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Groundwater evolution, chemical sedimentation and carbonate brine formation on an island in the Okavango Delta swamp, Botswana

T. S. McCarthy and J. R. McIver
Department of Geology, University of the Witwatersrand, P. O. Wits, Johannesburg 2050, Republic of South Africa

and

B. Th. Verhagen
Schonland Research Centre, University of the Witwatersand, P. O. Wits, Johannesburg 2050, Republic of South Africa

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Abstract—The Okavango Delta of semi-arid northern Botswana is a large alluvial fan (22,000 km^2) covered by permanent and seasonal swamps from which 96% of the annual discharge is lost by evapotranspiration. Many small islands (~1 ha) within the permanent swamps are the sites of accumulation of sodium carbonate salts and many contain saline pans. The associated alkaline soils are toxic to vegetation. An understanding of the processes involved in alkalinization could be of potential benefit to long-term conservation planning in this unique ecosystem. The relation between soil chemistry and mineralogy, and swamp and groundwater chemistry were investigated on an island in the swamps. The study revealed that the water table beneath the island is depressed and swamp water enters the groundwater regime of the island from the margins and below, and flows toward the centre. The water becomes progressively more saline, initially owing to transpiration by trees and ultimately by evaporation in the central parts of the island. As a result of increasing salinity, amorphous SiO_2 and magnesium calcite precipitate in the soils beneath the marginal zone of the island, raising the land surface, while the more soluble alkali carbonates are concentrated in the centre of the island as surface crusts and brine ponds. Leaching of these salts into the soil during the rainy season and gravity-driven flow of saline brines in the dry season causes the downward movement of Al and Fe in the central zone of the island. K-feldspar and possibly amorphous allophane develop in the deeper soils under the central zone of the island.

INTRODUCTION

Brine lakes, characterized by the precipitation of trona, usually occur in intra-continental settings and may be seasonal or permanent (Sonnenfeld, 1984). The essential requirements for such lakes are: a suitable climate in which evaporation significantly exceeds inflow and precipation, a closed basin, and a plentiful supply of water rich in HCO_3 (Eugster and Hardie, 1978). The entire water body is usually alkaline and trona deposition occurs around the margins or over the entire lake. In some instances, the water body may be of low salinity, with trona precipitation occurring in smaller depressions flanking and supplied by the lake, for example, on the northern margin of Lake Chad (Eugster and Maglione, 1979). In contrast to these situations, McCarthy *et al.* (1986b) described the occurrence of trona on small islands (typically <1 ha) within an extensive, fresh water swamp in the Okavango Delta of semi-arid northern Botswana. The trona occurs mainly as efflorescent crusts on the soil surface, but locally, small saline pans are also present on the islands. These areas are devoid of all vegetation, indicating that the soils and groundwater have reached toxic levels of alkalinity.

The Okavango Delta is a prime conservation area, and one of the most spectacular nature reserves in southern Africa straddles its eastern margin. While salinity buildup does not appear to be a problem at present, it is important that the processes which cause it are understood so that future trends can be assessed. These may have implications for the long-term planning of the conservation area as well as for agricultural areas in the southern and western regions of the delta. This work reports the results of the first detailed investigation into salt accumulation and brine formation on an island, and focuses on the chemical relation between swamp water and the groundwater regime beneath an island, and the process leading to carbonate brine formation.

THE OKAVANGO DELTA

The Okavango Delta (Fig. 1) is a large alluvial fan (22,000 km^2) lying within grabens of the southern extension of the East African Rift system (Hutchins *et al.*, 1976; Scholtz, 1975). The Okavango Delta currently represents the terminal depository for the Okavango River system which drains central Angola. The Okavango River degenerates into a series of

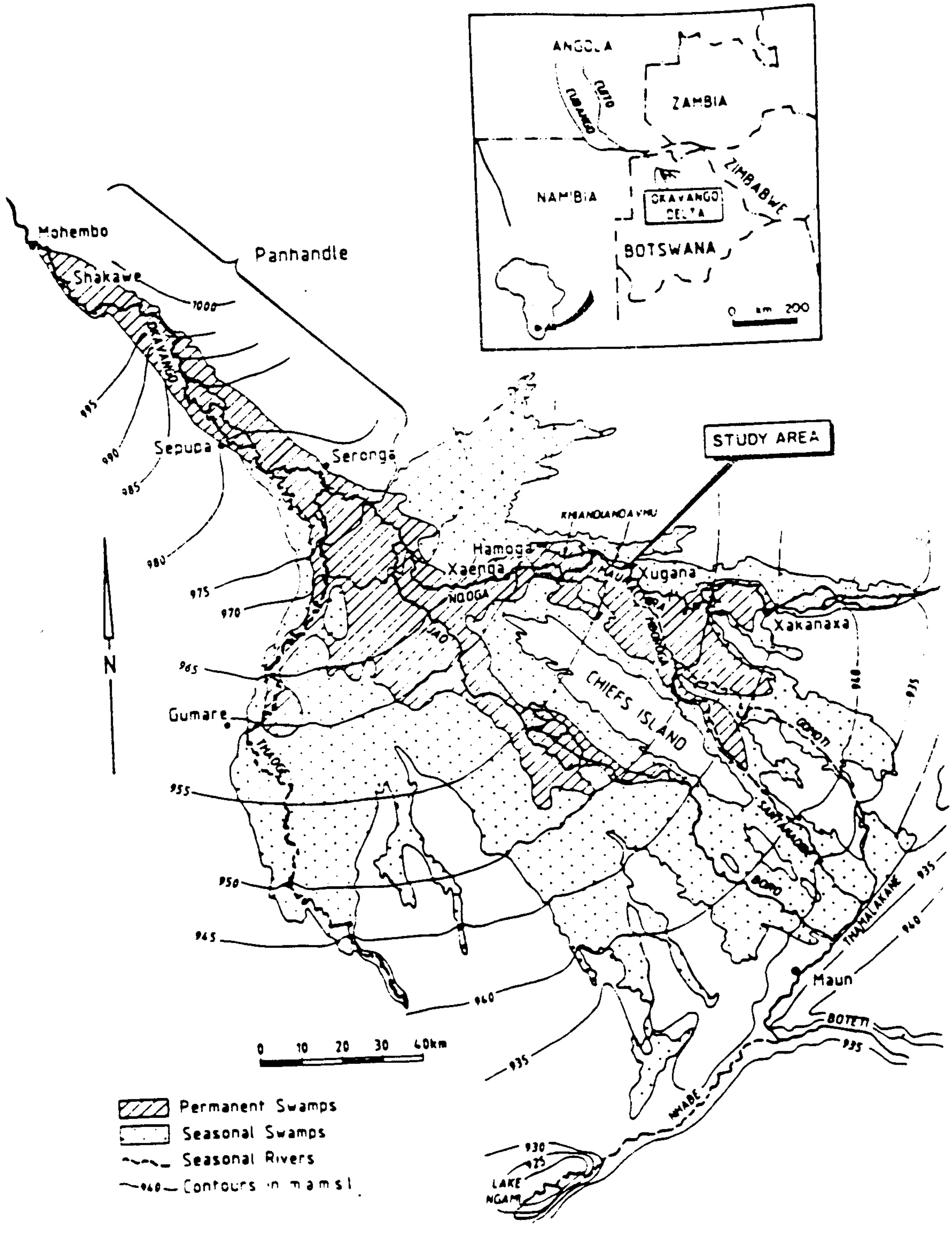

FIG. 1. The Okavango Delta, Botswana.

anastomosing channels on the fan surface which are bordered by extensive permanent swamps (6000 km^2). These give way to seasonal swamps along the distal margins of the fan. Evapotranspiration from the swamps exceeds precipitation by a factor of three and ~96% of the annual discharge is lost to the atmosphere (DINCER *et al.*, 1981).

Although fluvial sedimentation is taking place actively on the fan (MCCARTHY *et al.*, 1986a, 1989, 1991), mass balance calculations suggest that the major sedimentation process is in fact chemical and is apparently caused by capillary evaporation of swamp water on islands, especially in the permanent swamp region of the delta (MCCARTHY and METCALFE, 1990). This leads to the accumulation of $CaCO_3$ and amorphous SiO_2 in the soils, and the resultant volume increase may be responsible for much of the surface topography of the delta. In addition, efflorescent crusts of trona and thermonatrite are a common feature of the islands (MCCARTHY *et al.*, 1986b), although these are probably transient (MCCARTHY and METCALFE, 1990). Many of the islands in the permanent swamps are characterized by the presence of isolated pans containing dark coloured, saline water which is saturated occasionally in sodium carbonate. These pans are usually surrounded by trona-encrusted soils which are devoid of vegetation.

STUDY SITE

The island chosen for the study is situated in the northeastern portion of the permanent swamps, north of Maunachira Lediba (Lake) (Fig. 2). The island is ~500 m long and 150 m wide and is surrounded by a shallow (~1–2 m), densely vegetated swamp. The elongate margins of the island are heavily vegetated by large trees and undergrowth. Species present include *Acacia nigrescens*, *Ficus natalensis*, *Garcinia livingstonii*, *Kigelia africana*, *Sclerocarya kaffra*, *Croton gratissimus*, *Tarconanthus camphoratus* and *Berchonia zeyheri*. On the fringes of the tree-covered areas, the grass *Cynodon dactylon* is abundant. The central axis of the island is lower than the margins and is largely devoid of vegetation and covered by an efflorescent crust. The grass *Sporobolus spicatus* survives on the fringes of the salt-encrusted zone. Small saline pans are developed along the lowest points of the central axis.

Water distribution in the swamps is changing continually (WILSON, 1973; SHAW, 1984; MCCARTHY *et al.*, 1986a) owing to alteration of the channel systems and possibly also to neotectonics (the area is seismically active; SCHOLTZ, 1975). The area of swamp surrounding the present study site is subject currently to a slowly rising water level. Figure 3 illustrates the hydrographic record for the period 1974–1984 for the Xugana Lediba, situated ~3 km southeast of the study island. Seasonal water level fluctuations are small in this area (<20 cm) but there is a steady rise in water level, owing to channel changes upstream or possibly to tectonic tilting, which is directing an increasing quantity of water to this region of the swamps (MCCARTHY *et al.*, 1989).

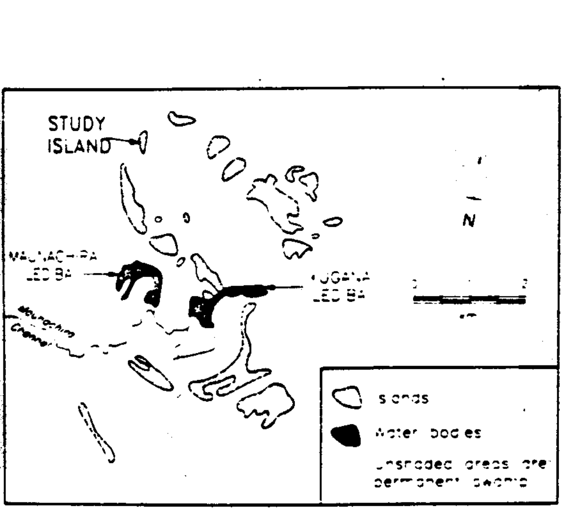

FIG. 2. Location of the study island.

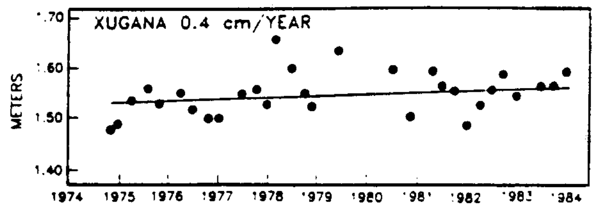

FIG. 3. Hydrographic record for Xugana Lediba.

STUDY METHODS

A topographic map of most of the island was made using a plane table and level. Pits and auger holes were dug on various parts of the island, especially around the central depression. Water levels in these excavations were allowed to equilibrate for 2 d and the water level surface was surveyed, as was that in the surrounding swamp. These elevations are accurate to within 2 cm. Samples of soil and surface crust collected from the excavations were subjected to mineralogical analysis using microscopic, X-ray diffraction and SEM techniques. Samples were also chemically analysed by X-ray fluorescence and atomic absorption spectrophotometric methods (MCCARTHY and METCALFE, 1990). Water samples collected from the pits and surface were analysed by the South African Bureau of Standards, Pretoria. Sodium, K, Ca and Mg were determined by atomic absorption spectrophotometry; SiO_2 by the molybdosilicate colorimetric method, SO_4 by a turbidimetric method using barium chloride; Cl by titrimetric method against $AgNO_3$ using a dichromate indicator; and CO_3 and HCO_3 by titration (APHA, 1989). Density of the water samples was determined using a pycnometer at 23°C. No analytical work was carried out in the field because of the remoteness of the area and the very primitive field conditions.

