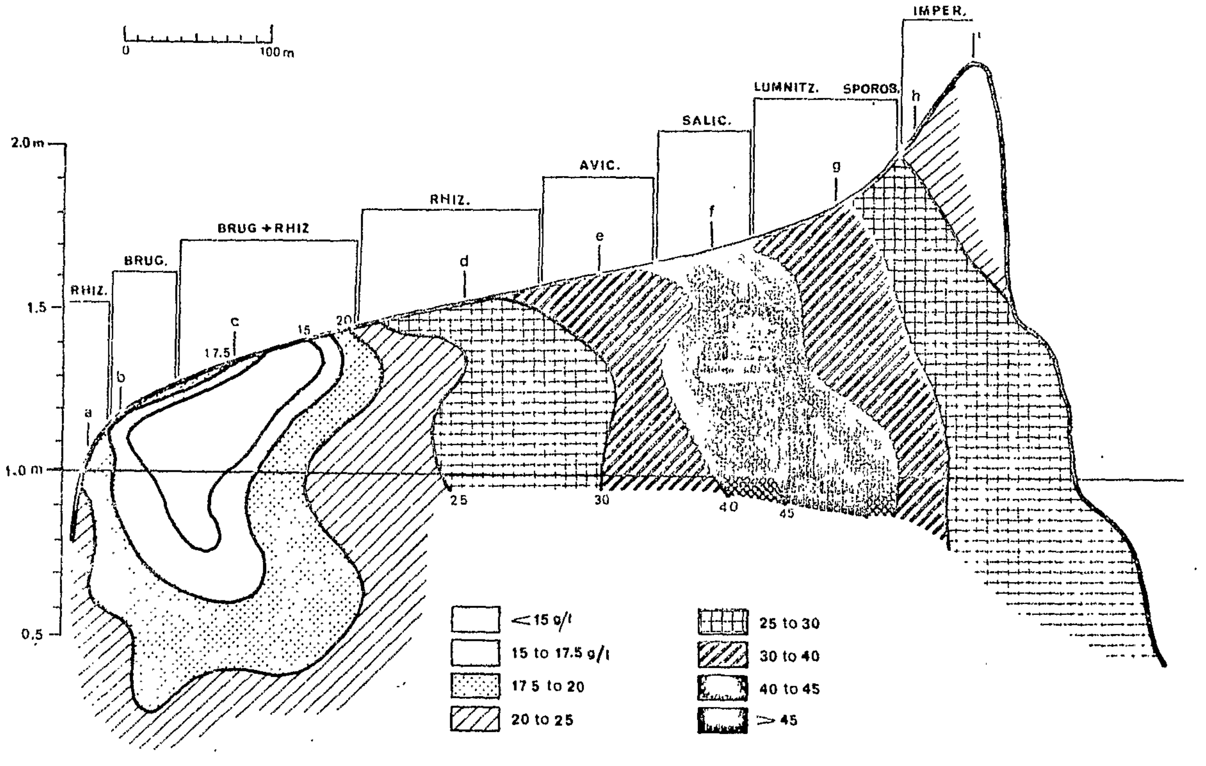

Figure 1. Distribution of plants, from levee to bay, and distribution of chloride ions in pore water of sediment.

STUDY OF SEDIMENTS

Sedimentary profiles were determined with an auger at places where an accurate measurement of soil level could be made. To keep a complete record of the cores, slices were cut lengthwise along them using direct current to keep the knife blade clean. Special samples for chemical and mineralogical analyses were collected at depths selected either by visual criteria or by regular spacing in the case of cores with little variation.

Pore water of sediments was obtained with a pressure membrane extractor at 30 bars. The water was analyzed quantitatively for Cl^-, SiO_2, SO_4^{2-}, CO_3H^-, K^+, Na^+, Mg^{++}, and Ca^{++}.

Mineralogical analysis was by X-ray diffraction methods. Chemical analysis was carried out on complete sediment samples without size fractioning. Results are given in percent of total mineral (loss on ignition deduced). Samples were treated with hot perchloric acid to dissolve secondary silicates. The residue was then dissolved in dilute sodium hydroxide solution. The quantity of silica after dissolution is referred to as "soluble silica." The main silicates that are unaffected by perchloric attack are quartz, pyroxene and talc. They are referred to as the "insoluble fraction." A comparison with the results of analysis for total silica (by X-ray fluorescence) demonstrated that "soluble silica" + "insoluble fraction" nearly equalled total silica. Most of the insoluble fraction was quartz, especially when this fraction was abundant.

Many quartz grains were observed through a scanning electron microscope equipped with an X-ray analyzer for chemical qualitative determinations. Examination of quartz was performed using principles of Le Ribault (1974).

Silty and clayey sands on top of the levee (Fig. 2) contain antigorite, quartz, goethite, pyroxene, maghemite, chromite and a little olivine. All these minerals originated in the ultramafic rocks. Sedimentary and volcanic formations downstream add quartz and feldspar. The finer fraction (smaller than 2 µm) is mainly antigorite, goethite, a little talc, kaolinite and smectite. Ferruginous gels and amorphous silica may account for one-third of the fine fraction.

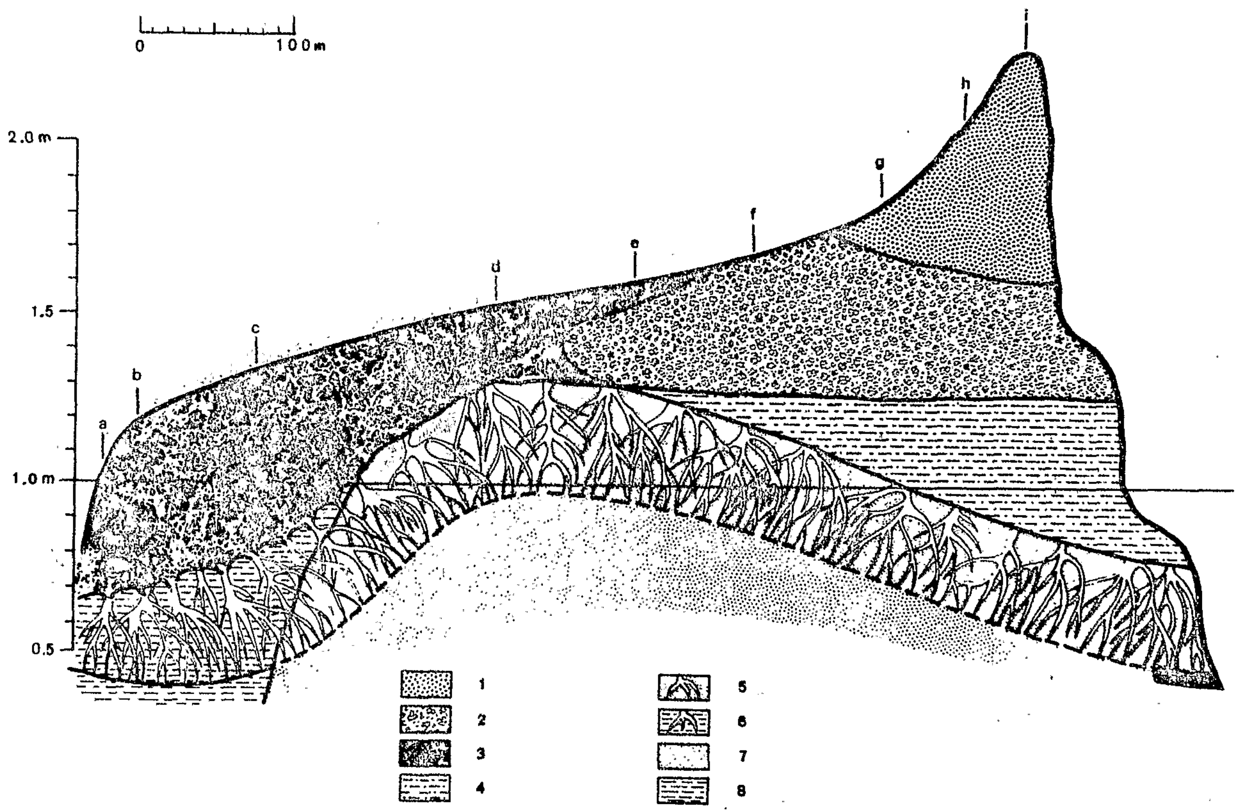

Figure 2. Distribution of sediment, plant debris and roots.

