CHAPTER IV

CYANOBACTERIAL MATS: MICROANALYSIS OF COMMUNITY METABOLISM

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Introduction

Stromatolites, trace fossils of microbial communities, provide the oldest evidence of life on earth; they represent the beginning of our 3.5 billion year old record. Stromatolites are by far the most abundant fossils found in the Archean and Proterozoic Eons (3.5-0.6 billion years ago) (BYA). The other major sedimentary record of the Prephanerozoic are Banded Iron Formations (BIFs) deposited 2.2-1.8 BYA. Cyanobacteria are postulated to play a major role in the deposition of both stromatolites and BIFs. Cyanobacteria-like fossils have been described from cherts in many Prephanerozoic and Phanerozoic sediments. Some BIFs are associated with stromatolites. Cyanobacterial iron-dependent photosynthesis related to the deposition of Banded Iron Formations has been postulated (Hartman, 1984).

Even though stromatolites are scarce in the Phanerozoic Eon, they are still found today in specific environments where grazing metazoans are excluded. Cyanobacterial mats are presently found in hypersaline lagoons, hot springs, and alkaline lakes. The study of mat-forming cyanobacteria aids in the understanding of the environment of deposition of Prephanerozoic stromatolites and Banded Iron Formations as well as our study of evolution of photosynthesis among the most ancient groups of oxygenic phototrophs.

Cyanobacteria have long been known as oxygenic photosynthesizers. Other kinds of photosynthetic modes have been demonstrated for several mat-forming cyanobacteria, possibly indicating the antiquity of this group.

Facultative anoxygenic photosynthesis operating photosystem II and the use of hydrogen sulfide or hydrogen as electron donors have been shown in some strains of benthic cyanobacteria (Padan and Cohen, 1982). Recently others demonstrated oxygenic photosynthesis under high sulfide concentration (Jorgensen, et al., 1985). Fe**+-dependent carbon dioxide photoassimilation has been shown for conditions of intermediate redox potential.

Delta 13C measurements of the cyanobacterial communities in recent mats have yielded the heaviest value ever recorded for per mil organic matter: -4 to -8 per mil. Yet similar measurements in ancient mats show values of 12 per mil to 16 per mil. The observed
discrepancy may be the result of the appearance of the bicarbonate pump in recent cyanobacteria that evolved in response to the decrease in atmospheric CO₂ concentration since the Phanerozoic Eon.

Two field sites were chosen for the study of cyanobacterial mats: the salt ponds in San Francisco Bay near the Dumbarton bridge where microbial mats develop under varying salinities, and the Alum Rock sulfur springs.

The microbial communities in these sites were studied using several approaches: a) light microscopy; b) the measurement of microprofiles of oxygen and sulfide at the surface of the microbial mat; c) the study of diurnal variation of oxygen and sulfide; d) in situ measurement of photosynthesis and sulfate reduction and study of the coupling of these two processes; e) measurement of glutathione in the upper layers of the microbial mat as a possible oxygen quencher; f) measurement of reduced iron as a possible intermediate electron donor along the established redoxcline in the mats; g) measurement of dissolved phosphate as an indicator of processes of break down of organic matter in these systems; and h) measurement of carbon dioxide in the interstitial water and its delta ¹³C in an attempt to understand the flow of CO₂ through the systems.

Using these approaches we have analyzed microbial processes of primary production and initial degradation at the most active zone of the microbial mat. Our results can be compared to those obtained by those working on SO₄ reduction (Chapter III) in the deeper part of the sediment column.

**Site Descriptions**

**Dumbarton Bridge Salt Ponds and Marsh**

**Salt Ponds**

The study sites were the Dumbarton Salt Ponds (salinas) north of the Dumbarton Bridge (Map 2). These San Francisco Bay Wildlife Preserve salinas represent several environmentally distinct microbial mat communities. There are several salt evaporite ponds increasing from 42 per mil salinity (pond A2) to 90 per mil in pond 5 to 150 (145) per mil in pond 4. Sedimentary surficial microbial mats, collected from water at depths of 10-20 cm in these ponds have been microscopically examined (see Table IV-1).

The overall trends observed include a general decrease in the diversity of cyanobacteria. Population densities of *Oscillatoria* and *Anabaena* also declined with increasing salinity. *Anabaena* appeared in the 90 per mil pond probably because a niche was created for it due to the abundance of *Aphanothece halophytica* which causes a depletion of nitrogen.
<table>
<thead>
<tr>
<th>MARSH</th>
<th>ORGANISMS</th>
</tr>
</thead>
</table>
| 20 per mil | Cyanobacteria  
Oscillatoria 1,4,5,6,7,30 μ: Dominant  
Anabaena 4 μ: Fewer  
Spirulina 2 μ: Fewer  
Gomacullar species: Fewer  
Other bacteria  
Beggiaoa (5 μ x 300 μ length): Abundant  
Spirochetes, Chroococci: Abundant  
Thiospirilla: Fewer  
Eukaryotes  
Diatoms: Dominant  
Ciliates and non-ciliated protozoa: Fewer |
| 42 per mil | Cyanobacteria  
Fischerella - heterocysts: Fewer  
Spirulina (tightly coiled and loose type): Fewer  
Other bacteria  
Beggiaoa: Fewer  
Eukaryotes  
Small and large diatoms: Dominant  
Green algae, heterotrophic protozoa: Fewer |
| 90 per mil | Cyanobacteria  
Oscillatoria 1,5 μ: Fewer  
Fischerella: Fewer  
Spirulina (tightly coiled and loose type): Fewer  
Anabaena 4 μ: Fewer  
Aphanathece halophysica (planktonic): Abundant  
Other bacteria  
Spirochetes: Fewer  
Beggiaoa: Fewer - Abundant  
Eukaryotes  
Diatoms: Dominant |
| 145 per mil | Cyanobacteria  
Aphanathece halophysica (planktonic): Dominant  
Oscillatoria 1,2,4 μ: Fewer  
Purple filamentous bacteria 0.3,1 μ: Abundant  
Other bacteria  
Spirochetes, Beggiaoa: Fewer  
Eukaryotes  
Mesostella (planktonic), Diatoms: Fewer  
Rod-shaped ciliated protozoa: Fewer |
| 200 per mil | Cyanobacteria  
Aphanathece halophysica: Fewer  
Other bacteria  
Halophilic bacteria: Abundant  
Eukaryotes  
Mesostella: Dominant |

