

Biochemical and Geochemical Aspects of the White Salt Pan--Bonaire, Netherlands Antilles

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ABSTRACT

The present study supplements recent reports on the Pekelmeer gypsum, dolomites, etc., by new data on the White Salt Pan evaporites. Where sampled, some 75 mm of evaporite encrusted a Cenozoic reefal (?) limestone in the area adjacent to Pekelmeer. The upper third consisted of halite hopper crystals; the lower two-thirds was dominantly gypsum with halite hoppers associated with gypsum (no halite was reported in Pekelmeer subsurface gypsum) and carbonates. Small subfossils are present in gypsum/carbonate.

A probable diurnal banding was indicated in the hopper crystals by hundreds of successive fine bands and a few coarse ones per crystal. Measurements show a daily growth increment of 0.10-0.14 mm, or $3 \pm$ mm per month.

X-ray analysis indicated the presence of aragonite, very small amounts of calcite, dolomite, and (not previously reported) magnesite in the lower two-thirds of the sampled section. The age of this Recent dolomite can be bracketed within the past 200 years--the lifespan of this artificial pan. This new age, taken together with that on Pekelmeer near-surface crusts that had a C-14 age of 1412--2190+ ybp (Deffeyes et al., 1965), indicates the recurrent availability and mobility of Mg cations over a span of some two millennia, especially in dolomitization.

Both surficial halite hoppers and subsurface crystals contained the same kind of organic content consisting of exceptionally well preserved three-dimensional skeletal and plant items. This Caribbean saltpan may serve as an analog of biochemical significance for study of ancient salt deposits. For example--4 to 5 of the same amino

acids reported in Upper Silurian rock salt from New York State were found in the Bonaire mixed evaporite (glycine, alanine, tyrosine, glutamic acid and possibly serine).

INTRODUCTION

During the late summer of 1965 the present investigator carried out a reconnaissance of salt deposits on the island of Bonaire, Netherlands Antilles. The plan was to make field observations relative to the incorporation of organic content in a modern evaporite. The White Pan was selected for this purpose since it approximates ancient evaporite deposits. Subsequent analysis of samples showed that mineralogical and geochemical data were of equal interest.

Recent publication of two definitive and excellent studies (Deffeyes et al., 1965; Lucia, 1968) prompted preparation of this supplementary account, in view of the widespread attention that has been given the Bonaire evaporites.

ACKNOWLEDGEMENTS

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Figure 1. White Salt Pan, Bonaire, halite crust 7.0 to 25.0 mm thick. Note pools and vegetation beyond Pan.



Figure 2. Evaporite/carbonate and overlying halite crust, White Pan.

remains. Professor Ernest Bubenick, (Wichita State University), a mycologist, consulted on fungi.

THE WHITE PAN AND SURROUNDS

A crust of white cloudy-to-clear halite ranges from 7.0 mm to 25.0 mm in thickness (Fig. 1). The crust overlays some 50.0 mm of poorly consolidated, lumpy evaporitic carbonate (Fig. 2). In turn the lowermost unit rests on hard coralline (?) bedrock. Previous work established that a Cenozoic reefal limestone underlies the area, and is covered by Recent supratidal deposits.

The thin salt crust was found to consist of masses of hopper crystals (Fig. 3). These crystallized out of an upper dense layer during evaporation of a shallow cover of Caribbean seawater. The Bonaire

White Salt Pan is artificial and has been in operation, on and off, for some $200 \pm$ years (Deffeyes *et al.*, 1965). (The oversized cement doghouses that quartered slaves who worked these deposits were located a distance from and in front of Fig. 2).

What was the age of this salt crust? The age of the top of the bedded gypsum, presumably equivalent to that found below the surficial halite on the White Pan, was 110 ± 130 years (Deffeyes *et al.*, 1965) as determined by the radiocarbon method. The upper age limit for the bedded gypsum of 240 years can be rejected since the Pan has been operative less than that time. The relative freshness of the incorporated organic skeletal and plant material in the White Pan lumpy gypsiferous carbonate would argue toward the smaller of these two figures. A remarkable freshness is also found in



Figure 3. Surficial hopper crystals. Size range 10-20 mm.

skeletal material in halite crystals suggesting even more recent accumulation than during the past two decades.