On the hypersaline marsh, sediments have a mineralogical composition which is very similar to the finer fraction.

Total silica content of the sediments of the levee is lower than 50%, which is low for a detrital sand (Fig. 3). It contains less than 20% of the insoluble fraction (Fig. 4) and 20 to 25% of the soluble silica. In the mangrove swamps, superficial sediment of the marginal basin contains much organic matter which gives it a peaty aspect.

The mineral fraction (non-carbonaceous compounds), although sometimes not easily seen, is always present as more than 50% of the dry weight, even in the most peaty soils. A superficial layer of clay, one cm thick, is often present on top of sediments of the inner mangrove swamp.

Total silica contents in all the superficial sediments of the swamps were greater than those on the levee. The insoluble fraction strongly increased in amount in the area of core "D", due to a great abundance of quartz grains (Fig. 4). Most grains are bipyramided automorphous crystals. Many of these crystals are coated with a film of silica (Fig. 5). Approaching the hypersaline marsh, the silica film becomes more constant. Under the surface in the hypersaline marsh, the film is so thick that only the general crystalline shape is reminiscent of a quartz grain (Figs. 5c and d). No faces can

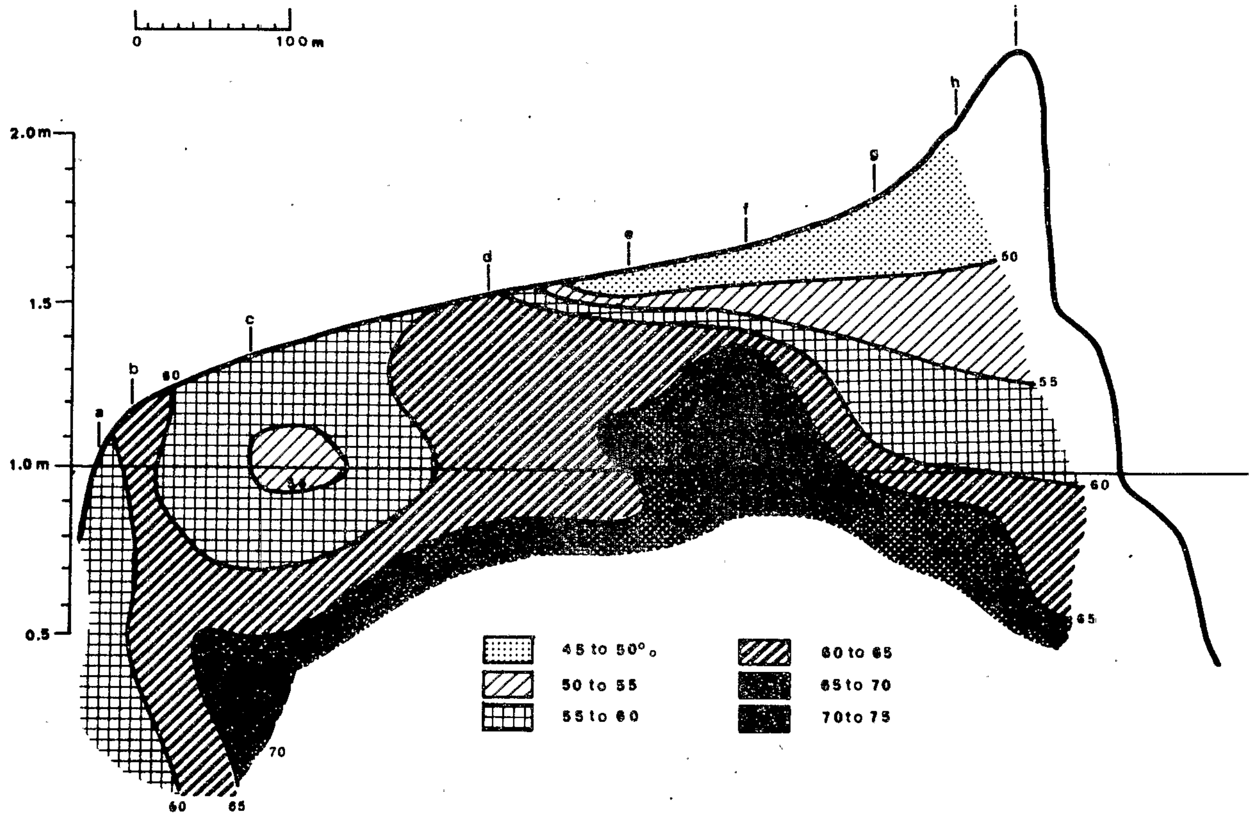

Figure 3. Distribution of total silica in sediments.

