Carbonate accumulation on islands in the Okavango Delta, Botswana

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Efflorescent crusts consisting predominantly of the sodium carbonate minerals trona [Na,CO,NaHCO,2H,O] and thermonatrite [Na2CO3.H2O] with minor sylvite [KCl] are commonly developed on less vegetated portions of islands in the Okavango Delta where the land surface is less than about one metre above water level. This efflorescence represents the end product of evaporation of swamp water. At intermediate stages of evaporation, small calcite [CaCO] crystals are produced. These are brought to the surface by ants for the construction of termitaria, degradation of which produces concentrations of calcite on the surface. The low total dissolved solid content of swamp water. suggests that evaporation of swamp water occurs predominantly from islands. Carbonate build-up will have a major impact on the Okavango ecosystem in the future.

Effloresserende korste wat hoofsaaklik uit die karbonaatminerale trona [Na2CO3.NaHCO3.2H2O] en termonatriet [Na2CO2.H2O] naas kleiner hoeveelhede silviet [KCl] bestaan, ontwikkel gewoonlik op die minder begroeide dele van eilande in die Okavango-delta waar die landoppervlak minder as 'n meter bo die watervlak is. Dié effloresserende kors is die eindproduk van die verdamping van moeraswater. Tydens tussenstadiums in die verdamping vorm klein kalsietkristalle [CaCO3] wat deur miere na die oppervlak gebring word om termietneste mee te bou, maar wat later kalsietopeenhopings op die oppervlak lewer as die miernesse tot niet gaan.

The Okavango river, the catchment of which is situated in the highlands of central Angola, discharges into the closed, internal framage system known as the Kalahari Basin. The waters disperse o form the Okavango Delta, situated in northern Botswana,

which is probably the largest delta of its type in the world. In the upper reaches of the delta, the Okavango river is confined in a relatively narrow, fault-bounded graben, known as the 'panhandle'. At the southern end of the panhandle, the Okavango divides into several secondary distributaries, which further subdivide down the delta. Topographic gradients within the delta are remarkably small: fall in land surface from the southern end of the panhandle to the toe of the delta, a distance of some 150 km, is only 45 metres.

The secondary, tertiary and higher order distributaries in the delta are relatively narrow, and cannot accommodate the annual flood waters of the Okavango river. Consequently, there is considerable overspill of a permanent nature in the upper portions of the delta, and seasonal in the lower portions. The water surface area at peak flood (July-August) constitutes some fifty per cent of the total area of the delta. Channels amount to some one per cent of the area. The remaining area, some forty-nine per cent of the total, consists of islands, which range in size from individual ant hills to the largest, Chiefs Island, which is some 60 km long and 20 km wide.

In the northern areas, islands consist of alluvial sand, and the distribution of islands suggests that they owe their origin to fluvial processes. However, in the southern portion of the delta, the islands may consist largely of aeolian sand, and appear to have resulted from inundation of an essentially aeolian landscape.

The vegetation on the islands is surprisingly sparse, consisting of tall trees, especially palms (Hyphaenae) with grass cover (Eragrostis, Cynadon and Sporobolus). Many of the islands contain pan-like depressions in which seasonal standing water, fed by ground-water seepage, occurs.

The majority of the islands are characterized by the development of a white, efflorescent crystal growth. This generally occurs on the fringes of islands as well as on the margins of pans, but occasionally may be found in the interior of smaller islands. The crystal layer is termed 'ntsongo' by the local Batswana. This phenomenon prompted the investigation, the results of which are reported in this communication. During the course of examining this efflorescence, we noted that, in addition to the usual sand-size material which forms the islands, local accumulations of fine, pale brown, powdery material were also present. These are sedimentologically unusual, and accordingly were also investigated.

Occurrence and mineralogy

The efflorescence occurs on the margins of islands and pans as well as on low-lying islands. It consists of a white crust which develops on the sandy surface and on any porous material (e.g. wood) embedded in the sand. It occurs only in regions which are less than about one metre above water level, thus being generally close to the water's edge. The underlying sandy substrate is often damp. The development of efflorescence is confined to areas where vegetation cover, both grass and trees, is sparse, i.e. in areas which receive full sunlight for most of each day. General-

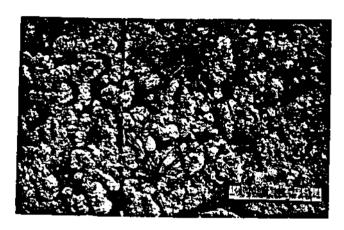


Fig. 1. Efflorescent growth of trona and thermonatrite amongst tufts of Sporobolus grass. Some sections of the evaporite crust have contracted into domical structures.