HOPPER CRYSTALS AND GEOCHRONOLOGY

The surficial hoppers range in size from 10.0 mm to 20.0 mm along the base of a single face. The pyramidal faces are striated and show successive stages of growth in bands (Fig. 4).

The striated faces merit some attention. Bands or incremental markings are of two types, coarse wider-spaced bands and numerous fine bands intervening between any two coarse bands. A few fragmented crystals were studied in some detail.

Specimen No. 1—length from base to top of hopper fragment is 30.0 mm; 16 coarse bands, and 187 intervening fine bands. Fine bands grouped as follows: a group of 14 fine bands recurred 6 times (37+ percent), a group of 11/12 (assumed to represent equivalents of the 14-group) occurred 4 times (25 percent), a group of 7/8/9 (assumed to represent half-units of the 14-group) recurred 6 times (31 percent).

Specimen No. 2—length from base to top of hopper fragment, 22.0 mm; 12 coarse bands and 188 intervening fine bands. The only recurring groupings were 18 bands, 3 times, and 19 bands, 2 times; other groupings ranged from 22 to 19 fine band units.

If the total of coarse and fine bands are divided into the maximum crystal length (measured perpendicular to the pyramidal apex), for Specimen 1 each increment represents 0.14 mm and for Specimen 2 each increment represents 0.11 mm. When a single unit between two successive coarse bands



Figure 4. Hopper crystal showing striae or growth increments in pyramidal face occurring in sequential units.

was measured on another crystal as a control, 17 bands occurred along a length of 1.65 mm, each band representing approximately 0.097 or 0.10 mm. Thus the growth increment of presently exposed hopper crystals on the Bonaire White Salt Pan, is in the magnitude of 0.10 to 0.14 mm.

What is the significance of the coarse as opposed to the numerous fine intervening bands? Such bands may denote more rapid addition of fine increments prior to sinking. A given coarse band, if this is the case, probably equates with two or more fine bands. Still, recurrence of certain fine band groupings of a given Bonaire hopper crystal, suggest some further control—possibly some semi-cyclical evaporative aspect.

Suppose we interpret the increment of 0.10-0.14 mm as diurnal. It would then follow, that in any 30 day period the added length of a given hopper would vary from 3.0 to 4.0 mm. To obtain the number of months represented, one need but divide this figure into the measured crystal length. A crystal length of 30.0 mm and an increment of

3.0 mm yields the chronologic value of 10 months as total growth represented in the given hopper fragment.

The increments of course may not be diurnal, and may represent longer or shorter spans than those of 24-hour duration. Still it is likely that they will have *some* time value related as they are to crystal-size increase. The density of such increments per unit space is high enough to suggest a daily increase. Similar bands are seen in thin sections of Salina hoppers (Dellwig 1953; 1969, personal communication). If one could firmly establish what time value to assign such bands, geochronologic application to hoppers in ancient salt deposits could readily be made.

GEOCHEMICAL DATA

Small carbonate inclusions in the surficial halite hopper crystals were reflected in the chemical analysis. Trace amounts of CaO (0.10 percent) and MgO (0.08 percent) were found. In the underlying gypsum/halite/carbonate sediment, CaO represented 20.68 percent, MgO, 1.97 percent.

X-ray analysis of the coarse insoluble residue of the surficial halite sample indicated that it was chiefly calcite. Analysis of the untreated sediment below the halite crust, at first did not reveal the presence of the magnesium carbonate. This was attributed to the wideness and masking effect of the halite peaks in the x-ray curves (Pei-lin Tien). Other x-ray study by Dah Cheng Wu showed that the first and second strongest peaks for dolomite were masked by the gypsum + aragonite curve, and by the gypsum curve respectively.

The powdered sample was dissolved in distilled water and an insoluble residue obtained. The result of the second x-ray analysis (by Pei-lin Tien) of the concentrated carbonate fraction showed small amounts of calcite, dolomite and magnesite. (Dah Cheng Wu reported an excess of aragonite over calcite).

Age dating by C-14 of Pekelmeer near-surface dolomitic crusts indicated an age of $1412 \pm 2190 \pm \text{ybp}$ (Deffeyes et al., 1965). The age of the dolomite reported above is likely to be within the time of the operative lifespan of the White Salt Pan, i.e., the past 200 years. Thus the two dates together provide a glimpse of the recurrent availability and mobility of Mg cations over the past $2000 \pm$ years. It should be stressed that the dolomite and magnesite were sparse in the evaporitic sediment below the halite crust.