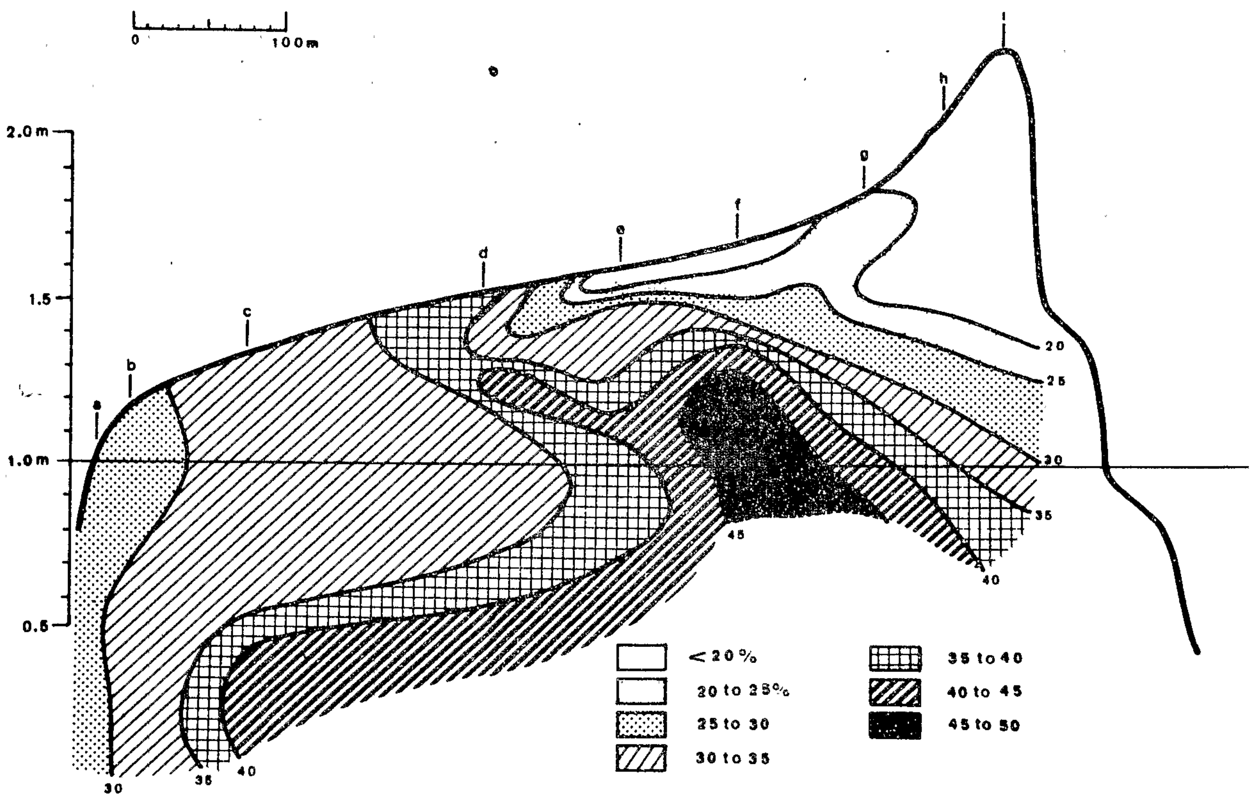

Figure 4. Distribution of the insoluble fraction in sediments.

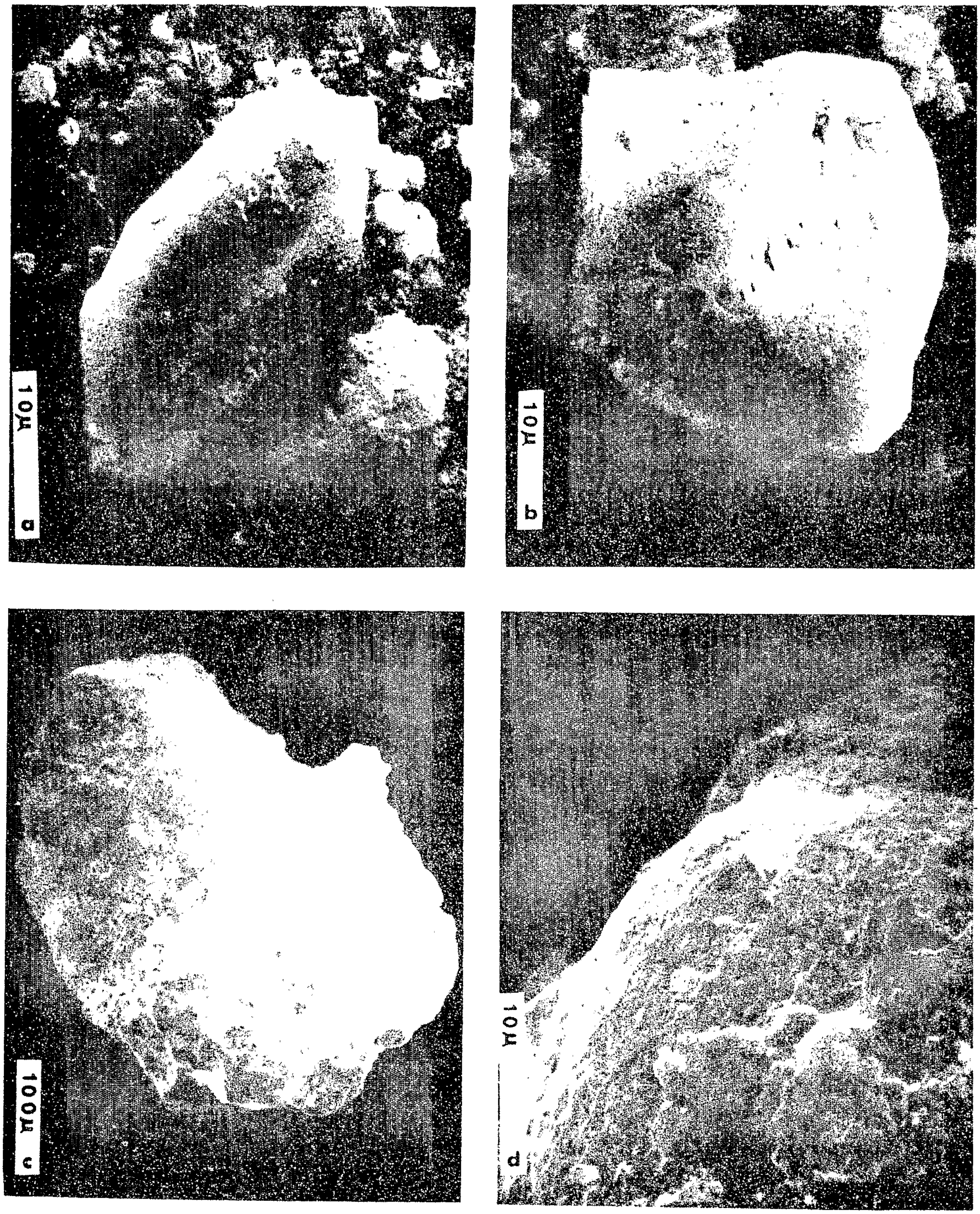

Figure 5. Quartz crystals. a) authigenetic crystal crystal from mangrove swamp ("D" core); b) crystal in silica ball (summits of quartz pyramides at upper left and lower right); c) crystal from hypersaline soil under the marsh, covered with layers of silica; d) upper portion of "c" showing detail of outer deposition of silica.

be seen. Soluble silica content of the sediment (soft mud) is maximal near the Baie Hoff. Sediments there contain many intact (Fig. 6) or fragmented (Fig. 10) diatom frustules. *Diploneis interrupta*, *D. ovalis*, *D. smithii*, *Melosira dubia*, and *Gyrosigma* were identified by Dr. Fusey on Scanning Electron Micrographs.

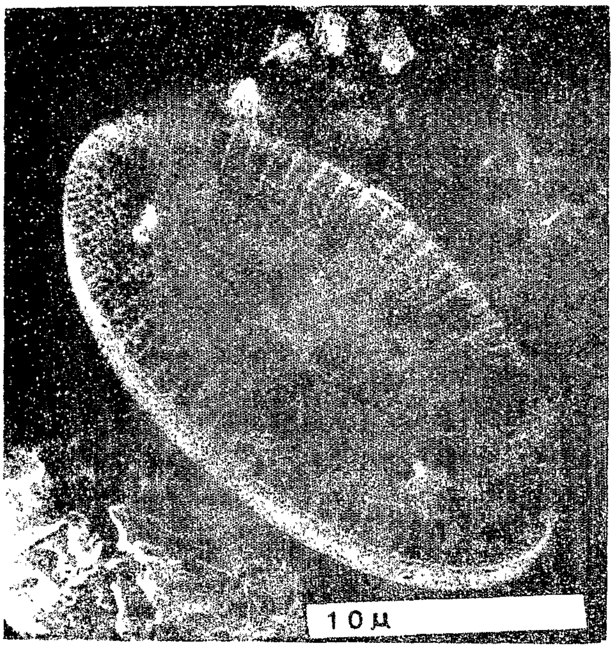

Figure 6. Preserved diatom (*Diploneis ovalis*) from sediment.

To sum up, I observed that newly-laid sediments on the levee are, as a whole, the poorest in silica whatever the grain size. On the contrary, very recent sediments of the mangrove swamp always contained more silica (total silica 60-65%). That content is due in part to deposition of diatom frustules and to a larger insoluble fraction due to quartz formation. Individual quartz crystals show features that strongly suggest growth was underway in the sediment (Fig. 7). Also, individual crystals are very small when the insoluble fraction is not abundant and are large when it is abundant.

