

## STRUCTURE AND GENERAL CHEMISTRY OF TABLE MOUNTAIN SANTA BARBARA PHOSPHATES, CURAÇAO, NETHERLANDS ANTILLES<sup>1</sup>

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### ABSTRACT

Stienstra, P. 1983 Structure and general chemistry of Table Mountain Santa Barbara phosphates, Curaçao, Netherlands Antilles — *Geol. Mijnbouw* 62: 275-284.

Rock-phosphates from Table Mountain Santa Barbara (Curaçao, Leeward Netherlands Antilles), were investigated in the field and by evaluating data from cores of 203 drill holes. The distribution of phosphate- and fluorine-contents and recovery were studied in detail. Arrangement of several zones of maximum mineralization suggests that phosphatization, caused by the influx of a guano-derived phosphate-brine, was mainly governed by (a) the primary stratification and other primary petrological trends, and (b) the hydro-geochemical environment as defined by a phreatic fresh water-salt water mixing zone. A direct relationship is suggested between the two main zones of mineralization and two specific periods of relative stable sea level during the Pleistocene.

### INTRODUCTORY REMARKS

#### *General setting*

Curaçao, the largest of the three Leeward Islands of the Netherlands Antilles (Fig. 1), consists of a core of Cretaceous and early Tertiary igneous and sedimentary rocks (BEETS, 1972; BEETS & MACGILLAVRY, 1977). These rocks are unconformably overlain by Mio-Pliocene limestones (Seroe Domi Formation), which are regarded to be accumulations of debris on the foreslope of an algal-coralline reef (DE BUISSONJÉ, 1974). Subsequent spasmodic sea level changes produced erosional terraces on the Neogene limestones along the coast, and denudational terraces in the centre of the island (Fig. 2) (HERWEIJER & FOCKE, 1978).

Table Mountain Santa Barbara (Fig. 3A) is the highest elevation of Neogene limestones (+ 196 m) in the southeastern part of Curaçao. It consists of a 30 to 50 metres thick succession of Seroe Domi limestones, resting on basalts of the Curaçao Lava Formation (BEETS, 1972). It is bordered to the north by a steep escarpment with a height of up to 50 metres and to the south by six stepwise arranged terraces. Apart from the terraces defined by DE BUISSONJÉ (1974) — Highest Terrace, elevation 90-110 m; Higher Terrace, el. 50-80 m; Middle Terrace, el. 15-45 m; and Lower Terrace, el. 0-10 m — the

Toplevel of the Mountain itself can be regarded as an erosive terrace (elevation 150-196 m). An extra escarpment (altitude 140 to 160 m) occurs along parts of the southern rim of the Toplevel. At present much of the original morphology of Table Mountain is radically changed due to mining of phosphate during the last century.

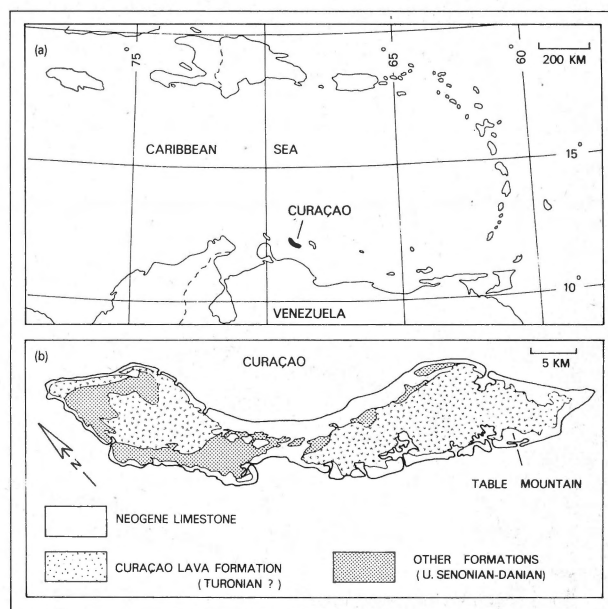


Fig. 1 Location of Curaçao in the southern Caribbean Sea, and general geological map of the island (after Beets, 1972).

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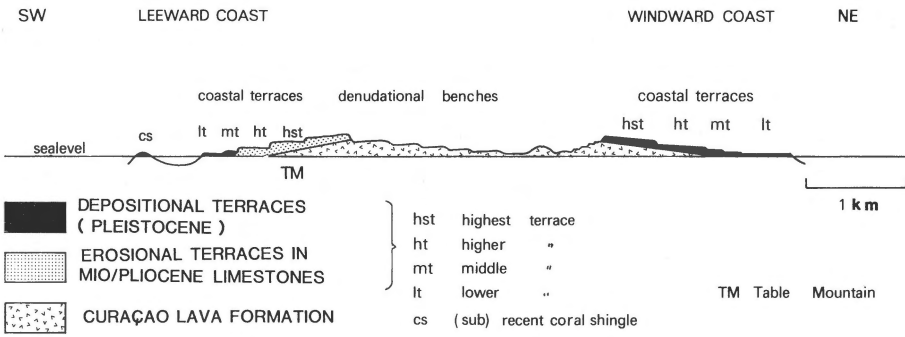


Fig. 2  
Schematic section across south-east Curaçao (after Herweijer & Focke, 1978)

*Earlier investigations*

Since the discovery in 1874 of extensive phosphate deposits on Table Mountain and the start of production in 1875 only little information on the phosphates has been published. Early

information is scanty and often second hand (GILBERT, 1877 in: MEYN, 1879; MARTIN, 1888; DUYPJES, 1910; GRUTTERINK, 1912). At first so-called 'rubble phosphates', usually present in 2-3 m deep karstholes on the Highest Terrace, were mined (KEILHACK, 1926; GRUTTERINK, 1928 in: HUTCHINSON, 1950). Later