FIELD OBSERVATIONS ON BIOTIC ELEMENTS ETC.

Small open pools in the halite crust and open water in parts of the White Salt Pan area were noted. Numerous small birds visited and moved through the water pecking for food morsels. (In the so-called Orange Pan a few miles to the South, the coloration is due to incorporated algae. Here many more flocks of birds were observed). Elsewhere along the Pekelmeer, flocks of flamingos were seen wading in the water and presumably exploring bottom muds for organic particles. Tropical vegetation rims the Pekelmeer/White Salt Pan area.

There were at least six possible sources for the organic content found in the Bonaire salt and underlying mixed evaporite (cf. Tasch 1963): (1) transport by birds—as congealed mud on their feet, fecal pellets, or bioturbation of sediments while probing for food morsels; (2) wind transport—most likely for spores and pollens and seed items, but also possible for many insects; (3) parasites—in or on insects, ostracods etc., fungi, bacteria and other microbial types; (4) *in situ* growth—as with algae on the Orange Salt Pan, brine shrimp and salt fungi; (5) original dispersed organic content in Caribbean seawater that filled the pan; and (6) contamination by man.

ORGANIC CONTENT AND BIOCHEMICAL ASPECTS

Appendages and other skeletal parts of insects and other arthropods, in a surprisingly fresh condition were retrieved from hopper crystals, and underlying evaporites during microscopic examination. Mostly, the items retrieved were fragments (Figs. 5, 6). Fragmentation of insect skeletons suggest possible predation by birds or other predators before incorporation into fully crystallized material.

Wind transport seems indicated for spore/seed items. Spherical egg items were brightly colored and in the range of 200 microns diameter. These were chiefly found in the underlying mixed evaporite. An occasional carbonized seed of larger size ($1100 \pm$ microns) also occurred. The intact valves of a modern Caribbean ostracod, with some dried organic content as well as subfossil ostracods and foraminifera were part of the biota of the mixed evaporite.

In order to facilitate separation of egg/spore/seed components in the mixed evaporite, it was dissolved in Millepore-filtered water and then passed through a Millepore filter into a laboratory

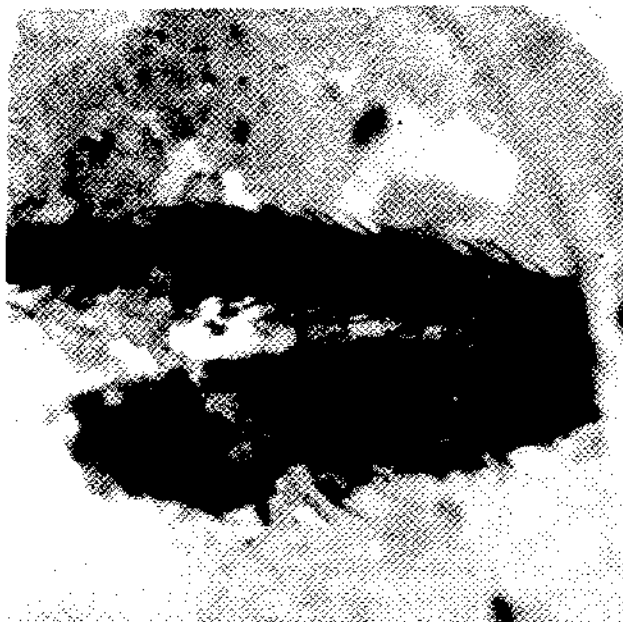


Figure 5. Insect appendage, photographed as it occurs in a hopper crystal. Note freshness of preservation, X80.

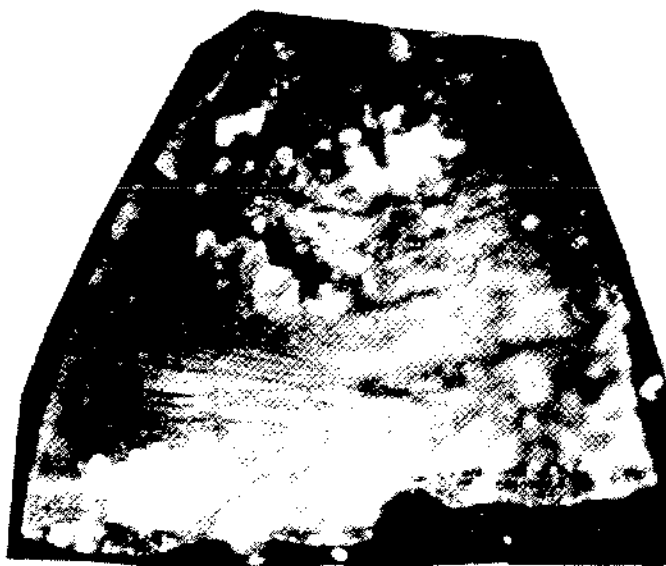


Figure 6. Arthropod skeleton fragment. Body and head segment, light tan, interior hollow and empty, preserved in evaporite carbonate, X46.6.