Isotopic analyses were carried out in the Environmental Isotope Laboratory of the Schonland Research Centre at the University of the Witwatersrand. Aliquots of the brines were quantitatively vacuum distilled prior to isotopic measurement, which was performed using standard techniques (EPSTEIN and MEYEDA, 1953). The samples for deuterium analysis were prepared using a modification of the method of COLEMAN *et al.* (1982). Results are expressed as per mille deviation from the SMOW standard.

RESULTS

Topography

The topographic map of the island is shown in Fig. 4a. Swamp water level is ~30 cm lower at the northern end of the island relative to the datum point in the south, and there is a general northward flow of swamp water. This flow is, however, very slow because of the density of swamp vegetation. The eastern and western margins of the island are elevated slightly relative to the centre. The highest points on the island are formed by termite mounds, which rise to a maximum of ~1.5 m above datum. The central topographic depression has four low points in which permanent saline water occurs (pans 1–4, Fig. 4a). The water surface in these pans lies at 32, 42, 54 and 59 cm below datum, respectively.

Large trees and shrubs are confined to the eastern and western margins of the island while the central zone is covered by grass (Fig. 4b), except for the area

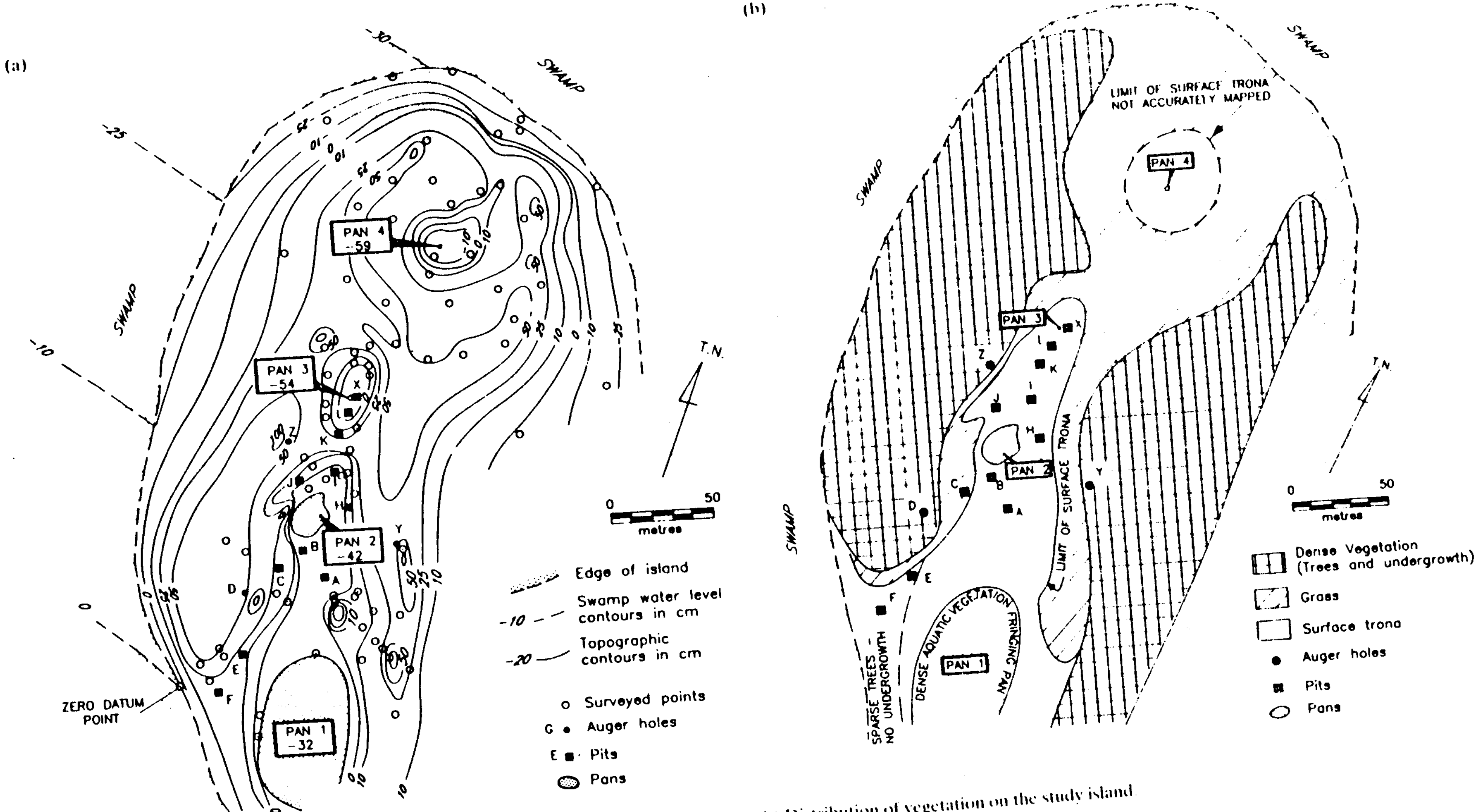

Fig. 4. (a) Topography of the study island. (b) Distribution of vegetation on the study island.

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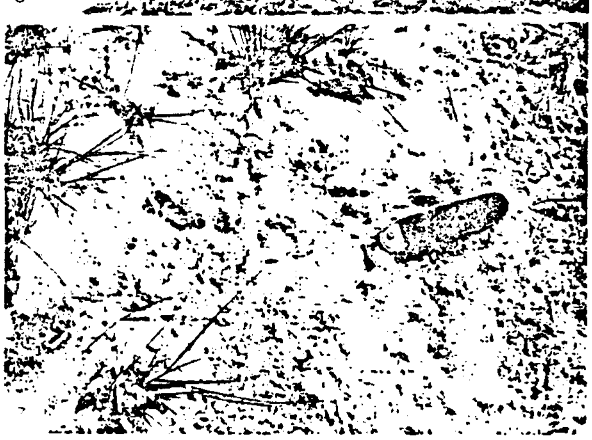

FIG. 5. View looking northward across the island: excavation C is in the left foreground and Pan 2 is in the middle distance.

FIG. 6. Trona-covered area around Pan 2. Note the trona-free seepage zone immediately flanking the water's edge.

FIG. 7. Trona crust, with a few tufts of *Sporobolus spicatus* grass. The penknife is 8 cm long.

around the pans which is largely devoid of vegetation and is covered by efflorescent crusts (Figs 5, 6, 7). Trees near the saline pans appear to be greatly stressed (Fig. 5).

Water level

A contour map of the water level elevation beneath the island is shown in Fig. 8. The groundwater surface exhibits a central depression, similar to the topographic surface, sloping down toward the pans. Pans 2, 3, and 4 are surrounded by seepage zones, which are free of efflorescent crusts, and in these zones groundwater seeps out at the surface and flows down toward the pans (Fig. 6). The groundwater and the water in the pans is coloured brown, becoming almost black in Pan 3, which had a crust of crystalline material covering part of its surface at the time of the survey. This was identified as trona by X-ray diffraction.

Soils

The soils remote from the pans are typically yellow-brown to light-grey in colour and are very sandy, being composed largely of well-sorted, fine quartz sand (average grain size ~0.2 mm). There is little obvious stratification. In areas around the pans, the upper few centimetres of the soil profile are stained dark brown to black. This stain is readily soluble in water and appears to be identical to that which colours the groundwater. The soil surface is usually covered by an efflorescent crust, normally white, but locally also stained. X-ray diffraction analysis indicated that the surface crust consists mainly of trona with minor thermonatrite. The soils are grey, becoming greenish-grey in depth, especially around plant roots.

Optical and X-ray diffraction examination indicated that the fine fraction (−200 mesh) of the soils consists largely of kaolinite, calcite and amorphous SiO_2 (opal A of JONES and SEGNIT, 1971). X-ray diffraction also revealed the presence of microcline in the fine fraction. Further investigation using scanning electron microscopy (with EDS) showed that this consists of very small, (~2 μm), irregular crystals.

Soil chemistry

Chemical analyses of soil samples are listed in Table 1, and localities of the profiles are shown in Fig. 4a. Profiles D, Y and Z are located in the heavily vegetated areas of the island and represent areas away from active trona accumulation. The remaining excavations were concentrated in the central depression of the island (Fig. 4a). The depth of the excavations and auger holes was limited by the inflow of groundwater, which caused collapse.

All of the soils analysed are very rich in SiO_2, reflecting the dominance of quartz sand. This is augmented by amorphous silica (MCCARTHY and METCALFE, 1990). The three profiles located in the vegetated fringe of the island (D, Y and Z) show pronounced increases in Ca and Mg with depth, reflecting increased abundance of magnesium calcite in the soils. This contrasts with profiles in the lower lying, central zone, which show a more uniform distribution of Ca and Mg with depth (Fig. 9). Pro-

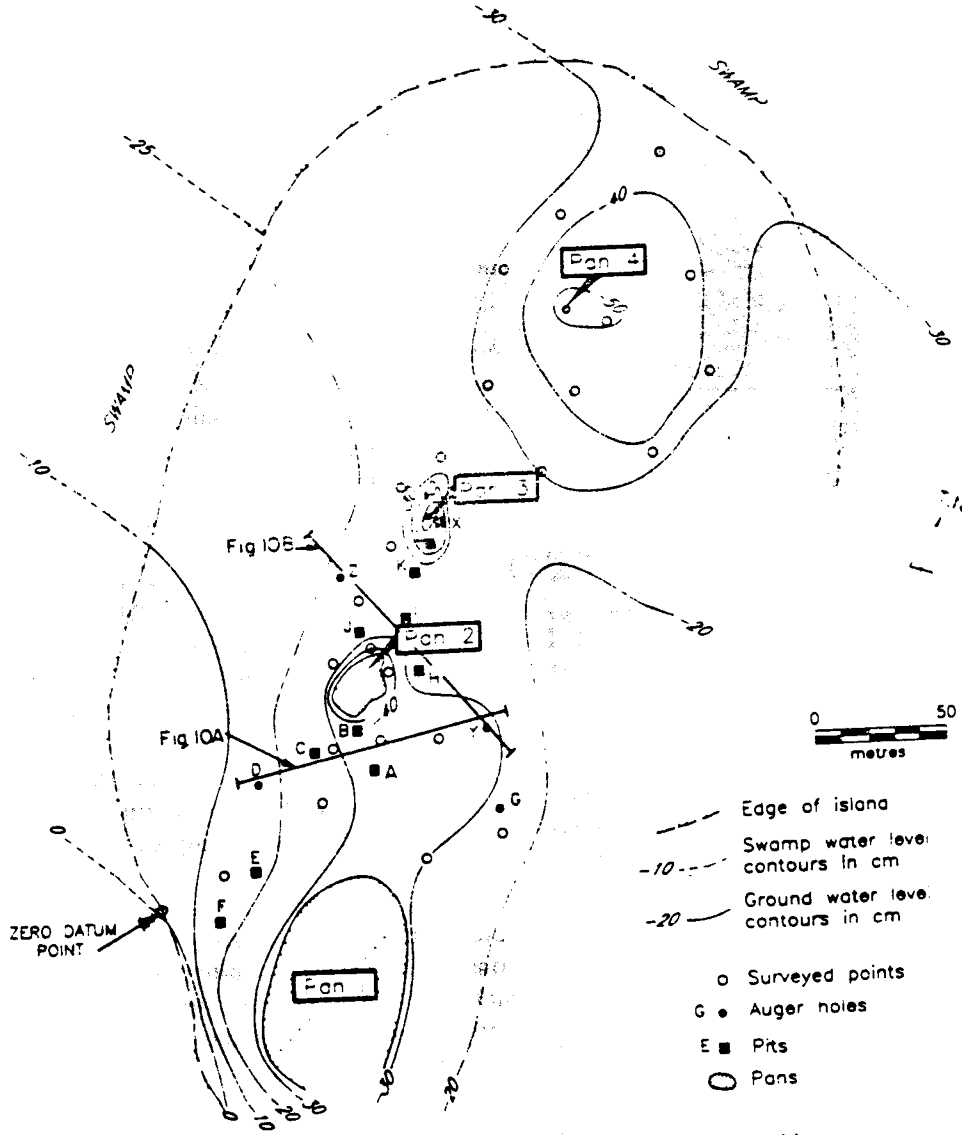

FIG. 8. Contour map showing elevation of the water table.

files across the island (Fig. 10) show that calcite is concentrated beneath the elevated margins of the island.