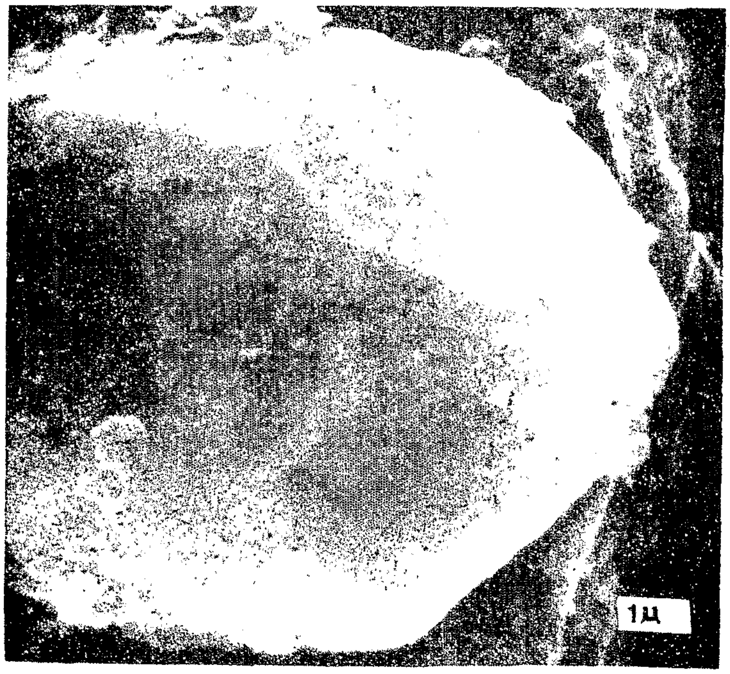

Figure 7. Small authigenetic quartz grain from the outer part of the mangrove swamp.

Deeper sediments of the levee are made of clayey sand and sandy clays. The fine fraction contained very abundant and well-crystallized smectite. Distribution of smectite in the fine fraction appears in Fig. 8 as an elongated isosceles triangle lying under the levee, with the bases parallel to the bluff of the channel bank. In the coarse fraction, polycrystalline quartz grains were present close to the channel. They were formed in situ (Baltzer and Le Ribault 1971).

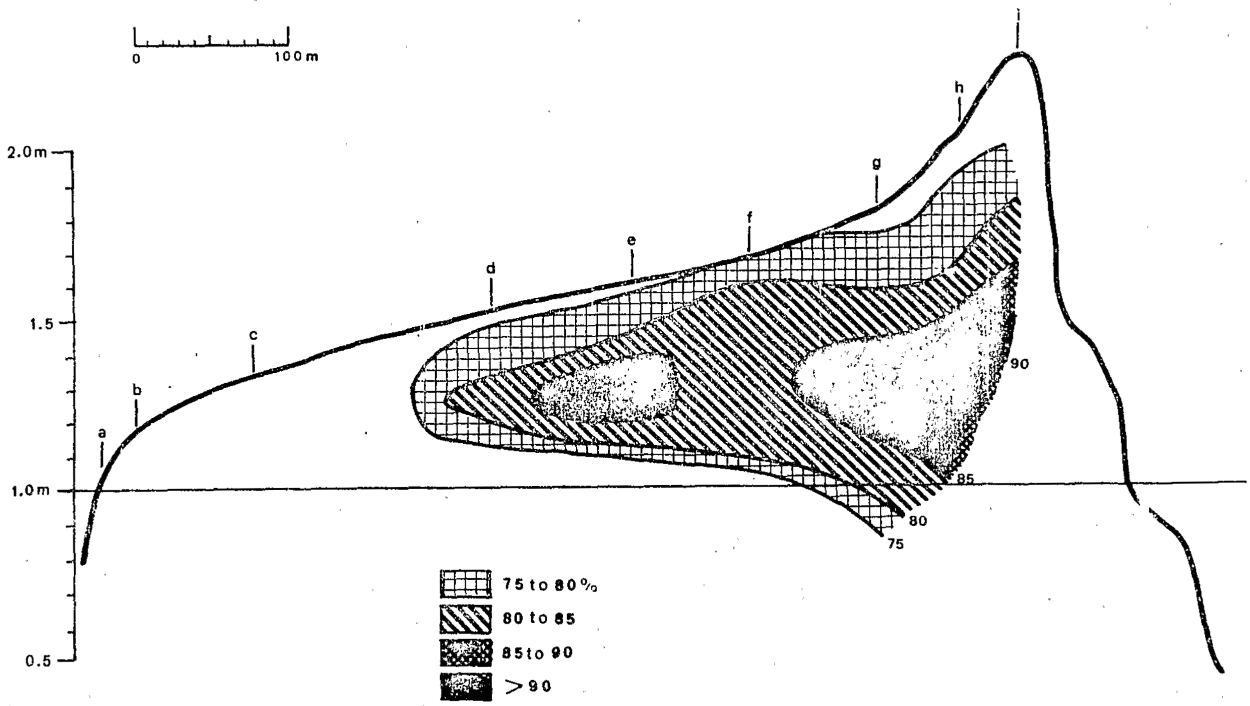

Figure 3. Distribution of smectite in the fine fraction (less than 2 μ) of sediments.

The total silica content increased from surface to bottom everywhere in the sediments of the levee (Fig. 3) and the maximum concentration was found under the hypersaline marsh. Distribution of soluble silica was in triangular isopleth patterns reminiscent of the smectite triangle. It is very likely that smectite is the mineral that contained most of the soluble silica in that area.

Isopleths of distribution of the insoluble fraction are generally parallel to soluble silica isopleths (Figs. 4 and 9), but are offset with respect to them. Isopleths of the insoluble fraction are deeper under the levee and further inside the mangrove (apart from the hypersaline marsh) than are isopleths of soluble silica.

In the mangrove swamp, the sediments under the surface were mainly a felt of rootlets and decaying vegetal matter with fine mineral particles. In the middle of the mangrove, intact diatom frustules were scarce but remnants were numerous (Fig. 10). Near Baie Hoff, diatoms were present in great numbers, either complete or in pieces. The content of total silica (Fig. 3) increased with depth across the transect. At intermediate depth (about 0.50 m) the content of total silica increased gradually from the bay toward the hypersaline marsh, except for an area in the middle of the mangrove swamp (under coring "C") where total silica content was low, almost as low as on the levee. The insoluble fraction content increased between Baie Hoff and the hypersaline marsh (Fig. 4). The soluble silica (Fig. 9), although it was higher everywhere in mangrove soils than on the levee, was remarkably low in the middle of the mangrove swamp (lower part of coring "C"). As we know that diatom frustules were dissolving, it is very likely that their dissolution was responsible for the observed decrease in the soluble silica content of the sediment. A comparison of distribution of diatom frustules with that of soluble silica suggests that incorporation of frustules added a significant amount of soluble silica to the mangrove sediments. It also suggests that part of this soluble silica dissolved later. Moreover, enrichment of the sediments by quartz and smectite was observed in the lower part of the levee, under the hypersaline marsh, and in the part of mangrove swamp close to it. This suggests that silica released by solution of diatom frustules is used in neoformation of quartz and smectite.