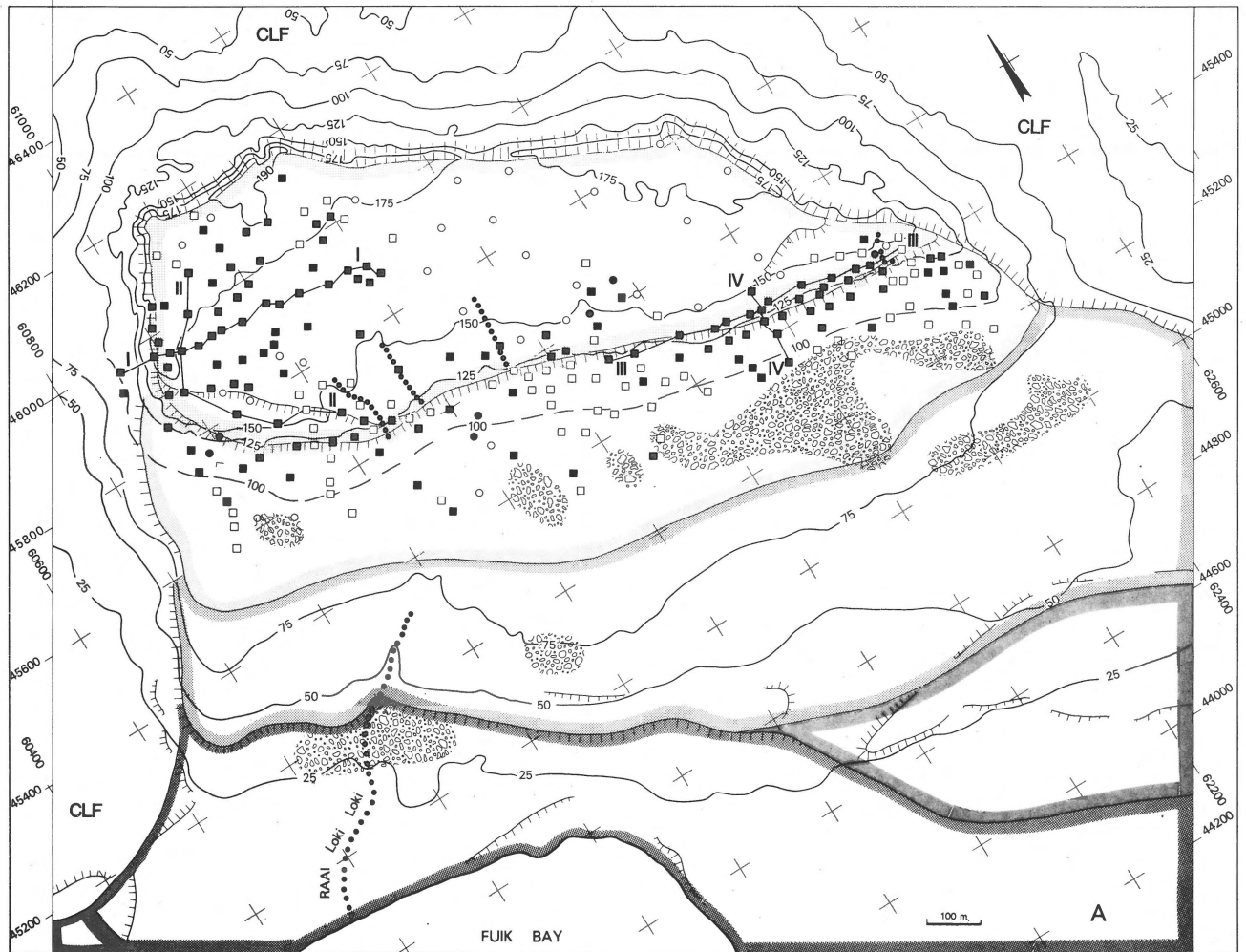


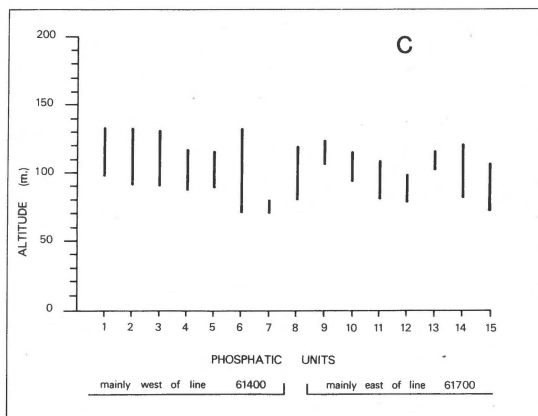
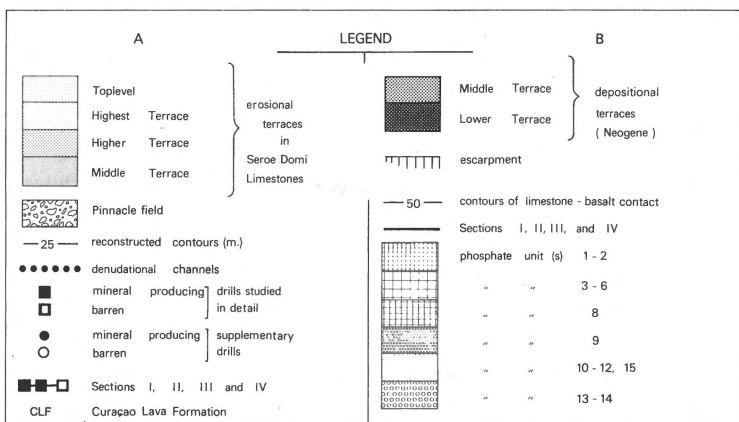
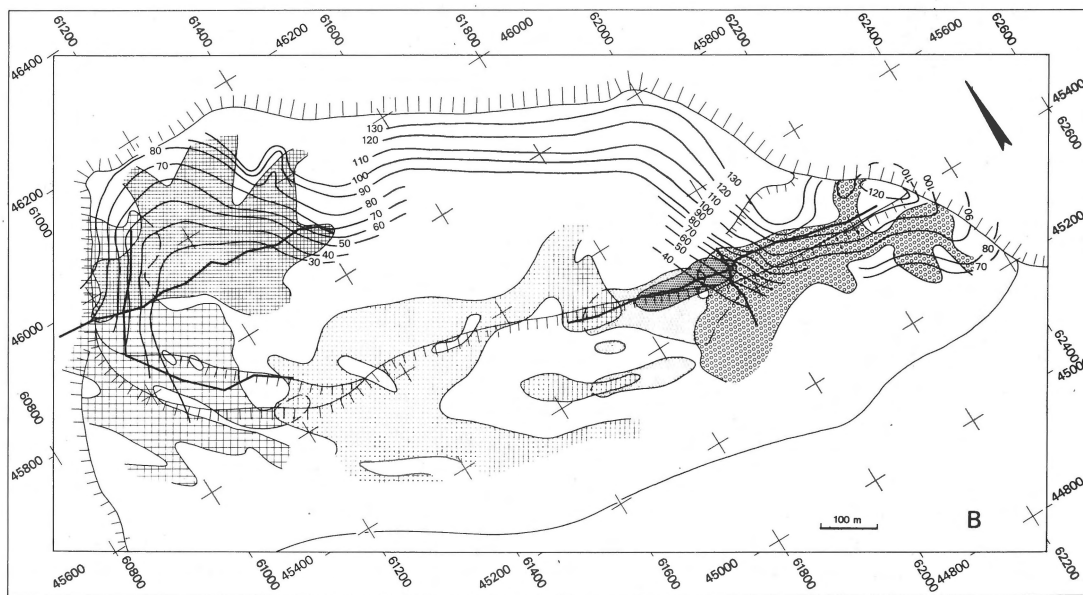
Fig. 3 (above and facing page)  
A; general geomorphology of Table Mountain Santa Barbara, and locations of investigated drill holes and sections. B; horizontal distribution of phosphate-units, and contours of the Seroe Domi Limestone Formation – Curaçao Lava Formation contact plane. C; vertical range of the phosphate units. (Area B is only part of area A).

exploitation expanded to 'rubble phosphates' at other locations. Similar phosphates were described from many oceanic islands (e.g. GULBRANDSEN, 1975; BRAITHWAITE, 1980) but also from continental areas (e.g. BATES, 1960; p. 183-186). By 1960 the depletion of the 'rubble phosphates' necessitated the exploration for a possible extension of the phosphate horizon in a northern direction (DE WIJS, 1962). Many diamond drill holes were lowered from the Toplevel of Table Mountain and confirmed such an extension. Apart from the phosphate contents, the fluorine of the rocks sampled was monitored continuously for economic reasons. Low fluorine phosphate receives a substantial premium in price above normal phosphate products because fluorine in certain uses is deleterious. Especially in cattle- and poultry-feed only low fluorine is permitted. DE WIJS (1963, 1964, 1966) found a rock phosphate horizon, sandwiched between barren limestones. He thought mineralization was caused mainly by the inflow of guano-derived phosphate brine along north dipping primary limestone stratification, a process partly directed by tectonic