Aluminium contents, which are controlled mainly by clay mineral abundance, are uniform in the profiles from the vegetated fringes of the island, but show a pronounced increase with depth in the trona-covered areas (Fig. 11). Iron and Ti follow closely Al (Fig. 12) but there appears to be a slight Fe enrichment in soils from the vegetated areas. Sodium and acid-soluble K are fairly uniform in abundance in the profiles from the vegetated areas, but show marked surface enrichment in the trona-covered portions of the island (Fig. 13). In contrast, acid-insoluble K is variable, showing a slight increase with depth in the trona-covered areas, but is relatively uniform in the soils from the vegetated areas (Table 1).

Water chemistry

Chemical analyses of water samples collected from the swamp, pans and excavations are listed in Table 2. Sample localities are indicated in Fig. 4a. The samples exhibit an extreme range in total dissolved solids (TDS), from 45 ppm in the swamp water to 240,000 ppm in water from Pan 3. Sulphate and Cl are low and the dominant anions are CO_3 and HCO_3. Such bicarbonate brines are typical of continental areas (GARRELS and MACKENZIE, 1967). Silica is a major constituent of the low salinity water, but is proportionally less abundant in the more saline water. Water samples from the pans and excavations are coloured brown. The samples were tested for tannins by boiling a mixture of the water and formaldehyde, which forms an insoluble polymer with tannins, but this failed to produce any precipitate, indicating an absence of this group of compounds. However, the colouring agent precipitated on acidification of the brines, indicating the presence of lignins. The concentrations of lignin in two samples were determined gavimetrically: Pan 3 contained 2525 ppm and Pan 2 contained 620 ppm.

Figure 14 shows a plot of Cl against Na for groundwater and surface water collected during the present study, and for surface water from the whole Oka-

Table 1. Chemical analyses of soil samples

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Loss on ignition	Total	Cl	Depth interval sampled	Mean depth (cm)	Acid-soluble MgO	Acid-soluble K_2O	Acid-insoluble K_2O
Va	62.19	0.05	0.44	0.22	0	0.03	0.21	20.24	1.22	0.07	15.59	100.25	11462	1	1			
A1	95.60	0.08	0.98	0.27	0	0.23	0.21	0.70	0.32	0.04	1.47	99.89	3253	4	2	0.04	0.22	0.10
A2	97.43	0.11	1.13	0.36	0.01	0	0.08	0.18	0.35	0.01	0.68	100.42	442	7	7.50	0.02	0.10	0.25
A3	90.78	0.19	3.67	0.91	0.05	0.26	0.35	0.49	0.83	0.04	2.35	100.07	726	3	12.50	0.06	0.31	0.52
A4	89.79	0.19	3.86	1.06	0.01	0.17	0.40	0.40	0.76	0.02	2.36	99.12	453	6	20	0.05	0.26	0.50
A5	93.24	0.18	3.24	0.86	0	0.09	0.16	0.20	0.58	0.01	1.61	100.24	454	10	25	0.04	0.17	0.41
A6	92.10	0.17	3.15	0.89	0	0.11	0.37	0.22	0.55	0.01	1.87	99.42	310	10	40		0.16	0.39
V5	50.32	0.06	0.70	0.28	0	0.15	0.32	25.52	0.61	0.09	21.38	99.41	12378	1	1			
B1	94.89	0.09	0.96	0.36	0.00	0.02	0.32	1.03	0.37	0.02	2.01	100	1380	1	1	0.07	0.14	0.23
B2	93.64	0.15	2.38	0.62	0	0.02	0.40	0.16	0.47	0.02	1.79	99.89	280	7	7	0.06	0.07	0.40
B3	94.72	0.14	2.11	0.61	0	0	0.36	0.16	0.38	0.01	1.52	100.09	112	18	30	0.04	0.08	0.30
B4	93.66	0.16	2.72	0.76	0.00	0.07	0.42	0.23	0.39	0.02	1.78	100.36	115	15	40	0.02	0.06	0.33
B5	92.62	0.17	3.34	0.86	0.05	0.16	0.26	0.24	0.38	0.03	1.88	100.20	147	5	50	0.04	0.06	0.32
V6	74.26	0.05	0.06	0.39	0.00	0	0.19	12.45	1.13	0.04	9.86	98.97	234	1	1			
C1	93.05	0.12	1.84	0.48	0.01	0.23	0.35	0.55	0.56	0.04	1.79	99.20	115	4	2	0.07	0.27	0.29
C2	97.40	0.12	1.49	0.37	0.04	0.05	0.14	0.16	0.34	0.03	0.84	101.01	53	10	9	0.09	0.21	0.13
C3	90.06	0.20	4.35	1.25	0.03	0.22	0.42	0.18	0.69	0.02	2.58	100.08	38	10	27	0.08	0.21	0.48
C4	88.71	0.20	4.14	1.23	0.01	0.30	1.23	0.07	0.62	0.01	3.35	99.97	36	10	35	0.16	0.16	0.46
C5	88.94	0.21	4.05	1.20	0	0.35	0.92	0.06	0.56	0.02	3.11	99.41	36	16	50	0.20	0.14	0.42
D1	89.45	0.15	2.30	0.90	0.03	0.07	0.96	0.03	0.40	0.05	5.27	99.62	102	20	15	0.07	0.09	0.31
D2	92.76	0.14	2.21	0.80	0.02	0.13	0.62	0.08	0.48	0.02	2.21	99.52	45	30	38	0.12	0.15	0.33
D3	90.80	0.16	2.78	1.01	0.03	0.34	0.91	0.08	0.54	0.01	2.63	99.32	38	30	74	0.27	0.18	0.36
D4	88.78	0.17	2.87	1.07	0.06	0.68	1.42	0.08	0.54	0.02	3.36	99.08	53	20	90	0.50	0.16	0.38
V3	61.34	0.06	0.55	0.39	0.01	0.02	0.24	18.61	1.36	0.05	16.56	99.18	124	1	1			
E1	93.08	0.10	1.27	0.47	0.02	0.10	0.62	0.62	0.75	0.03	2.42	99.52	138	4	2	0.14	0.40	0.35
E2	92.66	0.15	2.12	0.93	0.03	0.13	0.61	0.16	0.62	0.02	2.45	100.10	57	5	6.50	0.15	0.25	0.37
E3	93.15	0.15	2.28	0.94	0.04	0.14	0.71	0.10	0.53	0.02	2.32	100.64	46	11	18.50	0.16	0.17	0.36
E4	90.87	0.17	2.88	1.12	0.04	0.37	0.75	0.09	0.55	0.02	2.77	99.74	48	13	27.50	0.36	0.17	0.38
E5	90.54	0.18	3.44	1.22	0.03	0.53	0.74	0.05	0.53	0.03	2.84	100.47	44	10	39	0.41	0.14	0.39
V2	78.25	0.10	0.95	0.72	0.01	0.07	0.36	8.01	1.13	0.09	9.45	99.13	380	1	1			
F1	92.44	0.11	1.23	0.72	0.02	0.07	0.52	1.19	0.66	0.03	3.12	100.05	157	2	1	0.11	0.31	0.35
F2	94.32	0.13	1.70	0.69	0.01	0.14	0.57	0.20	0.54	0.03	2.46	100.96	100	6	5	0.12	0.19	0.35
F3	93.81	0.14	1.74	0.76	0.01	0.04	0.43	0.12	0.41	0.02	1.92	99.47	44	7	11.50	0.09	0.11	0.30
F4	91.81	0.16	2.39	0.97	0.01	0.31	0.53	0.11	0.44	0.02	2.36	99.28	48	26	28	0.29	0.11	0.33
F5	93.47	0.14	2.45	1.04	0.03	0.38	0.39	0.06	0.36	0.03	1.91	100.44	41	9	45.50	0.32	0.14	0.22
H1	92.89	0.10	1.45	0.06	0	0.11	0.58	0.95	0.84	0.02	3.12	100.55	228	2	2	0.09	0.48	0.36
H2	92.72	0.13	2.19	0.61	0.02	0.18	0.95	0.12	0.64	0.04	2.88	100.56	78	4	4	0.12	0.26	0.38
H3	91.34	0.14	2.17	0.75	0.02	0.18	1.37	0.14	0.48	0.03	3.86	100.49	52	24	20	0.13	0.15	0.33
H4	91.52	0.16	2.87	0.88	0.03	0.49	0.95	0.78	0.50	0.20	2.74	100.20	31	10	35	0.09	0.48	0.02
H5	91.05	0.17	3.42	1.00	0	0.42	0.71	0.04	0.45	0.01	2.50	99.78	34	20	45	0.27	0.08	0.37
V9	67.94	0.04	0.22	0.26	0.02	0	0.09	18.47	0.85	0.02	12.90	100.80	3994	1	1			
I1	97.06	0.06	0.65	0.25	0	0	0.25	0.21	0.24	0.01	0.94	99.70	163	5	2.50	0.03	0.05	0.19
I2	97.66	0.11	1.07	0.29	0.02	0	0.21	0.07	0.29	0.02	0.67	100.59	97	15	15	0.02	0.04	0.25
I3	95.95	0.14	1.60	0.55	0.03	0	0.10	0.08	0.35	0.01	0.85	99.67	62	10	24	0.02	0.06	0.29
I4	92.08	0.17	3.35	0.96	0.02	0.12	0.36	0.18	0.56	0.01	1.98	99.78	65	10	32	0.06	0.14	0.42
I5	90.72	0.17	3.86	1.16	0.01	0.15	0.22	0.20	0.57	0.01	2.21	99.43	74	10	47	0.04	0.15	0.42
I6	91.29	0.17	3.96	1.20	0	0.15	0.20	0.22	0.58	0.01	2.22	100.13	83	10	56	0.04	0.15	0.43
V8	77.56	0.08	0.70	0.53	0.00	0	0.18	10.56	1.32	0.04	8.72	99.69	278	1	1			
J1	94.91	0.09	1.14	0.43	0.03	0.03	0.31	0.64	0.69	0.02	1.79	100.05	120	2	1	0.07	0.38	0.31
J2	96.20	0.12	1.45	0.48	0.03	0	0.28	0.09	0.51	0.01	1.36	100.53	105	5	4.50	0.06	0.18	0.33
J3	96.62	0.13	1.40	0.38	0.02	0	0.13	0.08	0.40	0.01	0.92	100.18	71	11	12.50	0.02	0.11	0.29
J4	89.99	0.20	4.16	1.16	0.02	0.24	0.63	0.20	0.82	0.01	2.73	100.19	38	17	26.50	0.15	0.29	0.53
J5	90.96	0.21	4.32	1.19	0.00	0.20	0.36	0.07	0.69	0.02	2.44	100.49	26	15	36	0.07	0.20	0.49
J6	89.59	0.21	4.31	1.23	0.03	0.26	0.36	0.05	0.60	0.02	2.69	99.42	34	10	60	0.09	0.17	0.43
V10	79.96	0.07	0.58	0.32	0	0	0.18	9.41	0.39	0.05	8.49	99.45	3491	1	1			
K1	94.45	0.11	1.23	0.29	0.02	0.05	0.36	1.32	0.34	0.03	2.01	100.15	1600	2	1.50	0.05	0.11	0.23
K2	95.08	0.12	1.42	0.44	0.01	0	0.50	0.24	0.32	0.02	1.41	99.57	279	8	6	0.05	0.06	0.26
K3	93.33	0.14	2.38	0.71	0	0.05	0.30	0.28	0.39	0.01	1.87	99.46	143	15	17.50	0.05	0.08	0.31
K4	91.54	0.18	3.54	1.08	0.01	0.11	0.36	0.31	0.47	0.01	2.27	99.95	122	20	40	0.09	0.10	0.37
K5	91.64	0.17	3.49	1.02	0	0.17	0.46	0.31	0.44	0.01	2.24	100	119	10	55	0.07	0.08	0.36
V11	71.97	0.07	0.69	0.32	0	0	0.21	13.64	0.59	0.04	11.58	99.10	3400	1	1			
L1	95.25	0.11	1.08	0.43	0.01	0.03	0.36	0.47	0.31	0.03	1.43	99.77	341	1	1.50	0.05	0.09	0.22
L2	97.74	0.11	0.71	0.31	0	0	0.16	0.10	0.27	0.01	0.68	100.06	347	3	2.50	0.02	0.03	0.24
L3	98.71	0.10	0.71	0.36	0	0	0.05	0.07	0.22	0.01	0.42	100.67	136	15	11.50	0.01	0.02	0.20
L4	93.80	0.17	2.82	0.77	0.04	0.13	0.26	0.15	0.42	0.02	1.68	100.70	99	6	21	0.05	0.08	0.34
L5	94.75	0.12	2.00	1.15	0.04	0	0.39	0.24	0.27	0.01	1.40	100.24	61	15	38	0.03	0.12	0.15
L6	93.08	0.18	3.03	0.93	0.01	0.07	0.21	0.32	0.41	0.02	2.11	100.41	151	12	52	0.03	0.06	0.35