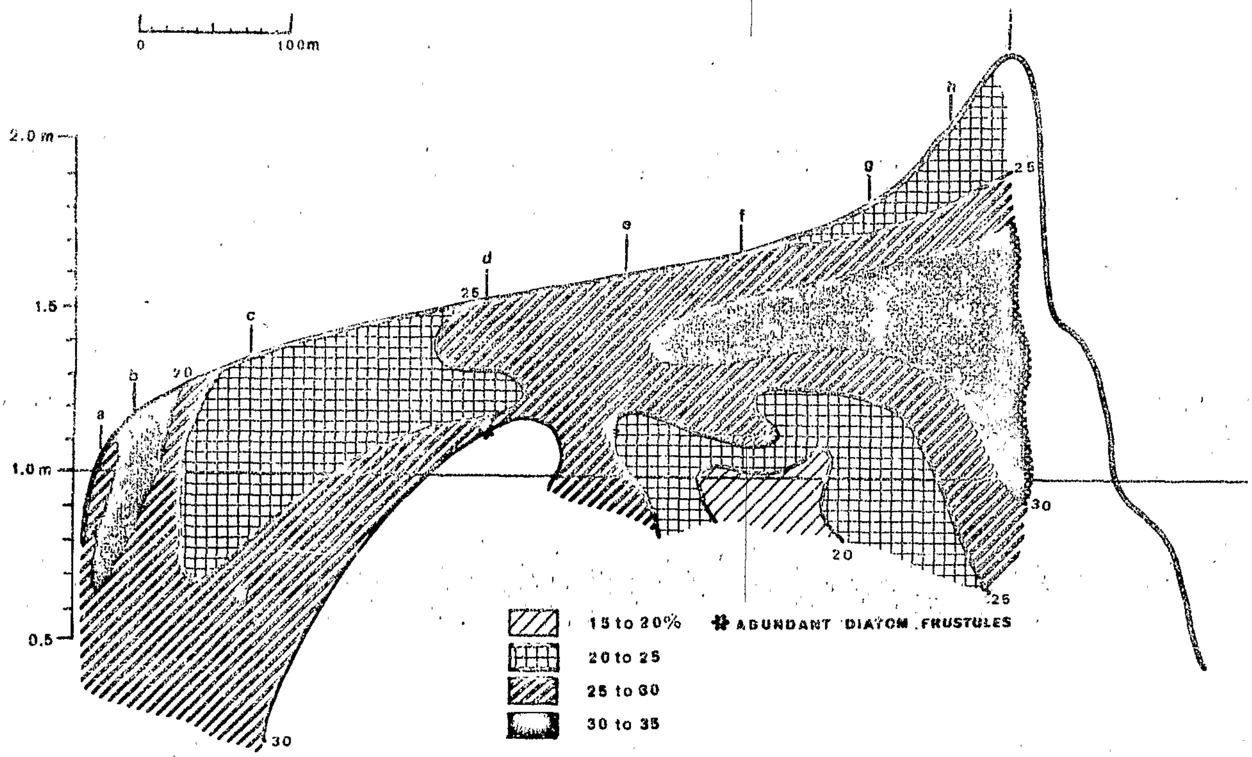

Figure 9. Distribution of soluble silica in sediments.

To test this hypothesis, we must consider: (1) surface water movements above the levee and the marginal basis, (2) pore water movements in the sediments, and (3) geochemistry of pore water in relation with geochemistry of sediments.

SURFACE WATER MOVEMENTS
(Figure 11)

Mangrove swamp soil is permanently wet or at least damp because of tidal penetration. The lower part of swamp, near Baie Hoff, was submerged every day but higher parts were progressively less covered with tidal seawater. The *Salicornia* and bare hypersaline march received only exceptionally high tides. The whole of the swamp and marsh was subjected to occasional rainfall. Orographic control of rainfall reduced the frequency of significant showers in low-lying areas. Nevertheless, during rainy seasons, a fair amount of fresh water reached the swamp.

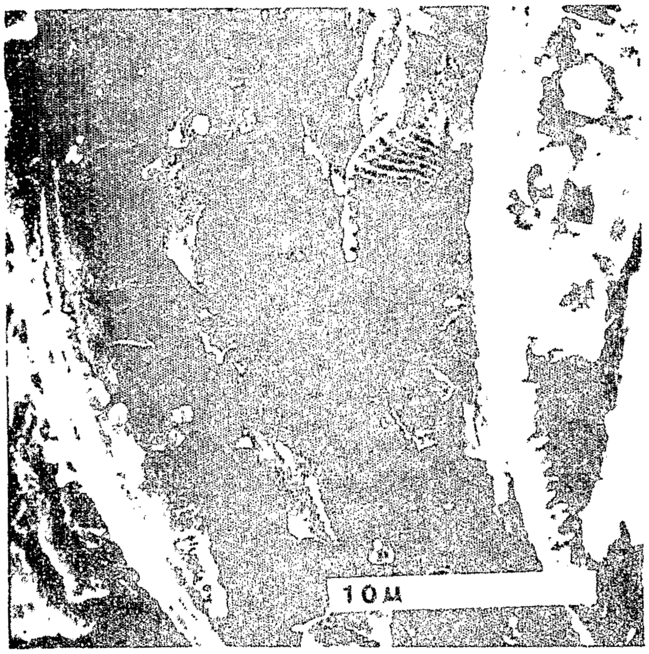

Figure 10. Fragments of diatoms in sediment of the mangrove swamp.

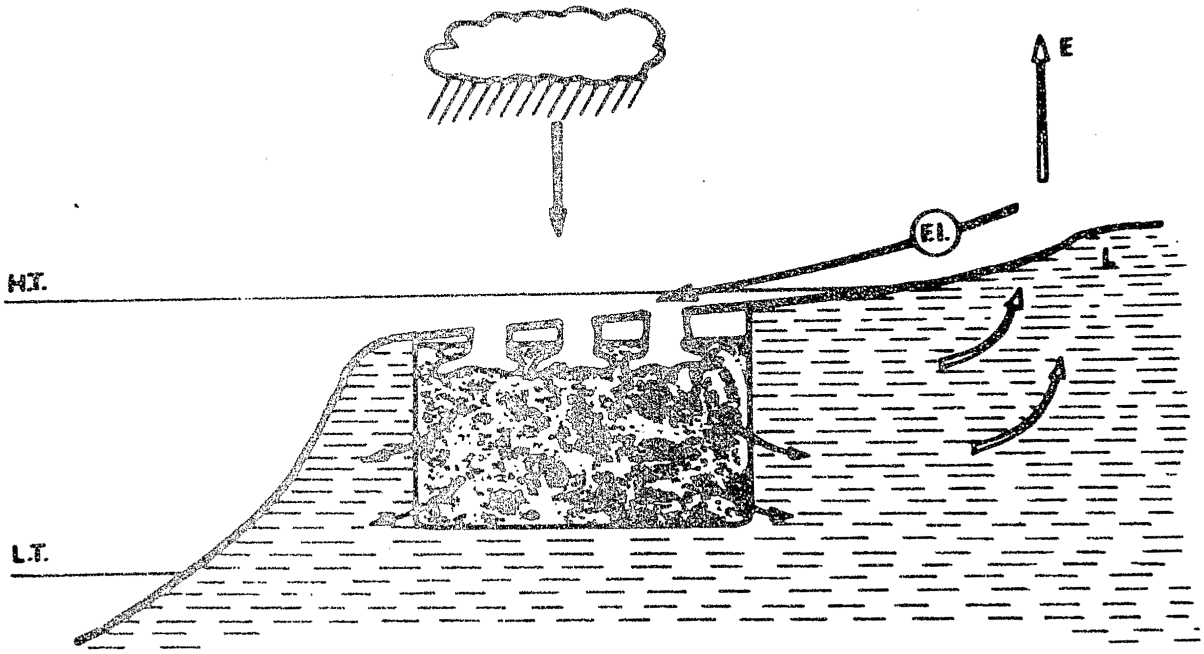

Figure 11. Sketch of surface and soil water movements by gravity (black arrows) and other processes (white arrows).