ly, the only vegetation growing in areas where crystals occur is a coarse, somewhat stunted grass [Sporobolus spicatus (Vahl) Kunth]. The surface crust usually has a pitted appearance, possibly due to dissolution by dew. Normally the crusts are white, but are sometimes stained brown by an organic agent. The crusts often exhibit contraction effects and in part detach from the underlying sandy substrate as small circular or elongate domelike features (Fig. 1). This is especially the case where the salts have grown in footprints (Fig. 2). Soil pH measurements were taken in the sand taken from beneath the white surface evaporite crusts. A pH of 10,6 was recorded in the upper five centimetres, whereas at a depth of 50 cm a pH of 9,4 was recorded.

Optical studies supplemented by X-ray diffraction techniques permitted identification of the surface evaporite minerals as trona (Na₂CO₃, NaHCO₁,2H₂O) and thermonatrite (Na₂CO₃,H₂O) together with minor sylvite (KCl). Previously, a UNDP project reported merely that the white efflorescence consisted of sodium carbonate and bicarbonate. Within the evaporite crusts vertical trona needles, typically three to four millimetres in length, are capped by a dull white, very fine-grained intergrowth of trona and thermonatrite. Investigation of the sand substrate indicated the presence of the carbonates trona and calcite (CaCO₄). The calcite occurs as a finely divided intergranular phase together with associated small needles of trona. No thermonatrite was encountered in subsurface samples.

Surface accumulations of calcite-rich material are, however, locally present as fine powder in the form of low mounds often occurring around the base of abandoned anthills. The mound

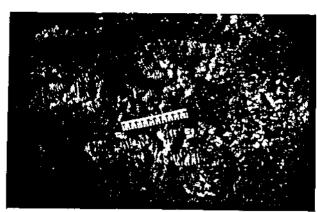


Fig. 2. Evaporite growth in footprints.

material comprises a mixture of quartz grains and powdery, vo finely divided calcite. Size analysis of this material reveals i distinctly bimodal character, which contrasts markedly with it typical island sand (Fig. 3). Mineralogically the coarse potting of the mound material consists of quartz with the finer portion (below 43 μ m) consisting essentially of calcite. Because of the cla spatial association of powdery calcite-rich accumulations wit anthills, samples of local anthills were investigated by means. petrographic thin-section study and X-ray diffraction. In thin sq tion (Fig. 4) the anthill material is revealed as consisting of assemblage of rounded quartz grains secured by a mortar of find divided calcite and a semi-opaque phase. Diffraction studies the $-43 \mu m$ fraction of lightly crushed anthill showed ti presence of a poorly defined but persistent diffraction peaks 4.45 Å in addition to the characteristic reflections pertaining quartz and calcite. No ready explanation for the presence of the peak, which was also observed in some substrate samples, w initially forthcoming until a study was made of the organic-rif mud-like accumulations of sediment trapped within papyn stands. In addition to an organic phase, these accumulations we found to consist of an assemblage of clay minerals dominate by kaolin accompanied by minor illite and smectite together will traces of quartz. The development of peat from organic materi relating to plant growth is widespread within the Okavango are It is also well known that spontaneous combustion of dry pa takes place at intervals. In burnt-out peat areas an inorgani

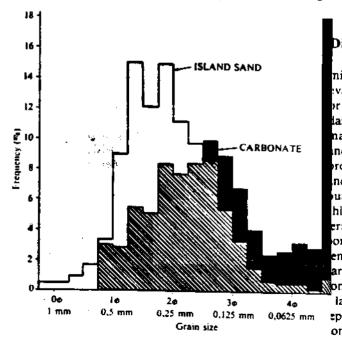


Fig. 3. Size distribution of fine-grained carbonate and a typical sand.

residue comprising a very fine-grained compact soil material is abundant. Diffraction study of this material showed it to be essentially isotropic to X-rays except for a diffuse reflection at 4,45 Å, a weak diffuse reflection at 3,52 Å and a weak indication of the presence of quartz.