Continued

Table 1. *Continued*

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Loss on ignition	Total	Cl	Depth interval sampled	Mean depth (cm)	Acid-soluble MgO	Acid-soluble K_2O	Acid-insoluble K_2O
V12	28.60	0.07	0.64	0.26	0	0.10	0.43	35.98	2.03	0.17	26.27	94.52	12512	1	1			
X1	84.49	0.22	2.69	0.97	0.05	0.36	1.56	3.17	0.87	0.06	6.16	100.51	1093	7	3.50	0.26	0.35	0.52
X2	96.74	0.09	0.98	0.38	0.01	0.01	0.56	0.30	0.27	0.02	1.48	100.85	284	3	8.50	0.09	0.07	0.20
X3	94.68	0.15	1.75	0.71	0.03	0.02	0.55	0.27	0.35	0.02	1.73	100.40	103	4	12	0.06	0.08	0.27
X4	91.18	0.19	2.78	0.91	0.03	0.12	0.90	0.48	0.48	0.03	2.71	99.80	146	16	24	0.09	0.09	0.39
X5	91.56	0.20	3.29	1.11	0.01	0.11	0.45	0.53	0.47	0.01	2.48	100.22	158	10	36	0.08	0.10	0.37
Y1	90.50	0.13	2.16	0.77	0.02	0.09	0.46	0.03	0.34	0.04	4.88	99.38	135	5	2.50	0.08	0.06	0.29
Y2	92.49	0.14	2.12	0.80	0.02	0.09	0.63	0.12	0.49	0.03	2.79	99.90	172	35	28	0.09	0.17	0.32
Y3	92.44	0.16	2.84	0.95	0.01	0.13	0.39	0.07	0.53	0.02	2.04	99.61	66	30	54	0.11	0.17	0.36
Y4	90.47	0.17	3.03	0.95	0.04	0.82	1.46	0.05	0.37	0.03	2.91	100.34	61	25	87	0.32	0.11	0.26
Y5	88.40	0.15	2.75	0.96	0.02	0.47	1.12	0.05	0.38	0.02	3.68	98.08	91	30	116	0.46	0.04	0.34
Z1	88.91	0.15	2.60	0.84	0.03	0.19	0.48	0.41	0.35	0.05	5.65	99.65	111	15	10	0.08	0.11	0.24
Z2	91.13	0.17	2.72	1.11	0.04	0.11	0.47	0.16	0.42	0.03	2.79	99.15	42	15	22	0.12	0.12	0.30
Z3	91.34	0.18	3.25	1.10	0.05	0.19	0.60	0.20	0.47	0.02	2.71	100.15	43	10	34	0.14	0.12	0.35
Z4	92.94	0.13	2.17	0.80	0.02	0.07	0.65	0.12	0.32	0.02	1.09	99.23	36	20	52	0.11	0.09	0.23
Z5	86.60	0.19	3.54	1.16	0.06	0.79	2.09	0.11	0.49	0.03	4.27	99.34	55	30	74	1.08	0.14	0.35
Z6	78.67	0.17	3.10	1.04	0.04	1.36	7.10	0.07	0.47	0.04	8.39	100.80	51	30	115	0.65	0.14	0.33

All values in weight per cent, except Cl, which is in ppm.

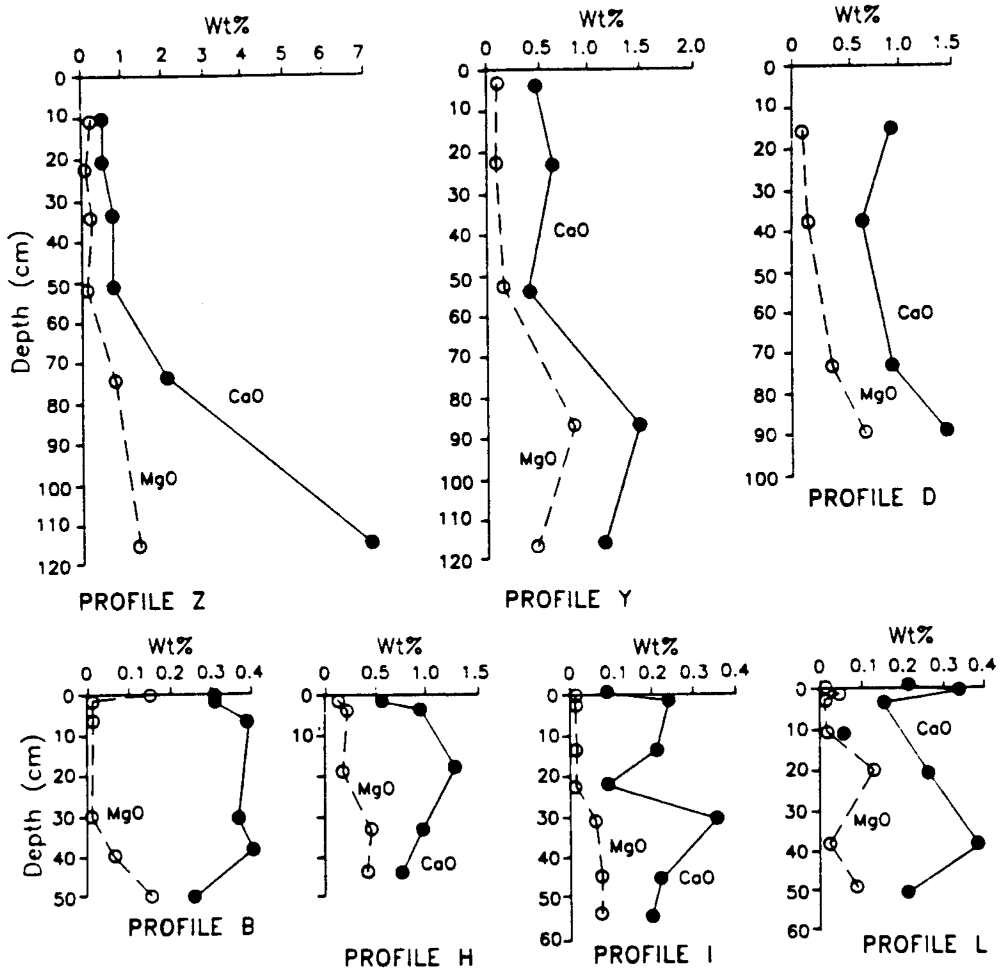

FIG. 9. Calcium and Mg contents as a function of depth in selected soil profiles. Profiles Z, Y and D were collected from vegetated areas. Locations of the profiles are shown in Fig. 4.

vango Delta area reported by HUTTON and DINCER (1976). There is a reasonable correlation; the scatter, particularly at low concentrations, probably reflecting analytical errors, especially with Cl. In spite of the scatter, it is evident that the rate of enrichment of Cl is less than that reflected by Na, indicating selective but continuous removal of Cl from the water relative to Na. As will become evident later, Na shows the greatest degree of enrichment of all species.

The rate of enrichment of K is also lower than for Na (Fig. 15), but a good linear relation exists between the two ($r^2 = 0.87$), indicating continuous removal of K from the brines relative to Na. In contrast to the plots of K and Cl against Na, the plots for Mg, Ca and SiO_2 are more complex. Magnesium increases initially with increasing Na (Fig. 16), with a slope close to unity, implying little selective removal of Mg from the water. Magnesium concentration peaks at ~25 ppm and with further increase in salinity its concentration falls, indicating strong selective removal. The plot of Ca against Na (Fig. 17) is very similar to that for Mg. The relation between SiO_2 and Na (Fig. 18) is complex and although the data are fewer, it appears that there is an initial increase in SiO_2 concentration with increasing Na to ~100 ppm SiO_2. The concentration of SiO_2 remains relatively constant with a further increase in Na until a concentration of ~4000 ppm Na, after which SiO_2 again increases. The pH closely follows the Na concentration (Fig. 19), rising to a maximum of 10.0 in Pan 3, which is saturated in trona.

Isotopic characteristics of the water

The $\delta^{18}O$ and δD values of the water span wide ranges (Table 2), with pan water being isotopically

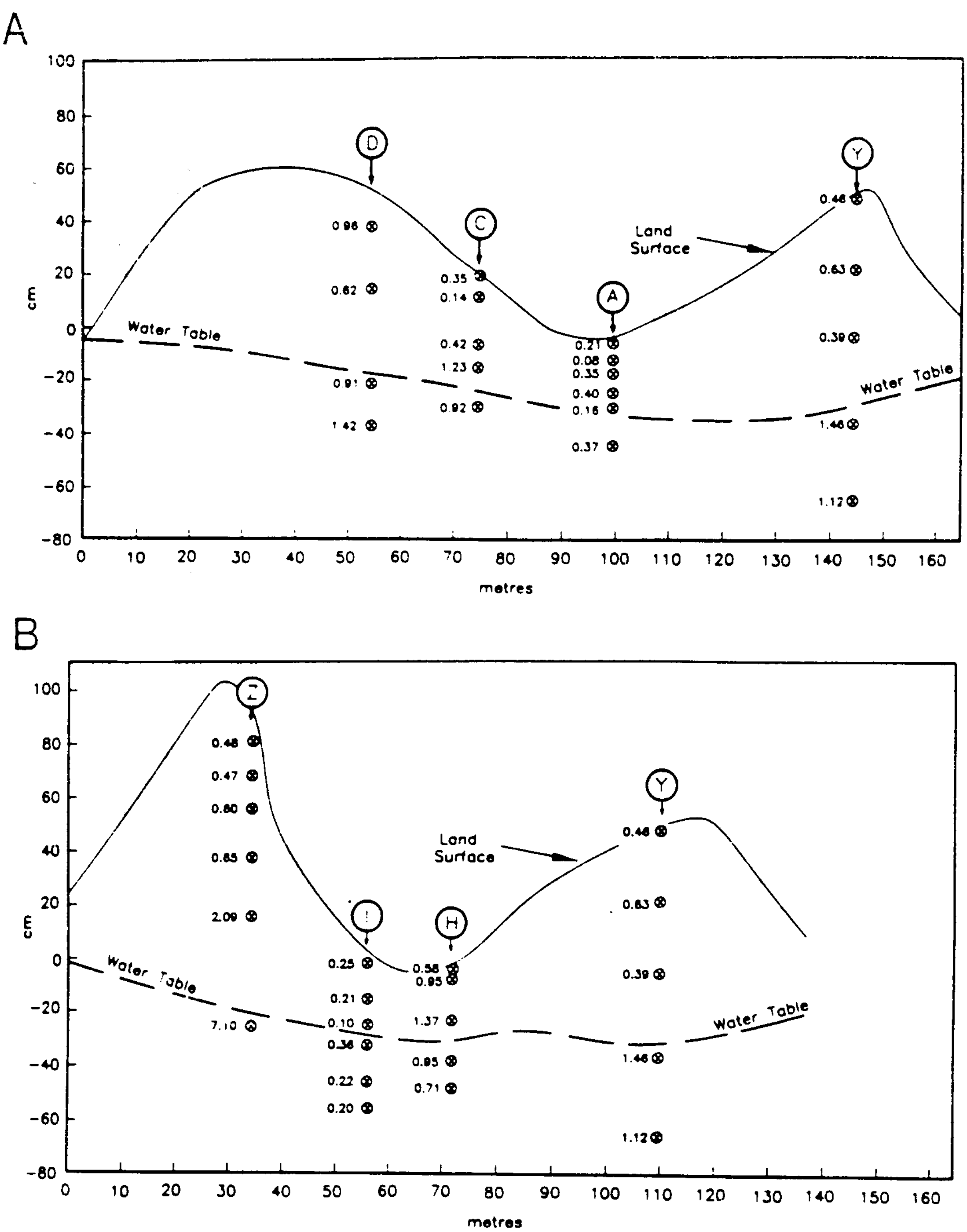

FIG. 10. Sections across the island showing the spatial distribution of Ca. Positions of the section lines are shown in Fig. 8.