controls, like fissures. Geomorphologic controls, like the drainage pattern, were thought to have been of secondary importance only. Following these data and theories new quarrying started, especially in the western part of Table Mountain. As late as 1976 an extensive sediment-petrological study was carried out (TEN HAVE & HEIJNEN, 1978; TEN HAVE ET AL., 1982). In the meantime the presence of a sandwiched phosphatized rock body was confirmed by mining. Its distribution, however, characterized by lenses of both differing phosphatization and porosity grades, was found to be more complex than expected.

*Purpose of this study*

Many questions on the shape and extension of the phosphatized body remained open. This paper provides new and detailed information on the distribution of mineralization within this body, and on the low grade mineralization of the surrounding barren Seroe Domi limestones. The relations



between phosphatization and primary stratification, tectonic control, geomorphology etc. are described in detail. Finally a genetic model is proposed, providing ample explanation for the features described.

## METHODS

### *Topographic maps*

To study the original and present morphology of Table Mountain, the following material was used: aerial photographs scale 1: 10 000; topographic maps of Curaçao (1963) scale 1: 25 000, surveyed by the Cadastral Department of the Netherlands Antilles and KLM-Aerocarto N.V. in 1960-1961; new topographic maps of Curaçao, scale 1:10 000, by the same surveyers, not yet published officially; detailed maps, scale 1: 1 000, surveyed by the Cadastral Department of the Netherlands Antilles, and several maps (scale 1:1000 and 1:2000) made by or by order of the N.V. Mijnsmaatschappij Curaçao. For tracing the boundaries of the terraces the Geological Map of Curaçao (Younger Cenozoic), scale 1:50 000 of DE BUISSONJÉ (1974) was used.