flask. It was surprising to observe the rapid growth of fungi in the flask fed by filtered water (Fig. 7).

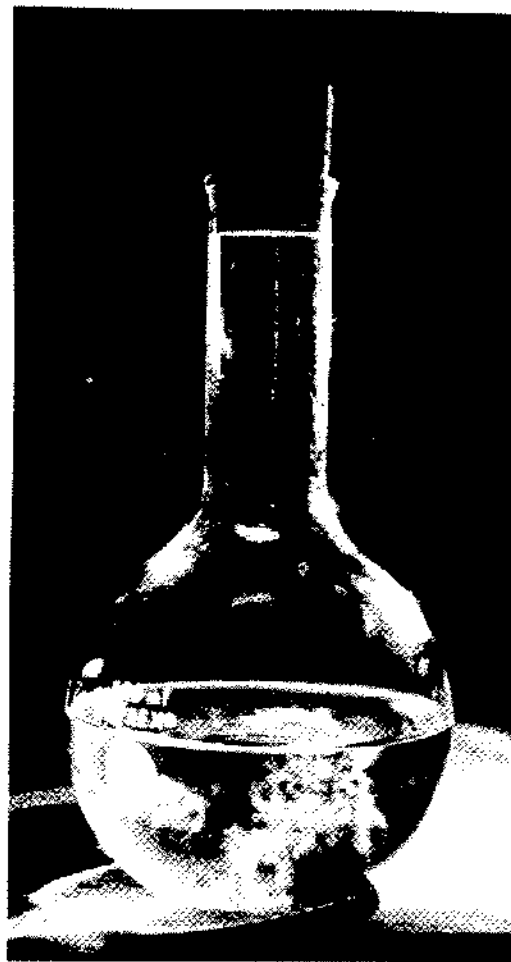


Figure 7. Fungal contaminant (cloudy mass in fluid) that grew instantly in Millipore-filtered evaporite/carbonate water poured into a flask.

Dr. Bubienic who is plating these, informs me that they are probably a common contaminant.

However, quite by chance the above finding may have wide application. The fungal growth which started immediately in the flask during the filtration process, could not occur unless critical organic components were in the filtered fluid. If so, one could introduce a known fungal contaminant into a laboratory flask, and quickly assay the presence of critical organic components in any filtered evaporite by observing if rapid fungal growth were sponsored.

There are of course salt fungi that live in salt environments and these are not to be confused with the common contaminants. These can be detected by plating.

BIOCHEMICAL ANALOG FOR ANCIENT SALT DEPOSITS

The critical organic components detected without analysis by the fungal-growth method, can of course be analyzed by paper chromatography. Preliminary study of the Bonaire evaporite by Flo Butler revealed an organic suite. The sample was taken from the mixed evaporite. Bound amino acids were indicated with the first ninhydrin test after ethanol extract in the residue. Three of the same amino acids (at the present stage of analysis) were characterized in two distinct paper chromatograms using two different solvents (percent volume): (1) phenol-79, water-19, NH_3 -1; and (2) butanol-70, formic acid-10, water-10.

The amino acids are characterized as most likely to be: glycine, serine, and glutamic acid. This determination is based on R_F values in the literature. (R_F value of an ion in a given solvent is the movement of the ion proportional to that of the given solvent.) There are of course other confirmations, color of spots, etc. (A subsequent analysis with Solvent 1—run at room temperature, with a six hour time of development, and a flow distance or solvent movement of 15+ cm—yielded five spots. Four of these clearly identifiable as glutamic acid, alanine, tyrosine, and glycine. The fifth spot has not yet been characterized. Analyses are being continued.)

Besides the fraction used for chromatograms there is a wash liquor fraction which contains amino sugars, amides and possibly some amino acids.