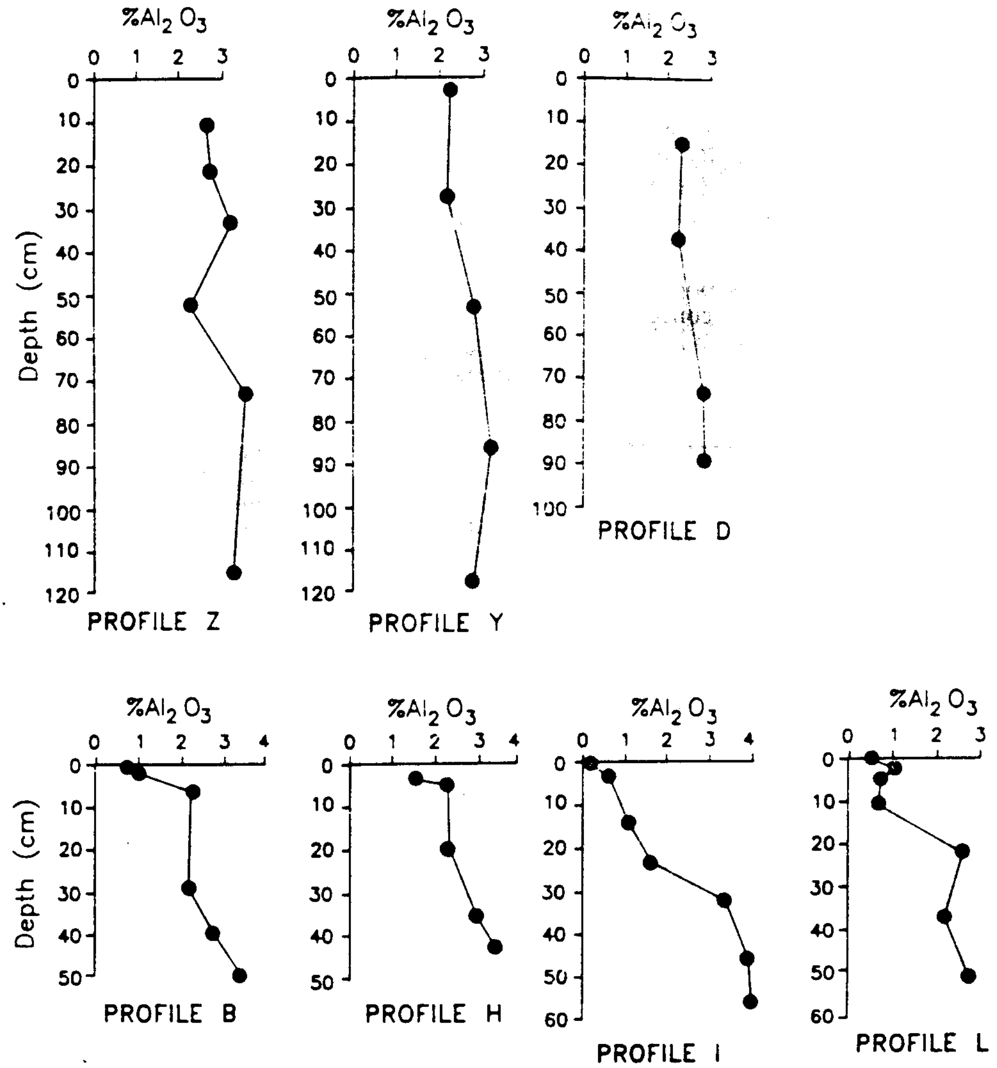

FIG. 11. Aluminium content in soils as a function of depth in selected soil profiles. Profiles Z, Y and D were collected from vegetated areas. Locations of the profiles are shown in Fig. 4.

heavier than groundwater. The results are plotted on a δD–$\delta^{18}O$ diagram in Fig. 20. Also shown as reference are the global meteoric water line and the "Okavango evaporation line" of DINCER *et al.* (1981). The results for samples taken at various times from closed water bodies and from rivers in the southern part of the Okavango system and the north-central Kalahari, obtained by MAZOR *et al.* (1977) are shown for comparison. Seen in this context the swamp, pit and pan samples from the island fall within the general pattern of evaporation for the swamp system. The pan samples reach the extreme enrichments observed in the residual water in Lake Xau (north-central Kalahari) just before complete desiccation. On a plot of salinity against $\delta^{18}O$ (Fig. 21), two groups are evident. Groundwater shows elevated salinities but with a limited range of $\delta^{18}O$ and is similar to local swamp water. In contrast, the saline surface water shows elevated $\delta^{18}O$ relative to groundwater of the same salinity, spans a greater range of values, and shows indications of a correlation between salinity and $\delta^{18}O$. It is of note that the $\delta^{18}O$ values of water from Pans 2 and 3 are similar ($\sim +17$) in spite of an order of magnitude difference in their salinities. This suggests that these water bodies may have attained an equilibrium condition in terms of evaporative isotopic fractionation.

DISCUSSION

The water table beneath the island slopes toward the central depression where it emerges at the surface producing active seepage zones around the smaller pans (Fig. 6). It follows, therefore, that at the time of the study, evaporation from the pans and from the capillary zone surrounding the pans exceeded the rate of inflow of water from the surrounding swamps, causing drawdown of the water table. Further, steady subsurface flow from the swamp toward the central depression was taking place, indicated by seepage zones around the pans. The study was carried out in August, mid-way through the long, dry season. During the summer rains (January–March), the pans accumulate rain water and a large proportion of the central depression becomes inundated (H. Robertson, pers. commun., 1989).

The groundwater around the area of the pans is not low salinity swamp, but is highly enriched everywhere in dissolved solids relative to the surrounding swamp (Table 1). This indicates that processes are operative which enrich the water in dissolved salts before it appears at the surface via seepage. This process clearly does not produce significant isotopic fractionation (Fig. 21).

The chemical evolution of the water is discussed conveniently in the context of Figs 14–18. EUGSTER and JONES (1979) and EUGSTER (1980) have described the application of similar plots in water evolution studies. In his work on trona lakes, Eugster has chosen to use Cl as the conserved species to monitor progressive evaporative concentration, because Cl remains in solution until the brine saturates in a Cl phase which occurs at a very late stage. EUGSTER (1980) points out that Na is also conserved in these lakes until a Na-bearing phase (usually trona) precipitates and hence could also be treated as a conserved element. In the present study, it has been noted that Na enriches preferentially to Cl (Fig. 14). Further, a plot of K against Cl shows unit slope, implying equal rates of enrichment, but there are indications that K is being removed from the groundwater to form K-feldspar. It is, therefore, concluded that Cl is not conserved in the water of the study

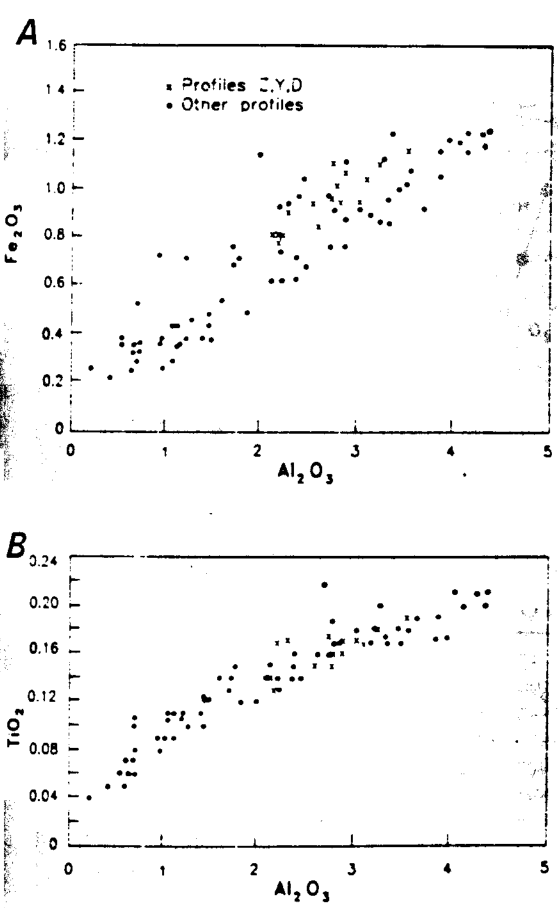

Fig. 12. (a) Fe_2O_3 vs Al_2O_3; (b) TiO_2 vs Al_2O_3.

island. For this reason, Na has been chosen as the conserved element rather than Cl. Its use in this context is applicable only up to the point where the water becomes saturated in trona. In this study, only the water in Pan 3 was found to be saturated in trona, but even in this water, the Cl/Na ratio has not been fractionated strongly (Fig. 14), indicating that only a small amount of trona could have formed from this brine.

Over the Na concentration range from swamp water (3–5 ppm Na) to 10 ppm Na, a concentration factor of about threefold, all dissolved species increase in concentration. Beyond this point, SiO_2 remains constant, indicating removal of a SiO_2-bearing phase. Calcium and Mg continue to increase in abundance with increasing Na but their concentrations peak at ~50 ppm Na, and with further increase in Na concentration, both Mg and Ca concentrations decrease. This indicates saturation in a single mineral phase (EUGSTER and JONES, 1979), in this case undoubtedly magnesium calcite. Potassium is enriched continuously, together with sodium, but at a slower rate, indicating continuous removal. EUGSTER (1980) suggested that cation exchange may remove K, but in the present case it seems more likely that K removal is the result of the formation of K-feldspar and possibly biological activity. At higher salinities, the content of dissolved SiO_2 increases again. EUGSTER and JONES (1979) attribute a pattern such as exhibited by SiO_2 (Fig. 18) to the formation of a compound, the precipitation of which is controlled by some other species. This seems unlikely in the present case. While feldspar does form, the quantity of SiO_2 removed is far greater than can be accounted for by feldspar formation alone. EUGSTER (1980) noted a similar behaviour for SiO_2 in the Lake Magadi area, which he attributed to buffering by volcanic glass. In the present case, the behaviour of SiO_2 may be due to a combination of precipitation of amorphous SiO_2 and buffering by an amorphous mineral such as allophane, but this is speculative.

All groundwater and surface water sampled in this study, including that from beneath the vegetated fringe, has salinities exceeding the saturation points of both calcite and amorphous SiO_2. This implies that some process operates which causes enrichment of dissolved salts in the groundwater as it flows from the swamp, beneath the heavily vegetated fringe and on toward the central depression. This process cannot be capillary-driven evaporation because such a process would lead to the local accumulation of the most soluble salts (sodium carbonates) in the soil profiles around the marginal zones of the island, which is not observed (profiles D, Y and Z, Fig. 13). Further, these areas are topographically elevated and heavily vegetated, both of which would tend to suppress capillary evaporation. Moreover, $\delta^{18}O$ and δD values are not influenced by this process, which also suggests that evaporation is not the cause.