### *Drilling survey*

Until 1975 the mining company lowered about 600 diamond drill holes into the Seroe Domi limestones from the Toplevel and the Highest Terrace. Data from all of these drill holes were used to reconstruct (a) the original morphology of Table Mountain and (b) the contact between the Seroe Domi Limestones and the underlying basalts of the Curaçao Lava Formation. Of these, 203 drilling logs provided information on amount and type of phosphatic material and were studied in detail (Fig. 3A). Drilling data were mathematically processed to produce continuous logs, containing information on recovery, amount of clean limestone (defined to contain less than 4.59%  $P_2O_5$ ), amount and grade of phosphatic material and fluorine contents. Trends in these logs could be correlated three-dimensionally, defining 15 phosphate units within the phosphatized horizon. Out of four of these units the mean BPL-contents (= Bone Phosphate of Lime, or  $Ca_3(PO_4)_2$ -contents) and the mean fluorine contents per drilling site were statistically compared, usually by Wilcoxon's Test and variance analyses, to establish horizontal and vertical variations. Correlations between mean BPL, mean fluorine, location and altitude above sea level were tested.

Similarly barren limestones from different locations and altitudes were compared.

## RESULTS

### *Geomorphology*

Table Mountain (Fig. 3A) is bordered to the north by an escarpment, at least 50 metres high, and to the south by

terraces. It has a shallow concave-up Toplevel, with a generally southeastward dipping trend (5-10°). Phosphatic pinnacle fields, containing 'rubble phosphate', occur all over the southern hillside.

The terraces are cut by denudation channels, in the antillean language called 'rooien'. The most distinct one is the Rooi Loki Loki. Nowadays the larger part of this Rooi is either covered by mining debris or has been mined out. Only the lower part close to Fuik Bay still exists. Some shallow tributary channels to this 'Rooi' could be recognized on aerial photographs. These minor 'rooien' follow the gradient of the Toplevel.

### *Limestone baselevel*

Unfortunately only the northern part of the Seroe Domi Limestone-Curaçao Lava Formation contact plain could be reconstructed (Fig. 3B). Most southern drill holes did not reach this plane. Contours suggest a concave-up surface. Undulations in the overall rather regular contour pattern may indicate erosional depressions formed on the basalt prior to infill by reef debris. Similar erosional features, possibly caused by - ? turbidite like - channelized flow have been described in Recent and fossil reef environments (ORME, 1977; SANTISTEBAN, 1980).

### *Seroe Domi Limestones*

Although this paper is not intended as a detailed description of the sedimentary petrology or other characteristics of these limestones some remarks are essential (see for comprehensive information DE BUISSONJÉ, 1974).

As to the stratification of the Seroe Domi Limestones on Table Mountain opinions have been contradictory. DE WIJS (1962) mentioned a northern dip of 10 to 30°. DE BUISSONJÉ (1974) reported the strata to dip more or less to the south. TEN HAVE & HEIJNEN (1978) did not present more than two dubious (cit.) bedding measurements. The present author agrees that, even in fresh quarry faces, a primary stratification can hardly be distinguished. At a few locations, all west of line 61800 (Fig. 3), only indistinct planes (like ones separating fossil-poor from fossil-rich zones) could be measured. The dips are plotted in Fig. 4a as solid triangles. Usually the bedding planes could not be measured directly, but only the apparent dip of bedding features in the steep quarry faces. These 'lineation' measurements are indicated in Fig. 4a by open triangles. A conspicuous feature is colour banding. Especially in the faces of the western quarries, distinct bands of whitish, pink and yellowish limestones alternate. In the central mining area bright pink banks can be seen, with abundant cream coloured coral fragments. Although diagenesis may have influenced limestone colours, DE WIJS (1963) found that the colour of red-pink limestones was caused by the presence of only 0.5% insoluble residue, mainly organic matter. As this can be regarded to be a primary petrological feature, colour bedding

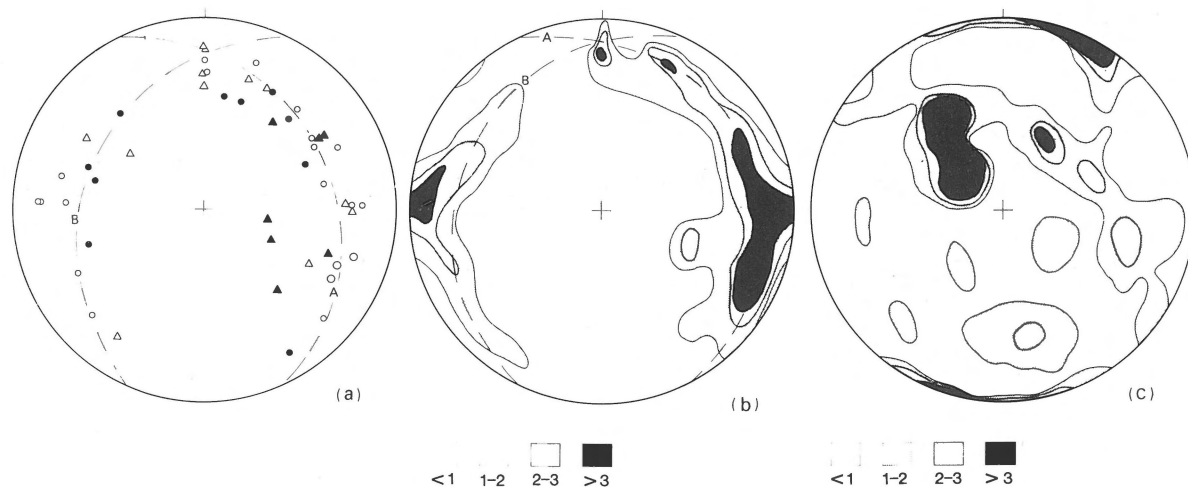


Fig. 4  
 (a): stereographic projection of poles of limestone bedding planes. (explanation of symbols in the text). (b): contoured equal area projection of poles of limestone bedding planes. (c): contoured equal area projection of poles of faults and fissures.