PORE WATER MOVEMENTS

Infiltration of sediment by superficial water and movements of pore water are controlled by the permeability of sediments. Sands on the levee were highly permeable, but were intermingled with silt and clay which become predominant near the hypersaline marsh. Also, the smectite triangle made the lower part of the levee impermeable, making the levee an impermeable body of sediments. Conversely, the small pores and canals between very small grains enhanced the capillary forces that moved water through clay layers.

Under the levee were black sands which contained remnants of mangrove roots (Fig. 2). They had a good permeability.

In the middle of the mangrove swamps the felt-like mangrove peat, which was penetrated at the upper part by innumerable crab holes, was highly permeable. The layer of clay on top of it contained many crab tunnels and was not efficient as an impervious screen. Toward the Baie Hoff, the soft mud was much less permeable than peaty soil. Nevertheless, at low tide, a significant amount of the water in the permeable peaty soil was able to filtrate toward Baie Hoff through the less permeable soft mud. It may also have filtrated under the levee through the black sands toward Dumbea Channel. At high tide, sea water from Baie Hoff reached the central mangrove and added to the water table (Fig. 11).

Distribution of chloride ions (Fig. 1) in the pore water was used to learn the main controls of movement of pore water through sediments. As a whole, the soils contained salty pore water. Near Baie Hoff and the Dumbea River channel, chlorinity was very nearly that of sea water (approximately 20 ppt Cl^-). In the areas rarely covered by sea water at high tide, evaporation permanently dried the soil surface (except during occasional rains and river floods). It concentrated the ground water up to 2.5 times that of seawater. Concentration in ground water was also evident in the part of mangrove swamps lying close to the hypersaline marsh. The content of Cl^- in the hypersaline area was higher at a few dm depth than it was near the surface. This was due to rapid decrease of the chloride ion content near the surface when rain or flood (river or tidal) covered the hypersaline marsh. The decrease in chloride content proceeded faster than did the increase in water content (Baltzer 1970b, Smith 1972, Vieillefon 1974). Sometimes salinity increased at the surface of the soil.

In the middle of the mangrove swamps, distribution of chloride in pore water indicated a lens of brackish water inside the felt-like mangrove peat and the lagoon clays under it (Fig. 1). The lens was similar to the Ghyben Herzberg lens of fresh water along sandy shores. It was limited to the central mangrove soil, i.e., to a soil lying under an intertidal area. The lowest chloride ion measurement was approximately 11 ppt in this transect, whereas it was 8 ppt in the transect where we observed the minimal value. The lenses of brackish water are certainly not transient features because they were found in all of the 6 transects through the Dumbea Delta mangroves. Also, distribution of *Bruguiera eriopetala* matched the areas where the chloride content of pore water was below 20 ppt. As *B. eriopetala* is known to prefer dilute seawater, this is evidence that the brackish lens is rather permanent.

The brackish water lens was insulated between sea water of Baie Hoff and the hypersaline marsh and subterranean water movement cannot explain its low salinity. Therefore, it is most likely that rains and serious river floods, when they occurred during low tides, refilled the reservoir constituted by the permeable peaty soil surrounded by much less permeable soils (Fig. 1). In this way, the water table remained somewhat higher at low tide inside the peaty soil because brackish water, which is lighter, rested on heavier salt water. That difference in height prevented replacement of the brackish water lens by salt water at high tide. Distribution of chlorinity across our transect suggests a pattern of movement of pore water through the sediments. There were (1) an area where pore water concentrated due to evaporation in the hypersaline marsh and (2) an area where seawater was diluted by rains and fresh water floods in the mangrove swamp. The brackish water lens was necessarily a high point on the water table in the swamp, at least during low tide. From that high point water permeated slowly toward Baie Hoff on one side and the hypersaline marsh on the other. At low tide, water from the brackish lens proceeded *per descensum* and *per lateralum*.

When dry weather prevailed, the movement was certainly accelerated by evaporation in the hypersaline marsh. Replacement of evaporated water in the area of core "F" induced two converging pore water flows which met under "F." One flow came from the brackish lens, the other from the Dumbea channel. Both currents were likely to be more effective in the black sand layer.

Electrochemical measurements provided us a means to check if that pattern of water movement occurred. Where organic matter is abundant, as in waterlogged soils, bacterial activity causes reducing conditions (Baas Becking et al. 1960). Distribution of Eh in the cross section (Fig. 12) demonstrates that mangrove soils, as a whole, are strongly reducing. The cross section also demonstrates that every possible oxidation process is very effective in increasing the Eh inside the sediment, even that in contact with much organic matter. Among these processes is the percolation of water which was previously in contact with the atmosphere through permeable sediments. For instance, contact of the water table of the mangrove with open seawater sharply reversed the reducing conditions near Baie Hoff. Similarly, percolation of water from the Dumbea River Channel toward the hypersaline marsh through the black sands resulted in higher Eh figures than would be expected based on organic matter content.

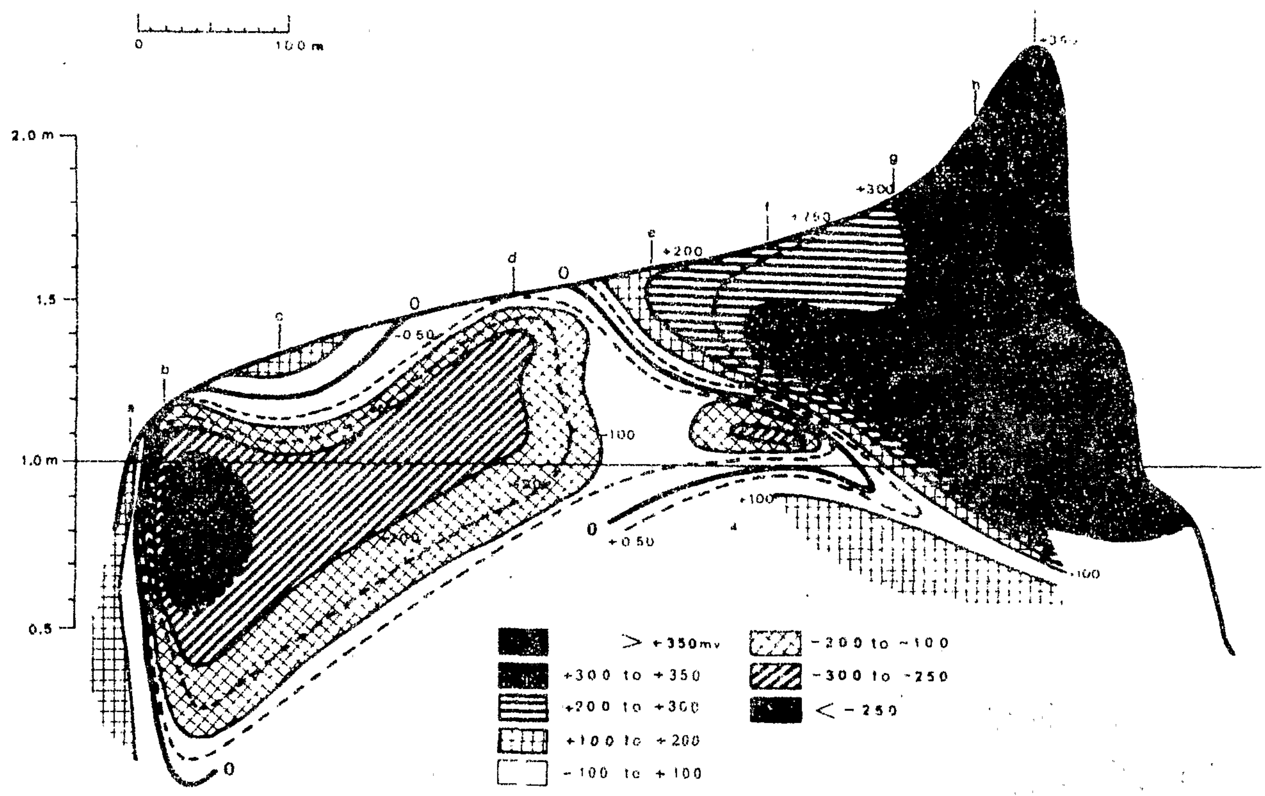

Figure 12. In situ measurements of Eh of sediments.