It is conceivable that rain water could contribute to

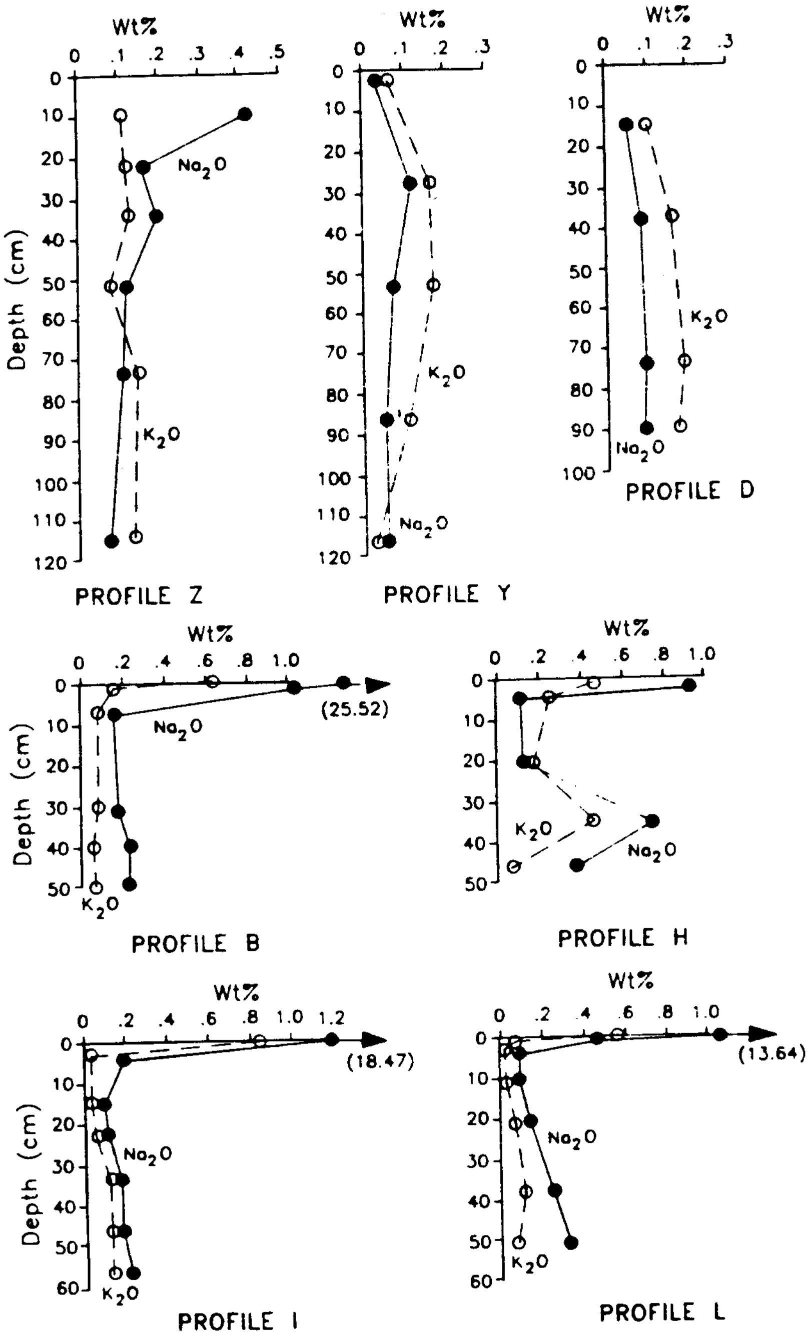

FIG. 13. Sodium and acid-soluble K in selected soil profiles as a function of depth. Profiles Z, Y and D were collected from vegetated areas. Locations of the profiles are shown in Fig. 4.

Table 2. Chemical and isotopic composition of groundwater and surface water

	pH	Na	K	Ca	Mg	Cl	SO_4	SiO_2	HCO_3	CO_3	TDS	Density	$\delta^{18}O$	δD
Swamp	7.40	5	3	6	1	5	5	13.3	37	0	45	0.9983	−0.92	−16.8
Pan 1	8.60	410	114	13	19	56	5	82	790	193	1250	0.9994	+4.88	+13.6
Pan 2	9.80	16,000	1560	2	1	2600	380	332	7583	15,598	33,200	1.0378	+17.40	+73.3
Pan 3	10.00	115,000	8700	1	1	6400	1700	1712	6572	140,200	240,000	1.2378	+16.96	+56.7
Pit A	9.50	4500	825	4	1	830	211	86	5907	2498	9500	1.0096	+0.75	−12.8
Pit C	9.10	620	148	10	17	12	5	93	891	385	1600	1.0002	−0.73	−15.9
Pit E	8.70	140	91	15	13	5	5	112	306	124	600	0.9987	−0.79	−22.1
Pit F	9.00	350	77	14	17	8	5	123	632	193	1100	0.9993	−0.55	−16.8
Pit H	8.60	78	56	28	34	5	5	131	301	56	500	0.9987	+0.21	−12.0
Pit I	9.50	2600	375	2	1	157	50	64	1548	2610	5800	1.0045	−0.20	−11.4
Pit K	9.30	4400	129	8	7	220	50	60	2970	3729	8100	1.0084	+0.53	−9.0
Pit L	9.60	6500	172	8	1	440	50	115	2338	6960	13,600	1.0130	+1.08	—

Concentrations in ppm, isotopic compositions in per mille.

elevated salinity in the groundwater beneath the island, in the following way. Rain water would dissolve surface trona crusts and accumulate in the pans where it may mix with saline pan water. This saline water could then seep into the ground under the hydraulic head of the flooded pan, producing a lens of saline water beneath the island. This possibility is discounted for two reasons. Firstly, it is highly improbable that the oxygen isotopic compositions of a random mixture of rain water ($\delta^{18}O \approx -5‰$) with pan water ($\delta^{18}O = +17‰$ in Pans 2 and 3) would be identical to that of swamp water. Secondly, a mixture of pan water and rain water which had dissolved trona crusts would have a lower Ca content than observed in the saline groundwater. Hence, it can be concluded that rain water has not contributed significantly to the high salinity groundwater beneath the island.

It seems more likely that the enrichment in dissolved solids occurring beneath the elevated margins of the island is caused by transpiration, particularly by the trees. The roots of these trees probably extend below the water table and they selectively remove water, causing progressive enrichment in total dissolved solids. This inference is supported by the absence of oxygen isotopic fractionation in spite of increasing salinity, because plants are known to abstract water without causing isotopic fractionation (GAT, 1981).

It is also probable that the plants remove selectively a proportion of certain of the dissolved species, notably K and possibly Cl as well. The resulting increase in total salinity results ultimately in saturation in amorphous SiO_2 and calcite. By the time the groundwater emerges from the vegetated margins of the island in its flow toward the central depression, it is already well beyond the saturation point of SiO_2 and calcite. Hence, much of the precipitation of these constituents would occur in the soils beneath the vegetated margins of the island. Reference to Fig. 10 indicates that the soils in these areas are indeed enriched in Ca. Following the suggestion of MCCARTHY and METCALFE (1990), it may well be that the elevated margins of the island are due to the precipitation of carbonate in the soils, which results in volume increase. Lignins, produced by decaying organic material, are dissolved by the water and are carried toward the central depression. Because of their high solubility, the abundance of lignins in the water increases with increasing salinity.

Once the groundwater seeps into the pans, it becomes subject to evaporation and, accordingly, isotopic fractionation occurs, with further increase in salinity (Fig. 21). The $\delta^{18}O$ appears to attain a steady-state condition at about +17‰ but this value must depend on a complex interaction between inflow, evaporation, rain dilution and salinity.

The soils around the central depression in which the pans are situated show a marked surface enrichment in alkali carbonate accompanied by lignin staining, indicative of terminal evaporation of water in the capillary zone around the pans. There are, however, marked vertical gradients in soil chemistry, particularly in Al (and Fe and Ti), which are not present in the soils from the marginal areas (profiles D, Y and

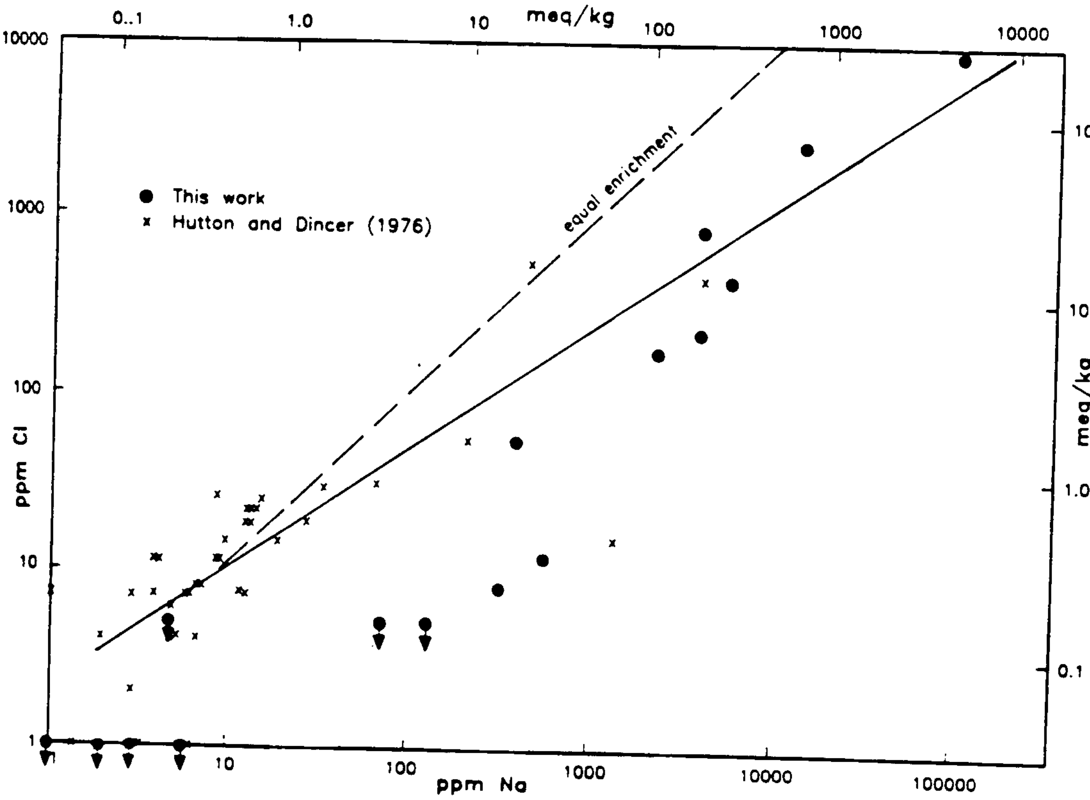

FIG. 14. A plot of abundances of Cl against Na for groundwater and surface water.

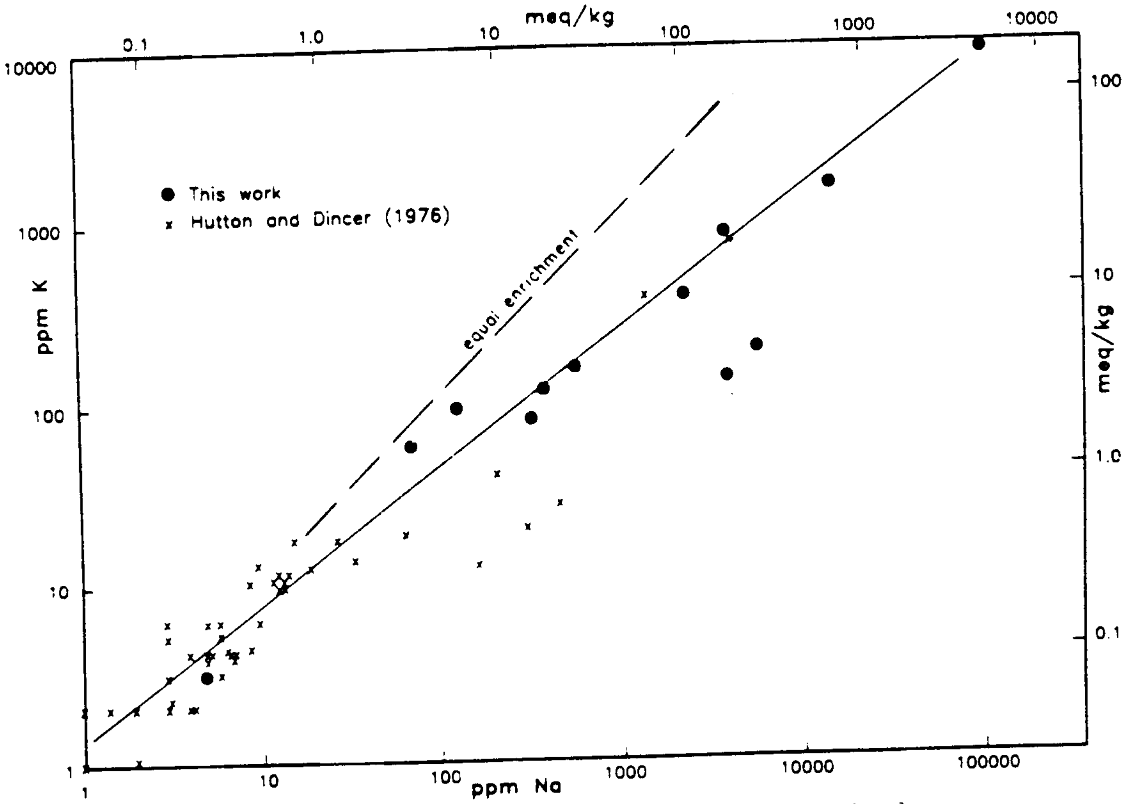

FIG. 15. A plot of abundance of K against Na for groundwater and surface water.