may be – at least partly – congruent to primary stratification. The orientation in concave-up colour zones, following the orientation of the limestone basal plain supports this. The dips of the colour beds and lineations are presented in Fig. 4a as closed and open circles, respectively. Contouring of an equal area plot of the measurements (Fig. 4b) indicates a shallow syncline, with northern axial dip of 4 to 25° (western flank averages N 065° E/21°, A in Fig. 4a-b; eastern flank averages N 293° E/28°, B in Fig. 4a-b). This agrees well with data presented by DE WIJS (1962). Additional information from the field indicates that this syncline is closed to the north. Fig. 4 and foregoing conclusions mainly concern the area west of line 61800 (Fig. 3). The area east of this line did not furnish enough information on stratification.

Poles of joints and fissures were plotted and counted on an equal area projection (Fig. 4c). Although data are rather scattered the maxima indicate planes oriented N 148° E/15 to 55°, N 211° E/30 to 40°, and (sub)vertical planes that strike about N 115° E.

To study the BPL- and fluorine-content of the clean Seroe Domi Limestones, data from logs of drill holes, from all over the area, were compared with each other. The data permit the following general conclusions:

1. mean BPL-values vary from 0.16 to 1.98%. However, approximately 70% of the measurements range from 0.1 to 0.5%. Apart from statistically significant higher mean BPL-values in clean limestones directly under phosphatized rocks, no differences could be confirmed statistically. It can be concluded therefore, that the mean BPL-contents of clean Seroe Domi limestones, apart from earlier mentioned enriched zone, is rather uniform.

2. Mean F content varies from 0.01 to 0.09%. Approximately 90% of the measurements range from 0.01 to 0.03%. Again, a statistically significant enrichment with respect to fluorine could only be proven in limestones directly underly-

ing phosphatic horizons. The barren limestones are very uniform in fluorine-content everywhere else.

Finally, the correlation between mean BPL and mean fluorine data was checked. In general, a significant positive correlation exists. However, fluorine- and BPL-values are less well correlated going from the north to the south and from higher situated limestones to lower ones. No significant trend was found in BPL/F-ratios.

## PHOSPHATIZATION

### *Morphology of the phosphate units*

As mentioned earlier, 15 separate rock-phosphate units could be defined. Their lateral extension and vertical range are indicated in Figs 3B and 3C, respectively. Strike and dip of the units on the Highest Terrace must be regarded with some reservations. At least part of the phosphatic material found here belongs to 'rubble phosphates' accumulated in karst-holes. Because these phosphates are excluded from this study, only phosphatic limestones more than 3 metres below the surface of the Highest Terrace, (i.e., below the average maximum depth of the solution holes) were taken into consideration. Along four vertical sections on the Toplevel (Fig. 3A) the units were studied in detail (Fig. 5). They occur as mineralization zones, usually no more than 6 metres thick. Locally thicknesses up to 20 metres are found. Some units can be traced horizontally over 200 metres and more. Usually they are separated by barren zones, but sometimes these are missing. In general the units follow the trend of the limestone basal plain (Fig. 6). Attention is drawn to the existence of two separate groups of units. Especially in the west this is very distinct (Section I, Fig. 5). Here units 1 and 2 are morphologically separated from units 3 to 6. In the eastern part of the Mountain such a subdivision is not clear.