In the middle of the mangrove swamp, in the area where we showed that fresh water occasionally filtrated to feed the water table, we observed that Eh was significantly higher in the neighboring parts of the swamp. This supports the idea that oxidized water permeated the soil of the swamp in this area.

In areas where circulation of pore water is impeded, reducing conditions are enhanced and induce very low Eh values in sediments with much organic matter. For instance, the brackish water lens permeated very slowly (through soft mud) toward Baie Hoff. This caused the lowest Eh found on the transect. Also, under the hypersaline marsh there was a point of convergence of pore water from the swamp on one hand and from the channel on the other hand. In this area, water probably stayed a long time before it eventually evaporated causing low Eh.

Sediments containing little organic matter, in the area of the levee and marshes, were oxidizing. The salt marsh, being covered periodically by tides and containing slightly more organic matter near the surface, had lower Eh's at the surface than at depth. The oxidizing conditions were obviously transmitted through the levee and salt marsh from the bluff of the bank on the river channel.

The distribution of Eh is in perfect agreement with the pore water movement pattern.

Distribution of pH (Fig. 13) obeys the same general rules as does Eh distribution. The waterlogged soils rich in organic matter of the mangrove were typically slightly acid (6.8). Dry areas containing little organic matter (levee and salt marsh) were typically higher than 7 (from 7.0 to 8.2) and were similar to both seawater and Dumbea River water. The higher figures were found in the most hypersaline conditions. A few other processes made pH distribution more complex. Shell debris reaching equilibrium with pore water gives high local pH measurements and marine water diffusion has a similar effect. Oxidation of sulfides of mangrove soils by percolating water lowers pH values. The low pH area (6.4) of the central mangrove in the area of the brackish water lens is a new confirmation that oxidizing water contributed to the lens in this region. Another interesting area was the frontier between the levee body of oxidized sediments and the old mangrove soil of the black sand layer. There, low (6.4) pH values marked the limit between oxidizing and reducing environments.

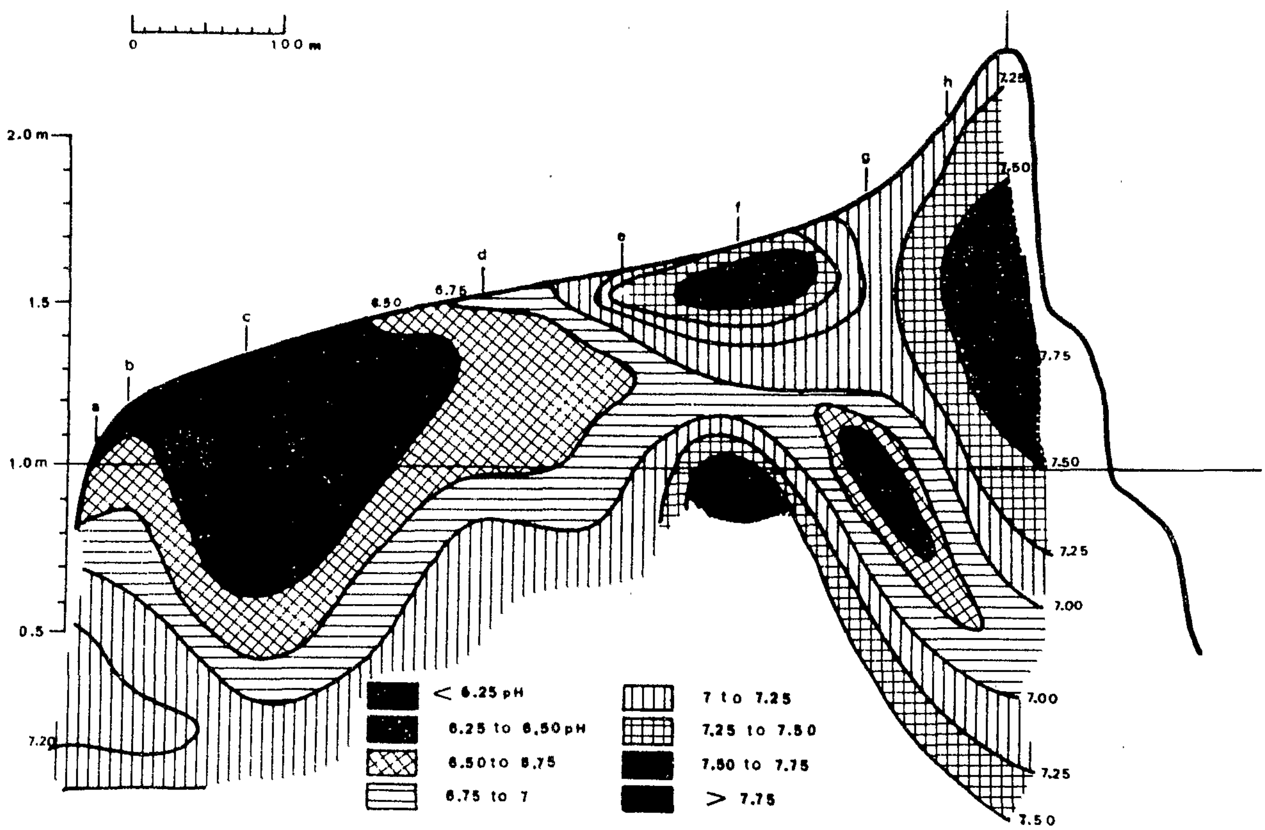

Figure 13. In situ measurements of pH in sediments.

Permeability of sediments, chloride ion distribution, and electrochemical conditions are all in good agreement with the scheme by which we propose to describe pore water movement. With the knowledge of that movement, we can now deal with the silica content of pore water.

THE SILICA CONTENT OF PORE WATER

The isopleths of silica content of pore water (Fig. 14) match the pattern of chloride ion distribution in the area of the brackish water lens, but the gradients are opposite: the silica content of pore water was maximal when the chloride content was minimal. According to what we know about pore water movement, the high silica content of the brackish water lens necessarily resulted from solution of a locally available source. As the maximal value of silica in pore water was found in approximate coincidence with the area where diatom frustules were subjected solution, it is very likely that they were the source of the large amount of silica in the brackish water lens.