Z. Fig. 11). In contrast, Ca and Mg show no strong vertical gradients in soils in the central area. These vertical gradients could not be caused by capillary-driven evaporation in the capillary zone because this process operates only in an upward direction, whereas the gradients in Al suggest downward movement. The somewhat higher concentration of Al in the deeper soils of the central zone, relative to the

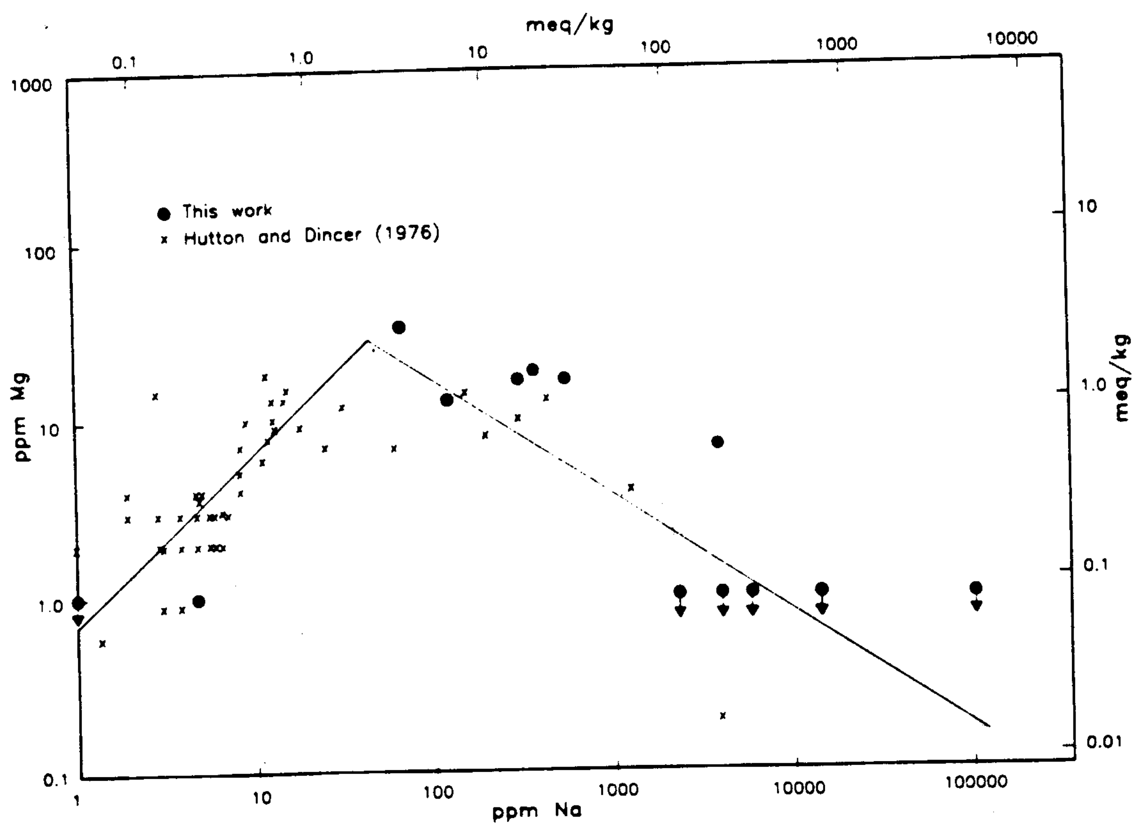

FIG. 16. A plot of abundances of Mg against Na for groundwater and surface water.

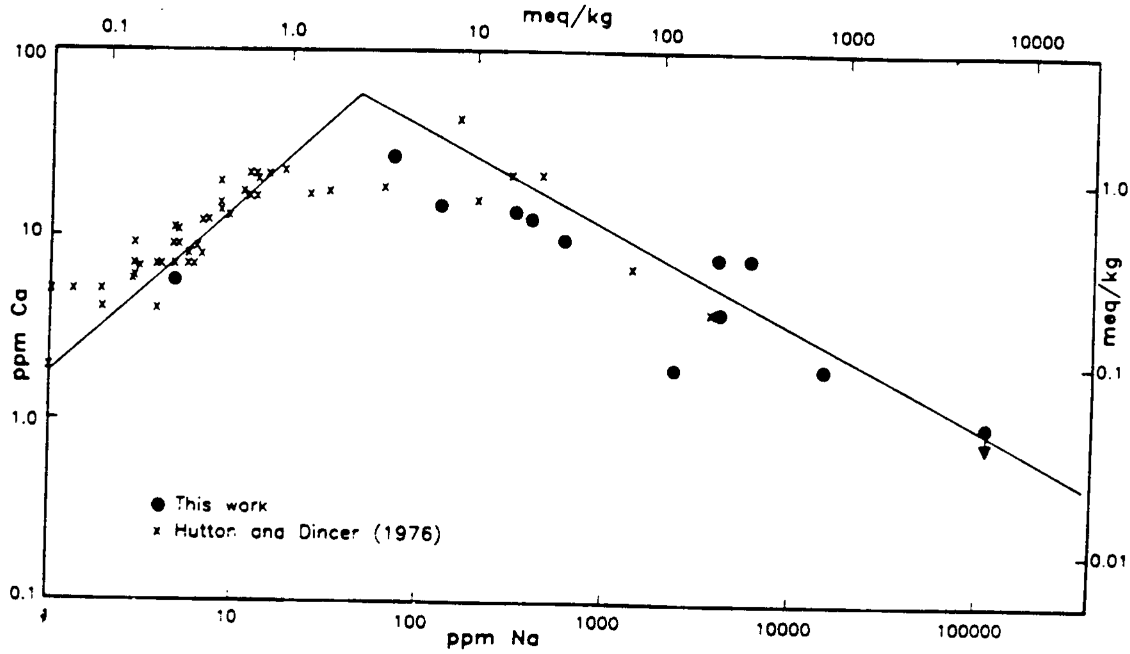

FIG. 17. A plot of abundances of Ca against Na for groundwater and surface water.

margins of the island (Fig. 11), even suggests the accumulation of Al in the former. Such downward leaching may be related to the accumulation of rain water in the central depression. Rain water would dissolve surface trona, producing a very alkaline solution which would be more dense than swamp water. Downward percolation of this water could leach Al, Fe and Ti into the soil profile. The absence of any isotopic signature of rain water in the groundwater indicates that rain water which enters the groundwater regime in this way is completely evaporated during the long dry period following the summer rains.

Mineralogical investigation of the soils suggests that the dominant host for Al is kaolinite but, in addition, small crystals of K-feldspar were noted and probably formed *in situ*. The formation of K-feldspar has also been recorded in the sediment beneath the trona-rich Searles Lake of California (HAY and MOIOLA, 1963). In the soils of the central depression, there is an increase in the amount of acid-insoluble K, suggesting an increase in the abundance of K-feldspar in these soils. Mass balance calculations indicate that the formation of this mineral alone cannot account for the increased Al content. For example, if the increase in insoluble K in profile I from 0.19 to 0.43 wt% were due entirely to an increase in K-feldspar content, the corresponding

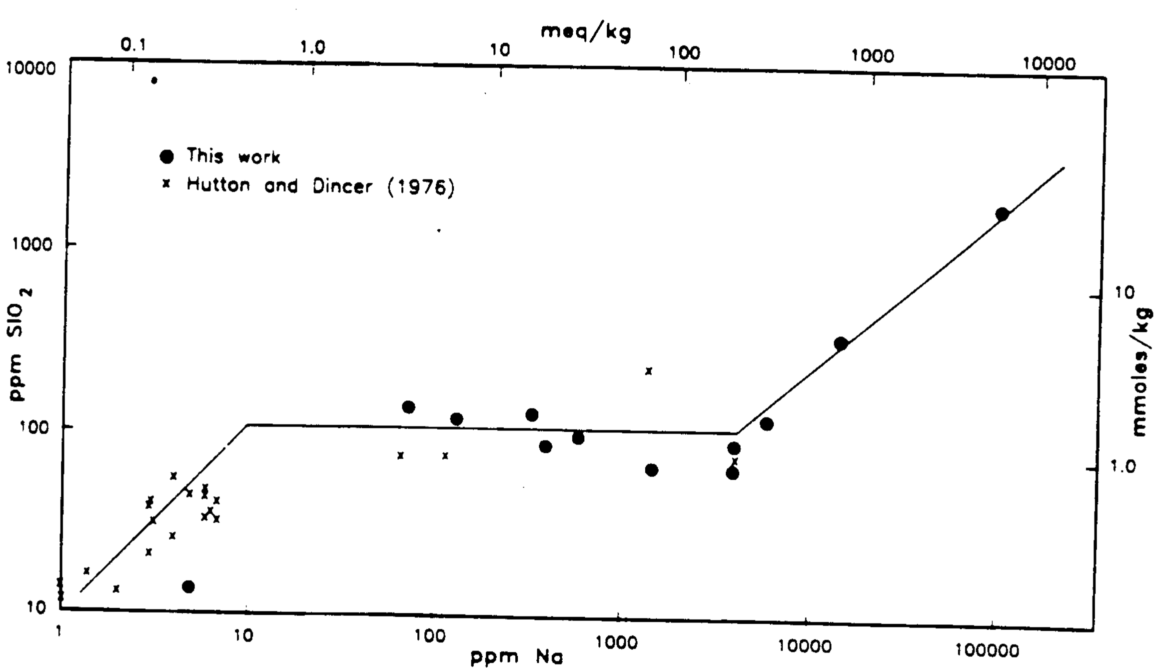

FIG. 18. A plot of abundances of SiO_2 against Na for groundwater and surface water.

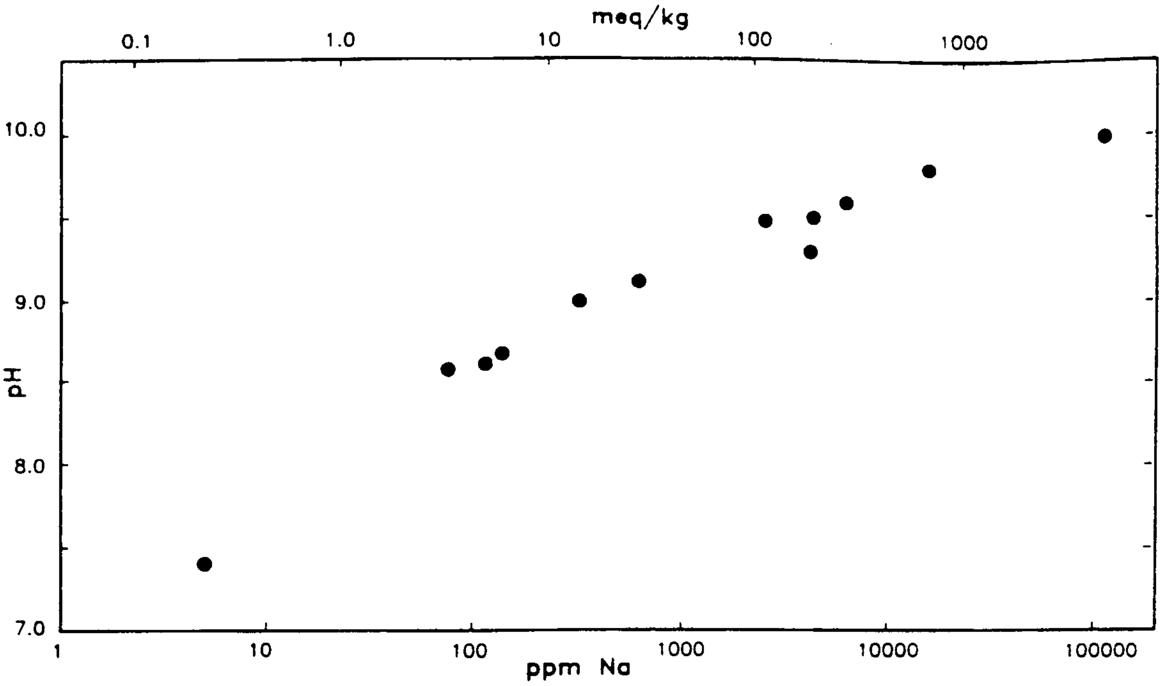

FIG. 19. The relation of pH to Na in groundwater and surface water

increase in Al_2O_3 would be 0.26%, compared with the observed increase of 3.31% (Table 1). Because there is no major change in the X-ray diffraction patterns of the deep soil compared with the near-surface soil, it seems likely that most of the leached Al is precipitatiing in an amorphous form, possibly allophane.