These diffuse reflections are characteristic of kaolin heated to dehydration temperature, resulting in the formation of metakaolin. According to Grimm, dehydration of kaolin takes place between about 400 and 525°C with the lower temperature range being favoured by small particle size and poor crystallinity. X-ray study of heated organic-rich material from the Okavango papyrus stands showed a breakdown of the kaolin structure between 350 and 400°C, with the heated samples yielding diffraction patterns similar to those given by the soil materials from the burnt-out peat areas. A minimum temperature of about 400°C may thus be assumed for the subsurface burning of peat-clay accumulations. It appears further that metakaolin of local derivation is present as a dispersed phase in the Okavango sands, and, being a water insoluble material, was employed together with finegrained quartz and calcite in the construction of the mortar phase of the anthills. Degradation of anthills can accordingly account for the presence of calcite-rich mounds situated well above the water on the islands.



Fig. 4. Photomicrograph showing the construction details of an ant hill where quartz grains (white) are cemented by a mixture of fine-grained interstitial calcite and an opaque phase. Plane polarized light.

Discussion

Trona is one of the most common non-marine evaporite minerals and is widespread in alkaline lakes formed by severe evaporative concentration of springs or rivers draining igneous or metamorphic terranes. 57 Such waters typically contain abundant bicarbonate or carbonate, calcium, alkalis and in some cases magnesium and silica. Depending on the source rocks, sulphate and chloride may occur in greater or lesser amounts. The end products of evaporation depend critically on initial composition. and end products may be dominated by carbonates with or withbut chlorides, or sulphates with or without chlorides or simply phlorides. Carbonate-chloride producing systems are characterized by an initial composition in which carbonate and bicarponate are dominant over sulphate and chloride. Evaporative concentration results initially in saturation with respect to calcium arbonate (calcite), which effectively maintains calcium at low concentration in the solution. Magnesium and silica are lost at later stage of concentration, generally by the precipitation of epiolite (Mg₂Si₂O₈.H₂O). Finally, sodium carbonates and bicaronates are precipitated, followed by halides.

Crystallization of sodium carbonates and bicarbonates from atural waters is subject to control by dissolved CO₂ and imperature (Fig. 5). In addition, kinetic effects, especially those

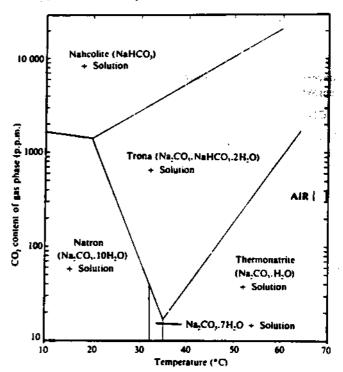


Fig. 5. Sodium carbonate phases in equilibrium with a saturated solution as a function of CO₂ content of the gas phase and temperature. (After ref. 9)

governing equilibration between dissolved and atmospheric CO_2 , are extremely important in determining the final form of the carbonates. The phase relationships illustrating the effects of evaporative concentration of sodium carbonates at 25°C are illustrated in Fig. 6.9 At higher temperatures, natron is replaced by thermonatrite (see Fig. 5). Evaporative concentrations under conditions of equilibrium with atmospheric CO_2 will follow path AB in Fig. 6. At B, trona will begin to crystallize. Crystallization of trona together with further evaporation should result in the solution composition moving towards C, i.e. it will cause a decrease in the HCO_3^-/CO_3^2 ratio, because this ratio in trona is greater than that in the solution. However, if equilibrium with atmospheric CO_2 is maintained, this ratio is buffered, and only trona is produced, because addition of atmospheric CO_2 stabilizes the HCO_3^-/CO_3^2 ratio as follows:

$$CO_3^{2-} + H_2O + CO_2 = 2HCO_3^{-}$$

Under conditions where atmospheric equilibration is inhibited,

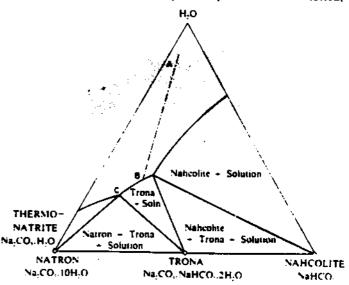


Fig. 6. Phase diagram for portion of the sodium carbonate, sodium bicarbonate, water system at 25°C. At higher temperatures, thermonatrite replaces natron. (After ref. 9)

i.e. where the HCO₃⁻/CO₃⁻ ratio is not buffered, path BC is followed, producing mixed thermonatrite and trona at C. The removal of HCO₃⁻ along BC under these conditions causes a marked rise in the pH, as the solution compensates for HCO₃⁻ removal by

$$CO_1^{2-} + H_2O - HCO_1^{-} + OH^{-}$$

In spite of this compensation, the HCO_3^2/CO_3^2 ratio falls well below that of atmospheric equilibrium (e.g. Fig. 5). The kinetics of equilibration are such that, during rapid evaporation, equilibrium with atmospheric CO_2 is normally not maintained.⁸