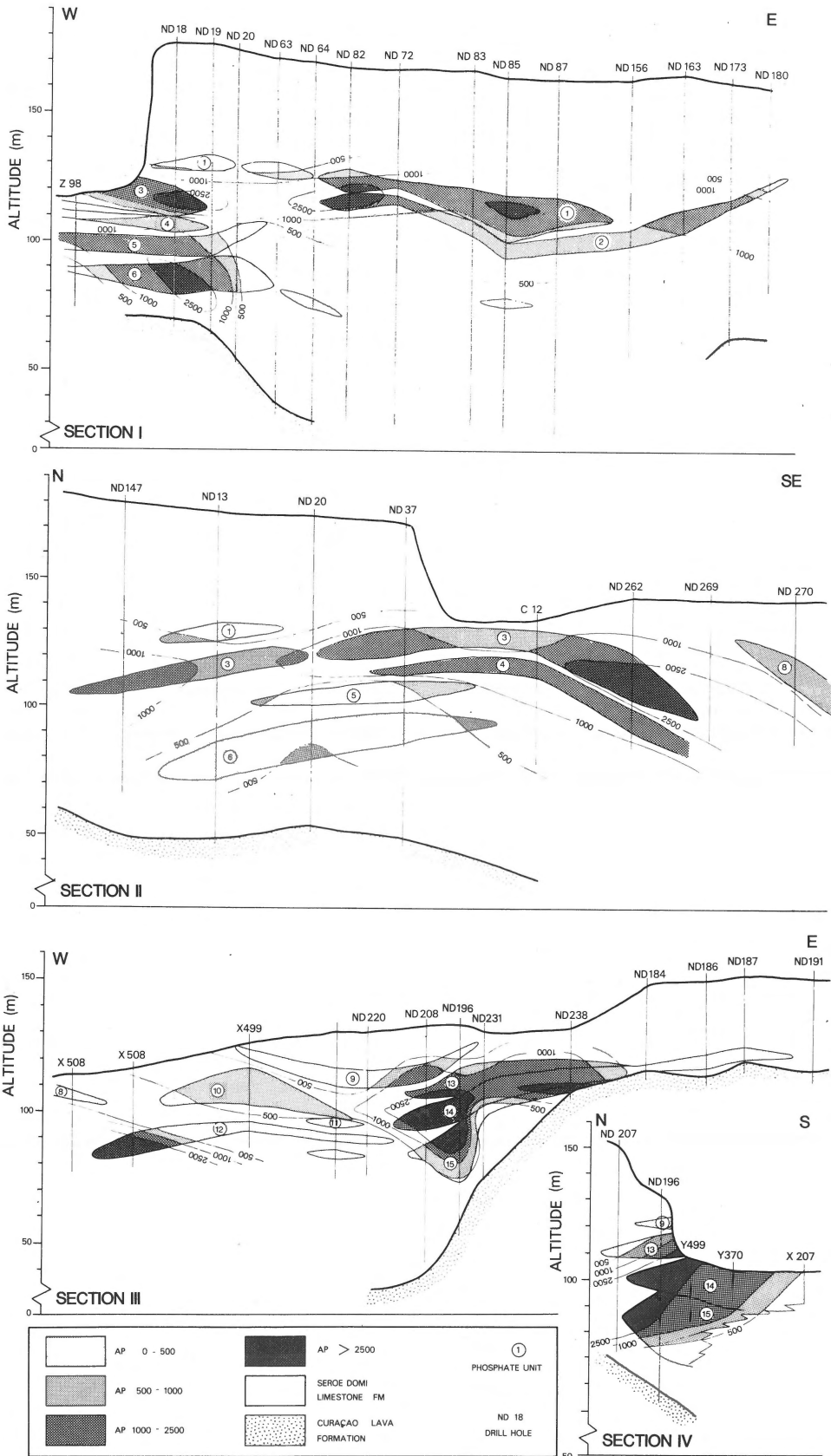


Fig. 5 Distribution of the phosphate units along Sections I, II, III and IV (Locations in Fig. 3) and 'amount of phosphate' (AP) within these units.

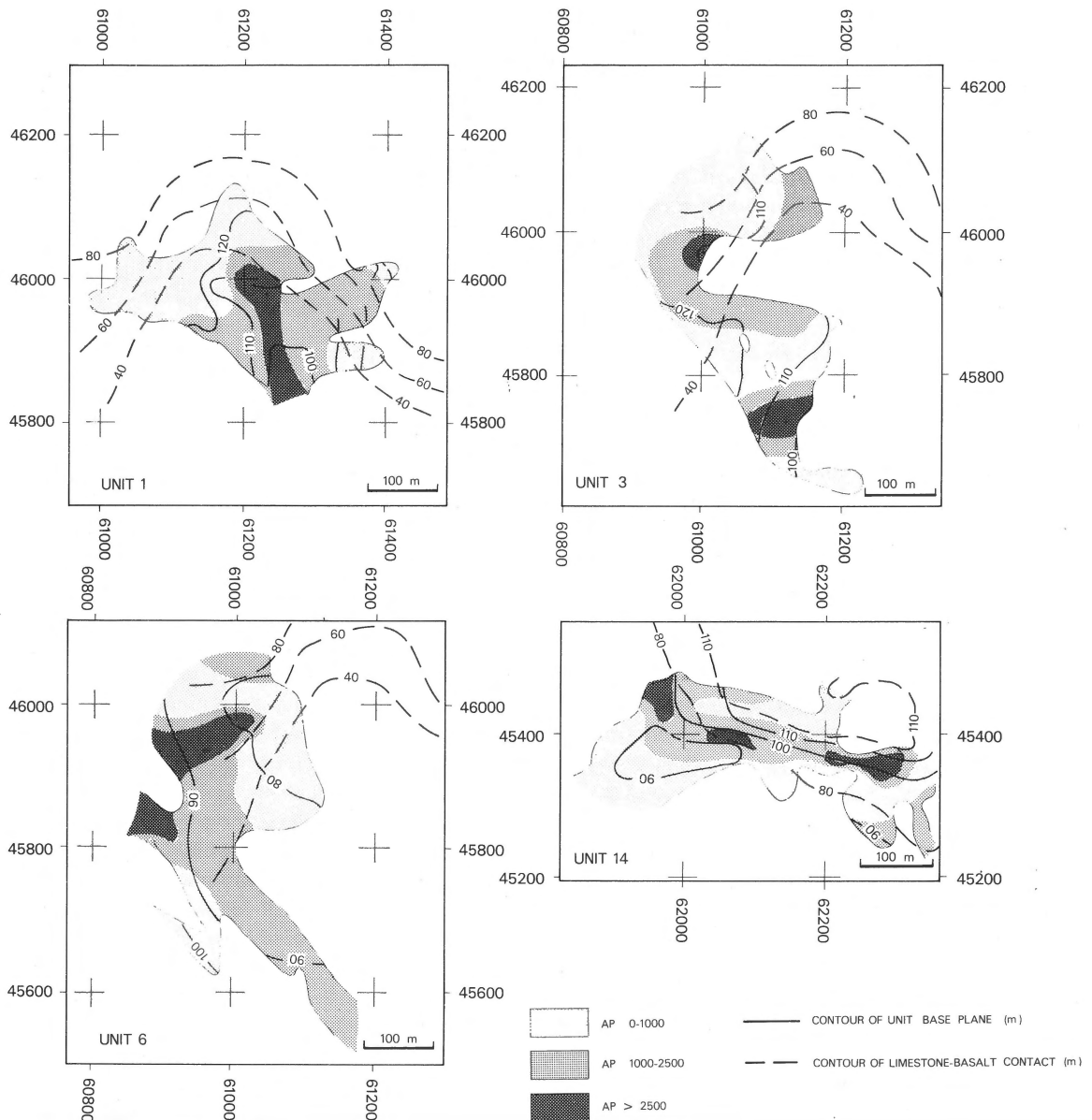


Fig. 6 Horizontal distribution of 'amount of phosphate' (AP) within phosphate units 1, 3, 6 and 14. Also indicated are the contours of the unit base-levels and the Seroe Domi Limestone base-level.