The data collected in this work suggest that during groundwater flow from the swamp toward the central depression, initial enrichment in dissolved solids occurs by transpiration, and indeed transpiration appears to be at least partly responsible for the lowering of the water table, which makes the flow possible. Saline water produced by transpiration seeps into the central pans where strong evaporative concentration occurs. Evaporation from the soil surface lying within the capillary zone around the pans causes the development of trona crusts. These relations are illustrated in the schematic cross-section of a portion of the island, shown in Fig. 22. Through-

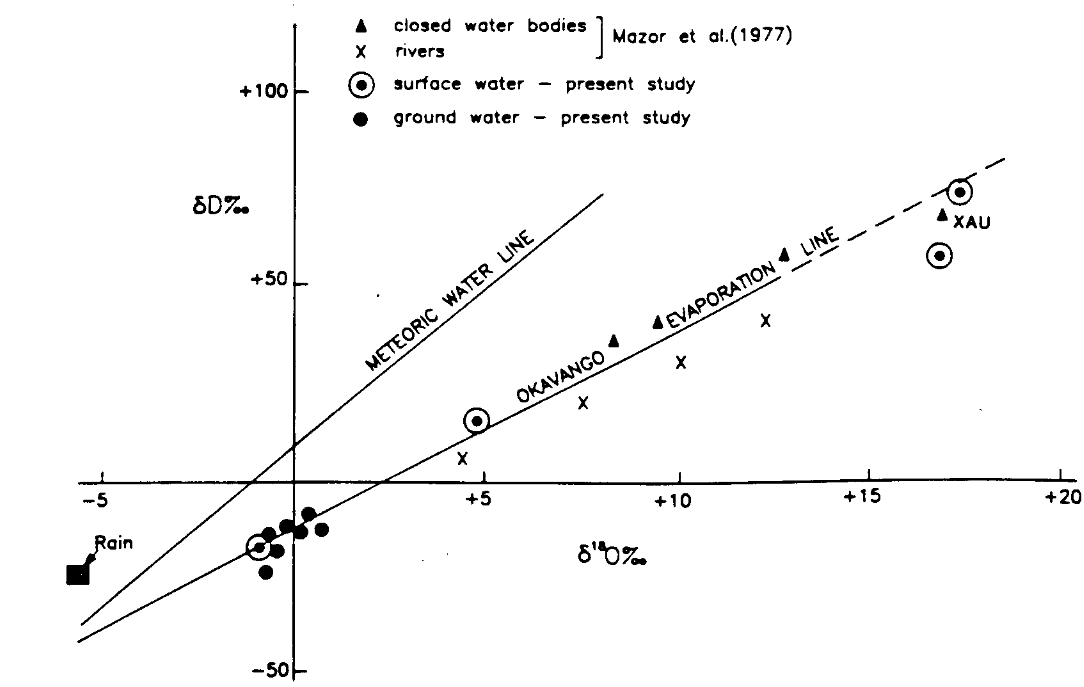

FIG. 20. Plot of δD vs $\delta^{18}O$ showing values for swamp, pit and pan samples from this study. Also shown are the meteoric water line ($\delta D = 8\,\delta^{18}O + 10$) and the "Okavango evaporation line" ($\delta D = 5.1\,\delta^{18}O - 11$) of DINCER *et al.* (1981). Shown for comparison are values for the southern Okavango system of MAZOR *et al.* (1977) obtained for closed water bodies and rivers.

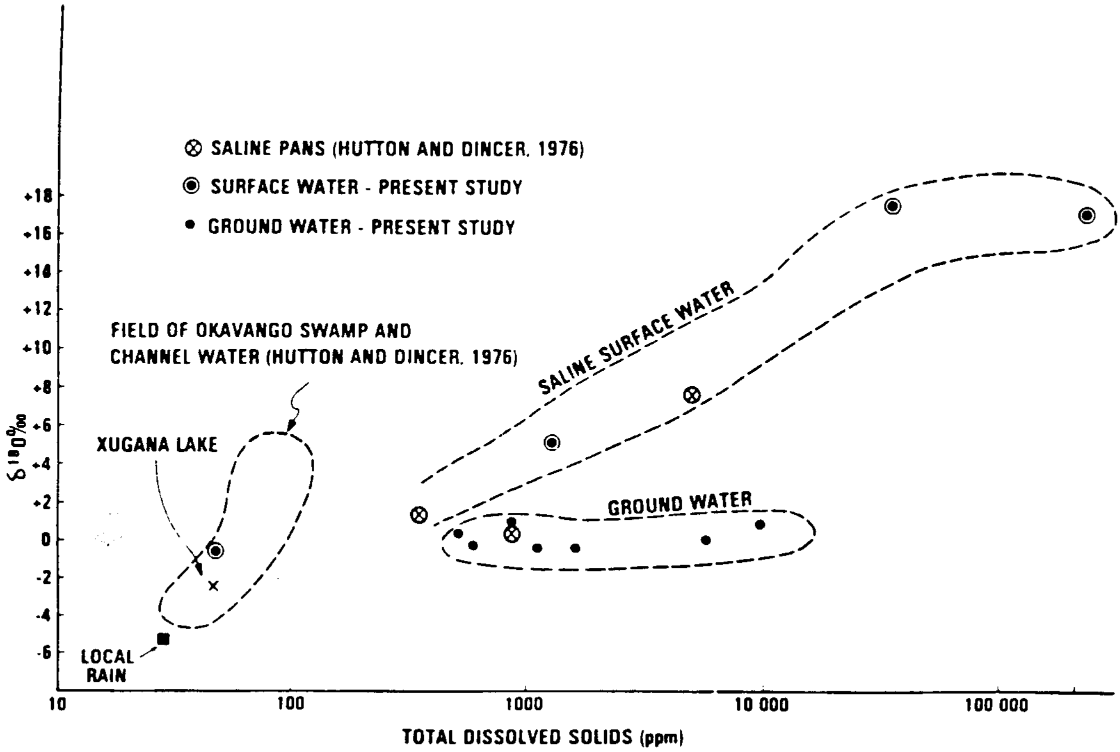

FIG. 21. A plot of total dissolved solids vs $\delta^{18}O$ for selected water samples from the Okavango region.

out this progressive enrichment in dissolved solids there is a concomitant increase in density of the brines (Table 2). Maximum increase in density occurs in the pans. Although the soils are rather fine grained, it is possible that these dense brines might percolate slowly downward, displacing less saline water below.

In spite of high evapotranspiration in the delta as a whole, extreme concentration of dissolved salts is observed only in groundwater and surface water of islands, particularly in the permanent swamps, and large saline lakes are not developed in the delta. A combination of seasonal flooding, uptake of solutes in peat (McCARTHY *et al.*, 1989) and probably groundwater leakage from the Okavango graben ensures that surface water in the swamps remains fresh (McCARTHY and METCALFE, 1990). In contrast, in the groundwater regime of the islands in the

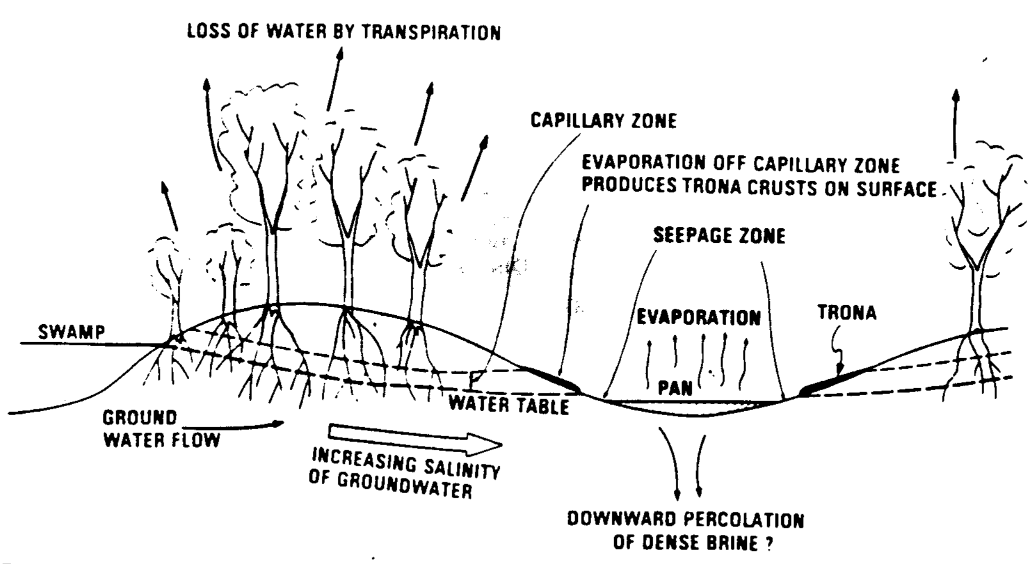

FIG. 22. Schematic cross-section of a portion of the island illustrating the processes inferred to operate which lead to brine development. Transpiration by trees and evaporation from the pan cause drawdown of the water table. Swamp water enters the groundwater regime and flows toward the central depression becoming progressively enriched in solutes owing to selective removal of water by transpiring vegetation. Saturation in magnesium calcite and SiO_2 occurs beneath the vegetated zone, leading to the localized accumulation of calcite and amorphous SiO_2. Evaporation from the capillary zone in the area around the pans causes trona precipitation at the surface. Groundwater enters the pan by seepage, where strong evaporative concentration occurs, producing dense brines which may percolate into the subsurface, displacing less-saline groundwater, and causing downward leaching of Al, Fe and Ti.

permanent swamps, water is held in the intergranular spaces and in isolated pans, and hence residence times of the water in the active evapotranspiration zone are far longer, allowing for the development of high-salinity brines.

CONCLUSIONS

The results of this study indicate an important interaction between the swamp and the island groundwater system which has implications for the evolution of islands in the permanent swamps. Water is lost from the islands by evaporation and especially by transpiration and is replaced by inflow from the swamp. Along the vegetated fringe, water loss is mainly by transpiration. This process increases dissolved salt content in the groundwater, leading to saturation in calcite and SiO_2 in this zone. Extensive precipitation of SiO_2 and especially calcite therefore occurs under the vegetated fringe. This may have the effect of raising the land surface, as suggested by McCarthy and Metcalfe (1990), and may be responsible for the elevated topography along the margins of the islands. Decaying roots, and possibly leaching of leaf litter, add lignins to the groundwater. Groundwater emerging from the vegetated fringe and flowing toward the central depression is, therefore, fairly saline, although depleted in Ca, SiO_2 and Mg. Along the barren, central axis of the island, evaporation must be the dominant process. This is in part capillary evaporation, leading to the development of surface crusts of trona and thermonatrite and to surface lignin staining. Groundwater emerges in the central pans, where extreme evaporative concentration occurs, leading ultimately to saturation in sodium carbonate. As salinity increases, density also increases, and it is possible that this very saline pan water may percolate downward, displacing lower salinity groundwater. The island may thus create a circulation system where fresh water enters from the marginal areas, becomes progressively more saline as it flows toward the central depression and finally sinks down into the subsurface beneath the central zone of the island as a hypersaline brine.

Accumulation of rainfall in the central depression seems to have a marked effect on the soils causing downward leaching of Al (and Fe). These constituents precipitate in the deeper soil horizons, possibly as amorphous allophane. In addition, K is lost to the soils by the formation of K-feldspar.

The fact that the centre of the island is at a lower elevation than the surrounding swamp water level warrants comment. Initially, the elevation of the entire island may have been above the swamp and the island entirely vegetated. During evolution of the island, the margins may have risen owing to carbonate and SiO_2 precipitation, while the interior was less affected by this process. Progressive increase in salinity in the central region of the island would eventually have killed the vegetation, leading to a change in this region from transpirative to evaporative processes. Progressive rise in the level of the water in the surrounding swamp (Fig. 3), and deflation of the increasingly barren central region, would lead ultimately to the present situation in which the swamp water level is higher than the land surface in the centre of the island.

The processes inferred to operate on the islands lead ultimately to the destruction of the vegetation. However, their effects are very localized and operate only as long as a ready supply of swamp water is available. Major shifts in water distribution cause swamp abandonment and it is likely that islands affected by salt accumulation are able to recover (McCarthy and Metcalfe, 1990). However, hypersaline sodium carbonate brines may be accumulating in the subsurface, which could pose a major environmental threat in the future.

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