Because in the Bonaire evaporite one can follow most of the stages leading to a chemically detectable organic fraction, it can serve as an analog for ancient evaporite deposits. The spectrum of stages related to the organic content of an evaporite includes:

(1) Incorporation. Entrapment of undecayed and unmineralized skeletal, plant, or spoor material (as well as amino acids and other non-proteinaceous components dissolved in or immiscible with sea water) in the crystallizing brine.

(2) Denaturing of Proteins. Critical organic components derived from (1) may be found in solution (Bioassay-fungal-growth method), and paper chromatography may reveal distinctive amino acids, and suites of the same, as well as other organic components.

(3) Sustenance of bacterial metabolism. This last stage, not evaluated for the present study but being examined in conjunction with other paleomicro-

biological researches of the writer, involves preservation of viable microbial forms in the evaporite.

(A) Recent contaminant microbial forms (viable).

(B) Dead and living microbial fossils.

Two examples of ancient evaporites that can be taken to show how the Bonaire data may serve as a biochemical analog are the Middle Silurian rock salt of New York State, and the Permian Wellington rock salt of Kansas and Oklahoma.

Brunskill and Vallentyne (1966) found the following amino acids in the water soluble fraction of the Silurian salt: serine, glycine, lysine, alanine, threonine, and aspartic acid (present in concentrations ranging from 107 to 26 $\mu\text{moles/g}$ in the order listed). In lesser concentrations they detected histidine, proline, phenylalanine, tyrosine, cystine, methionine, valine, leucine, isoleucine and glutamic acid.

Comparison of the Silurian salt inventory of amino acids to that found in the Recent Bonaire mixed evaporite indicates that the following components are shared in common: glycine, alanine, glutamic acid and tyrosine and possibly serine. Perhaps more of the whole Silurian evaporite suite of amino acids are present, but additional data must await ongoing analysis of the Bonaire samples. The significance of this equivalence in even several components can be seen when one relates the Bonaire White Pan stages, where all steps leading up to the ultimate amino acid assay can be followed, to the Silurian evaporating basin, in which case we have only the end result—the amino acid suite characterized by Brunskill and Vallentyne.

Thus one must postulate for the Silurian basin:

(1) Incorporation in crystallizing brine of organic debris, and organic compounds, both soluble and insoluble in seawater.

(2) Denaturing of proteins (perhaps achieved in whole or part by bacterial activity on included skeletal, plant, or spoor items) leading to the amino acid suite of the above study.

(3) Sustenance of bacterial metabolism. The suite of amino acids in the Silurian salt was deemed adequate to sustain bacterial metabolism within the salt—if any had been incorporated from the Silurian sea—or in organic debris that was derived by one or several of the methods reviewed earlier for the Bonaire White Pan. No bacteria were reported in that study. Nevertheless, the amino acid suite suggests their probable presence in the Silurian basin, if the Bonaire White Pan can be considered a modern analog.

It is of some importance to establish whether microbial life could be sustained in a viable state inside of evaporite crystals through geologic time. The whole question of viable fossil bacteria of great antiquity (hundreds of millions of years) was explored at an earlier date (Tasch, 1963). In the Permian Wellington Formation salt some viable bacteria were discovered.

Tasch (1960) postulated a seaside swamp on the margins of the Wellington salt basin to explain the source of organic debris (carbonized wood, etc.) found in the salt. However, taken alone, without the new data on the Bonaire Salt Pan and the Brunskill-Vallentyne study, viable bacteria of Permian age seemed difficult to comprehend. (It is still a highly debatable issue.) That difficulty is now considerably diminished, if we take the Bonaire Pan as a biochemical analog of the Wellington salt. Thus, viable bacteria of the Permian Wellington salt (equivalent to Bonaire Pan Stage 3) reflects, as does Bonaire Pan Stage 1, the incorporation of undecayed organic debris, some of which could have served as host to select Permian sea swamp bacteria. These could have penetrated fleshy parts of undecayed and unmineralized skeletal items, or been attached to hairs, bristles, etc. (Figs. 5, 6). Subsequent denaturing of proteinaceous substance in such debris, by bacterial intervention, would yield an amino acid suite.

It follows from the above discussion that comparative study of biotic components in the Bonaire White Pan, and the resulting amino acid suites in

the evaporite, can have significant analog value when applied to ancient salt deposits.

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