### Distribution of phosphate and fluorine

To investigate the distribution of phosphate and fluorine, BPL- and F-values from each of the units 1, 3, 6 and 14 where studied in detail. These units represent most of Table Mountain phosphate-types. The data permit the following conclusions:

1. mean BPL-values vary from 18.7 to 81.4%. However, about 60% of the measurements range from 30 to 60%. With regards to the BPL-contents, no statistically significant differences between the four investigated units could be found.

2. mean F-content varies from 0.08 to 0.96%. About 73% of the measurements range from 0.1 to 0.6%. Between the units no significant differences could be established, apart

from a significantly higher mean fluorine-content, which is probably coupled to a higher porosity in unit 6 compared to units 1, 3 and 14. Similarly, from unit 1 to unit 3 the BPL/F-ratio appears to decrease. However, this trend is not statistically significant.

This method of studying phosphate- and fluorine-distribution of the phosphates does not take into consideration the great differences in recovery that were encountered. Small amounts of high grade phosphates in high porosity rocks cannot be distinguished from large amounts of high grade phosphates in low porosity rocks. To better account for such differences, the distribution of phosphate can also be expressed as the distribution of 'the amount of phosphate' (AP). AP is defined as mean BPL-value times the percentage

of non-barren rock. For every occurrence of each of the units 1, 3, 6 and 14, AP was calculated. AP-trends are indicated in the units in Fig. 5. Two zones of relatively high AP-values appear to exist, separated by a lower grade zone. This zonation intersects the morphological trend of the 15 phosphate units. Although the situation is more complex in the east than in the west, this general organization can be recognized here too.

## DISCUSSION

The general morphology of the Santa Barbara rock phosphates appears to be strongly predetermined by primary limestone stratification. The mineralized zone as a whole, as well as the different phosphatic units, follow the trends of both the limestone-basalt contact and the pattern set by bedding and colour-stratification. This agrees with the strong correlation between depositional carbonate facies and phosphatization, as determined by TEN HAVE ET AL. (1982).

The patterns of fissures and faults and phosphatization, respectively, do not suggest a direct genetic relationship. Additionally, faults (sometimes with a clear dip-slip displacement of 2 m at maximum) were found to dissect phosphatized limestone zones. They are thus younger than phosphatization. Phosphatic material found in a fissure about 25 m below the Toplevel did not contain more than 7.5%  $P_2O_5$  (16.3% BPL). This does not suggest preferential downward transport of phosphate brine along this or similar fissures. Likewise, no direct relationship could be established between rock phosphates and geomorphology. The occurrence of rubble phosphates in pinnacle fields, however, sometimes seems to be related to the pattern of 'rooien' (Fig. 3A, along rooi Loki).

Although phosphatization seems in part to be defined by primary petrologic trends, like stratification, there must be another, secondary genetic process, because zones of maximum mineralization appear to transect stratification. The mixing zone of phreatic fresh and salt water is a geochemical/hydrological environment, where such a mineralization could become established. Many longitudinal shaped caves have been described on the Netherlands Antilles (ZONNEVELD ET AL., 1977; WAGENAAR HUMMELINCK, 1979) and elsewhere (RUDNICKI, 1980). This indicates the importance of solution along limestone coasts. In the eastern Table Mountain a level of preferential groundwater flow (at an elevation of about 110 m) is marked by distinct algal growth on the quarry face. This suggests the presence of a zone of high (secondary?) porosity. A striking feature is that this level seems to separate the lower more phosphatic rocks from the higher clean ones. Other cavernous levels were drilled, which sometimes contain artesian groundwater. Numerous caverns and caves can be seen in phosphatized zones of the present quarry faces.

PLUMMER (1975) has demonstrated that mixing of high-ionic strength, low  $PCO_2$ , saline water with low temperature, high

$PCO_2$ , nearly saturated carbonate ground water, leads to undersaturation of the mixed solution with respect to both calcite and aragonite. Consequently, limestone in contact with this solution will be dissolved and thus high porosity and permeability levels can be formed within the fresh water-salt water mixing zone.

Levels like these are open to allochthonous chemical solutions. On Table Mountain such a phosphate rich brine had been furnished by bird guano. This brine percolated down from the Toplevel to the high porosity zone. Phosphatization took place as replacement, cementing and depositing multiphase phosphate crusts within and directly below the solution zone (TEN HAVE ET AL., 1982).

Locally dissolution of the limestone and phosphatization seem to have been synchronous processes. In many locations preferential solution and consequent phosphatization occurs in 'pockets', that are characterized by a relatively high coral (aragonite) content and are surrounded by largely unaffected algal-micrites which mainly consist of calcite (TEN HAVE & HEIJNEN, 1978). AS WALTER & HANOR (1979) stated, the presence of dissolved orthophosphates may strongly inhibit the dissolution of biogenetic magnesian calcites without substantially influencing dissolution of aragonite. This seems to have been the case on Table Mountain. The resulting mineralization, therefore, will be the combined product of primary petrological composition and dissolution/phosphatization processes connected to a mixing zone.