Surface waters of the Okavango Delta are dominated by carbonate and bicarbonate: these constituents amount to some 70% of the total, with sulphate and chloride making up the remainder. Cationic species are dominated by alkalis and calcium, together making up about 80% of the total. Magnesium makes up the remainder. Surface-fed ground-water is drawn up around the islands by capillary action and, provided the ground surface is below the top of the capillary fringe, evaporation takes place. This may be enhanced in areas of poor vegetation cover. Initially, the water becomes saturated with calcium carbonate, producing fine-grained calcite in the interstices between sand grains. Locally, this calcite actually cements the sand grains together. Rapid final evaporation of water near the surface initially induces saturation with respect to trona and finally with respect to both trona and thermonatrite, together with minor sylvite in the final stages. This is associated with an increase in soil pH towards the soil surface. Sulphate minerals have not been identified, possibly reflecting low sulphate abundance in the water. The fate of the magnesium has also not been ascertained, but it is likely that a magnesium-rich clay also forms in the subsurface sands along with calcite.

Because the islands typically consist of well-sorted alluvial (and in some cases aeolian) sands (Fig. 3), which lack natural cohesion, fine-grained materials necessary for the construction of termitaria are at a premium. The ants, therefore, evidently make use of the calcite precipitate, selectively bringing it to the surface where it concentrates as the anthill degrades.

Surface sodium carbonates examined in this study were observed during the winter months. It is likely that summer rains dissolve these carbonates and carry them downwards into the sandy substrate. Evapotranspiration in the delta exceeds precipitation by a factor of about three: therefore, there must be a net accumulation of these carbonates in the soils of the islands with time, although the surface expression of the evaporation may vary seasonally.

It is of some interest to examine mass balances relating to the accumulation of the sodium carbonates in the light of the hydrological model proposed for the delta. On the input side, a water influx of 10.5×10^9 m³/yr and precipitation of 5×10^9 m³/yr are proposed, while on the output side a loss due to evapotranspiration of 14.9×10^9 m³/yr, a surface outflow of 0.3×10^9 m³/yr and a ground-water outflow of 0.3×10^9 m³/yr are proposed. Total dissolved solids in waters entering the delta amount to about 40 p.p.m. (ref. 10).

The net addition of solids to the delta each year, in terms of these data, is therefore 4.2×10^5 tonnes. Assuming that some 4% is lost due to outflow (surface plus underground), the net addition of dissolved solids to the delta each year is around 4.0×10^5 tonnes.

Over a period of, say, one thousand years (probably much less than the age of the present delta), some 4.0×10^8 tonnes of dissolved solids will accumulate in the delta. In terms of the annual water input (inflow plus precipitation), this would yield a concentration of 2.6% total dissolved solids if all were taken up in solution, or about 1.5% if calcium and magnesium were removed. Yet total dissolved solids in surface waters of the delta (even near

to the toe) rarely exceeds 600 p.p.m., except possibly in ranisolated pans. Furthermore, ground water within the delta are is also of low salinity. These calculations imply that an extremely efficient mechanism exists for removing soluble salts from the hydrologic system, thus preventing their accumulation in the waters of the delta. The only plausible mechanism is one in which most of the evapotranspiration takes place through the island rather than from the standing water. Alternatively, the proportion of water lost by evaporation may have been grossly over estimated, which seems unlikely on the basis of available isotopicals.

Conclusions

Trona and thermonatrite, which crystallize as a surface of florescence on islands in the Okavango Delta, represent the en product of evaporative concentration of swamp water drawn within the sands by capillary action. In the process of evaporation, calcite precipitation occurs below the surface, together wissome trona, whereas trona and thermonatrite form above surface. Crystallization of salts raises the pH of near-surface sat to 10,6. Termites make use of small calcite crystals for the construction of termitaria on the islands, degradation of which lead to local surface concentrations of calcite.

In terms of the hydrologic model proposed for the delta, may balance calculations suggest that most of the evapotranspiration which takes place in the Okavango Delta occurs from the island. This has the effect of removing accumulated carbonate from coetact with the seasonal flood waters, thus maintaining high water quality, and prolonging the survival of this magnificent coesystem. Carbonate accumulation must, however, inevitably have a serious impact on the vegetation. This raises an important question in regard to the vegetation density on the islands: does the surface efflorescence occur as a result of sparse vegetation, of is the vegetation sparse because of the presence of high salt concentrations? In the longer term, accumulation of carbonate must radically alter the character of the Okavango.

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