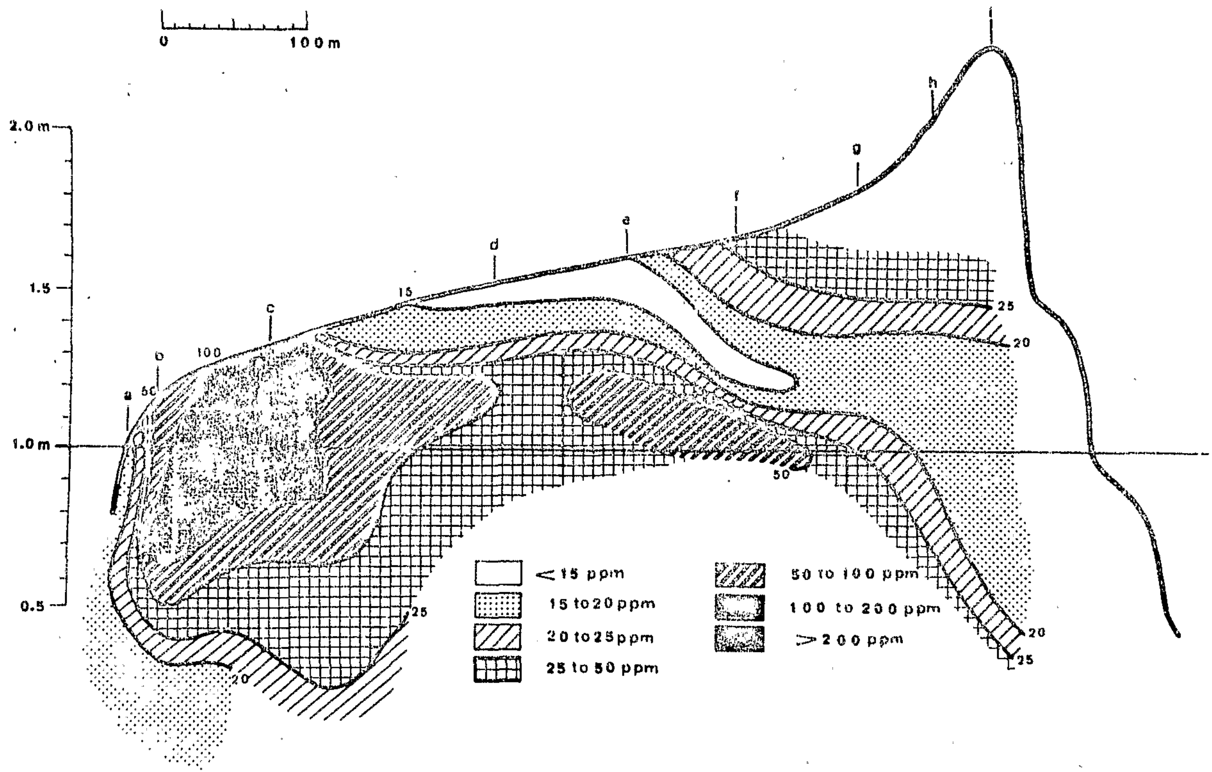

Figure 14. Distribution of silica in pore water of sediments.

Lewin (1960) studied solution of diatom frustules under carefully controlled conditions. He showed that solution proceeds very slowly when the alga is alive, faster when it is killed, and much faster when the frustule is cleaned in nitric acid or when the experiment is carried out in the presence of EDTA. He showed that Al and Fe cations considerably reduced solution of frustules except when EDTA was present. The chelating agent favored solution of frustules by inhibiting reaction of cation with the amorphous silica and production of insoluble compounds.

In mangrove sediments, highly complexing organic acids such as humic acids are present in great abundance. It is likely that they act as chelators in mangrove swamps.

Lewin (1960) also showed that older frustules were less soluble than younger and that in a living population of diatoms, some individuals could inherit fairly old half-frustules. This could explain why the lowest content of soluble silica sediment was slightly offset with respect to the highest content of silica in pore water. When frustules are leached by water a time comes when only the less soluble are left and the concentration of silica in water is reduced.

The highest content of silica in solution in pore water of mangrove sediments greatly exceeded those usually recognized for saturation of water with amorphous silica. We found more than 200 ppm, whereas according to Morey et al. (1962) 115 ppm is saturating for water at 25 C. It is difficult to imagine evaporative concentration of brackish water resulting in such a high concentration. Therefore, it is more likely that organic matter enhanced the solubility of silica of the frustules by adding oligosilicic acid to the orthosilicic acid in the water.

In such areas where silica concentration was higher than the saturation value of amorphous silica, loss might be due to autocondensation of silica (Baumann, quoted by Pascal 1965). Increase in Cl^- concentration in solution accelerates formation of gels by autocondensation. Increase of pH has the same effect and also enhances the effect of Cl^-. Br^- is even more effective, but is present in much smaller amounts. Chloride distribution in pore water and pH distribution are in good agreement with the requirements for an increased autocondensation process. However, the very complex ionic composition of pore water and the great amount of various organic compounds in it make this highly speculative.

From the central part of the lens of brackish water, where the silica content is maximal, we observed (Fig. 14) that silica content continuously decreased during the percolation of the water table toward the sea or toward the hypersaline marsh. When we reach values below saturation with respect to amorphous silica, the process of autocondensation of gels cannot operate and we have to conclude that a process of deposition of silica probably operated everywhere in the mangrove swamp. Small quartz crystals between mangrove rootlets are very likely to be neogenetic and would have that origin.

The area where the silica content of pore water was minimal (13 ppm) was a belt which lay where the maximum "soluble silica" content in sediment overlapped the maximum content of the "insoluble fraction." Therefore, it is probable that soluble and insoluble fractions were increasing due to addition from incoming water. Neoformation of quartz in that environment is puzzling. Quartz crystals formed in the environment where much silica in solution was present were clean, whereas quartz crystals formed in the area where there was only 13 ppm in solution were coated with layers of "amorphous silica." This is not in agreement with laboratory experiments and probably resulted from secondary effects of organic matter in the swamp and of ion hydroxides in the marsh.

CONCLUSION

We knew that the water of the Dumbea River carried enough silica to produce siliceous minerals under the banks of the channel (Baltzer 1971, Baltzer and Le Ribault 1971). We found here that mangrove swamp is probably even more effectige in accumulating silica from the fluvial discharge. The estuarine and deltaic environments under tropical conditions favor active growth of diatoms in mangrove swamps because silica, nitrates, phosphates, and iron are abundant (Patrick 1967). Moreover, diatom growth is likely to be stimulated by humic acids in mangrove swamps (Prakash and Rashid 1969).

Silica enrichment of swamp sediments is not based only on availability of diatom frustules. The special hydrogeological conditions prevailing under dry tropical climate induce movement of pore water through sediments of the proper composition. Diatom frustules dissolve in the middle of the mangrove swamp, perhaps generation after generation, because the amount of silica in the enriched sediments exceeds the amount in living diatom frustules.

The silica-rich brackish water of the central swamp permeated slowly toward more saline waters. In the meanwhile, its silica content gradually decreased to a minimum of approximately 15 ppm. This could be due to combination with cations at the bottom of recent sediments of the levee and salt marsh adjacent to the swamp. It is likely that the contents of soluble silica and smectite (nontronite) in the sediment are a result of that mechanism. In the sediments below the levee or the salt marsh, or closer to the central part of the mangrove swamp, mineral particles were not abundant and iron was trapped in pyrite. There, no nontronite could form, but quartz crystals did.

Thus, the silica of the frustules, which was a very soluble form in a very permeable environment, recrystallized as much less soluble forms and, under the marsh, in a less permeable environment.

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INTERNATIONAL SYMPOSIUM ON BIOLOGY
AND MANAGEMENT OF MANGROVES

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1975