Large-scale petrological trends, such as bedding, are important and the general morphology of zones of maximum mineralization is defined for instance by the dip in stratification whether seaward or landward – i.e. opposed to or concordant to marine-fresh water mixing trends, respectively. The first case is shown schematically in Fig. 7a. Here, zones of maximum dissolution and subsequent phosphatization are only limited in lateral extent. The second possibility (Fig. 7b) will produce more extended mineralizations. Both types can be recognized within the units of the westernmost area (Fig. 5, Section I) and the easternmost area (Fig. 5, Section III), respectively.

It is obvious that a prolonged genetic process as described above will strongly depend on a stable sea level. Successive periods of varying stable sea level positions may be recorded as a mineralization phase each. In case of small sea level changes, successive mineralizations may occur at one level – although that will be difficult to recognize. The presence of multipartite phosphates probably suggests such a process on Table Mountain. Large – e.g. eustatic – sea level changes, alternating with long periods of stable sea level will result in clearly separated mineralization zones. The presence of two phosphate-unit series and two superimposed high AP-zones thus may suggest – at least – two periods of relative stability; one at about 150 m, the second at about 110 m above present sea level. This agrees well with the 140-160 m escarpment and the Highest Terrace (90-110 m) respectively. Both are erosional features that can be attributed to periods of

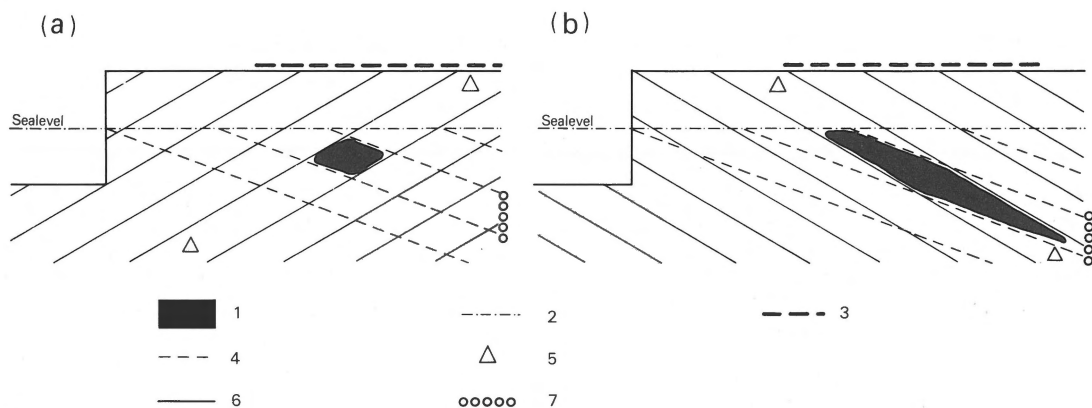


Fig. 7

Schematic coastal sections, indicating different configurations of the zone of maximum mineralization, due to seaward (a) or landward (b) dipping strata. 1. zone of maximum mineralization; 2. sea level; 3. guano cover; 4. fresh-salt water mixing gradients; 5. limestone bed, preferentially susceptible to solution and subsequent phosphatization; 6. stratification; 7. zone of most favourable geochemical conditions for mineralization.

relatively stable sea level. Correlation with the proposed local sea level curve for the Netherlands Antilles suggests an Early-Pleistocene age for the two successive mineralizations (2.3 Ma. to 1.3 Ma., and 1.2 Ma. to 900.000 a. B.P. respectively; STIENSTRA, 1983).

Because of these two mineralization-phases, it is not surprising to find that simple lateral and vertical AP-trends do not occur. Slight enrichment in BPL and fluorine in the barren limestones is related to directly overlying phosphatized levels. A decrease of mean BPL/F ratio from unit 3 to unit 6 within the phosphate units suggests an increase in marine influence in that direction. In an arid climate, as prevails presently in the region (KOK, 1978), seawater will be the main source of fluorine (CARPENTER, 1969). The fluorine-contents of a fissure infill (about 25 m below the surface) amounts to only 0.025%, and does not indicate a high fluorine input by rainfall.

## CONCLUSIONS

- A detailed investigation of the Santa Barbara rock phosphates confirms the existence of a high-grade mineralization level, sandwiched between, and laterally bordered by, phosphate- and fluorine-poor limestones of the Seroe Domi Formation. In general this agrees with the ideas of DE WIJES (1962) and TEN HAVE ET AL. (1982). However, the unit boundaries appear to be sharper than thought by the authors last mentioned. Internal morphology is very complicated, related to a complex genetic process.
- Genesis of the phosphates seems to be closely related to sea level stages as proposed in general by DE BUISSONJÉ (1974) and in more detail by TEN HAVE & HEIJNEN (1978). This study, however, revealed a much more complicated process than envisaged by the forementioned authors.
- 15 Morphological phosphate units could be defined, which, at least in the west, can be clearly subdivided into two separate groups. A similar subdivision, transecting morphological

trends, was recognized in the chemical characteristics (BPL-distribution).

- The highly complex distribution pattern can be attributed to a process of dissolution and mineralization.
- A phreatic fresh water- salt water mixing zone determines the geochemical/hydrological environment, favourable for dissolution of calcium carbonate and deposition of phosphate. Phosphate is derived from bird-guano, present on the surface.
- Based on this morphology, and supported by geomorphological characteristics of Table Mountain, two successive periods of mineralization could be distinguished, directly related to two sea level stages with a vertical difference of about 40 m.
- Within each of these two zones small scale intermittent phosphatization phases probably indicate minor (? seasonal) sea level fluctuations.

## ACKNOWLEDGEMENTS

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