Table IV-1. Abundance and variety of organisms present in marsh sites of various salinities.
Yet *Aphanathece halophytica* increased as salinity increased. Diatom population densities also appear to decrease as a function of increasing salinity. The occurrence of *Beggioa* and spirochetes in all salinity ponds suggests that there is a relatively shallow oxygen/sulfide interface in these mats.

Marsh (33 Per Mil) Site

In addition to these saline environments a salt marsh with salinity around 33 per mil was studied. Mats from this site were collected as described above and examined microscopically (Table IV-1) (for site description see Chapter III).

Alum Rock Park Sulfur Spring Site

The site chosen at Alum Rock Park (Map 3) was a sulfide stream flowing down a rocky bank leading into a larger fresh water stream about 1.5 meters wide. The main sulfide stream split into two small streams about 35 cm down from the source and continued flowing down the bank. White filamentous bacteria grew along the two branches of the stream while cyanobacterial mats bordered the streams. The source water smelled strongly of sulfide. Elemental sulfur was evident along the edge of the stream leading from the source. Samples of microbial communities were taken along one of the main streams and across the dryer section between the streams (Figure IV-1). Communities appeared to vary significantly from high to low sulfide regions.

Materials and Methods

Microelectrode Calibrations and Data Calculations

Oxygen Microelectrode Calibration

The oxygen microelectrode (see Cohen, Sulfur Transformations, Chapter 1) was calibrated using three solutions of known oxygen concentration. The first consisted of distilled water that had equilibrated having N₂ gas bubbled through it. Similarly the second solution was distilled water that had had air bubbled through it, and the third was distilled water that had been equilibrated with O₂ gas. To determine the oxygen content of the solutions in micromoles a Keithley 480 picoammeter current meter hooked up to an electrode was employed. Winkler titrations using the iodometric method (Standard Methods for the Examination of Water and Wastewater, 15th ed.) were done for each of the three solutions. The values thus determined allowed the construction of a calibration curve for each electrode. Oxygen microelectrodes were recalibrated individually and frequently since in most media some agents pass through and poison the semipermeable membrane tip, causing a nonlinear response to oxygen concentration (Revsbech and Ward, 1984).
Figure IV-1. Schematic diagram of Alum Rock sulfur stream site 3.
Calculation of Sample Oxygen Concentrations

For a given profile and a given electrode the particular conditions at the time of profile measurement must be taken into account; otherwise O₂ concentrations from the ammeter readings may be invalid. An ammeter reading in the overlying water was taken and a corresponding Winkler titration done to determine the oxygen concentration of the water. Eventually, with depth in the profile, a constant baseline reading was achieved. This reading is taken as corresponding to a zero O₂ concentration value in this medium. This zero value reading is usually not the same as that in the calibration (N₂ solution) since the calibration was done in distilled water whereas the readings are done in complex ionic natural waters. The electrode still has a linear response to oxygen concentration but its absolute value shifts in response to the chemical environment. By taking the overlying water meter reading and subtracting the baseline reading, a value is obtained that corresponds to the O₂ concentration of the overlying water. Dividing these values into one another yields a slope factor. Therefore to obtain an oxygen concentration for a given reading one must first subtract the baseline reading and then multiply by the given calibration factor. Knowing that the electrode has a linear response, the effect of the given medium can be taken into account.

Sulfide Microelectrode Calibration

To calibrate sulfide electrodes readings were taken (in millivolts on a Keithley 160 B Digital Multimeter) for newly made standard solutions. As a check on the known standards methylene blue sulfide determinations (Pachmayr, 1960, modified by Trueper and Schlegel, 1964) were made on the standards. A calibration curve was drawn on 3 cycle log paper. The microelectrode measures S²⁻, so to determine the H₂S profile one needs to take into account both pH and salinity. A pH profile should be taken with each sulfide profile. However, since the pH profiles we took showed that pH varies little with depth it was sufficient to determine the pH of the overlying water and assume constancy with depth. The simplest way to take pH and salinity into account is to follow the graphical determination presented in the Journal of Marine Research, 23, number 55 (1965), which shows the relationship between pH, salinity, and decimal fraction of undissociated hydrogen sulfide at 25°C. Readings were then taken on the meter (mV), converted to S²⁻ concentration via the calibration curve and then to H₂S concentration taking salinity and pH into account.

Unfortunately, the sulfide electrodes were not very sensitive below about 100 um and so many of our profiles which showed distinct trends in sulfide with depth could only be described as showing trace amounts.
pH Calibration

pH readings were taken in millivolts on a Beckman Model 3500 Digital pH Meter for solutions buffered at pH 5, 7, and 9. Good linear calibration curves were seen for all the microelectrodes although the values varied widely due to differences in the making of the electrodes.

Photosynthetic Rate Determinations

Light and Dark Profiles of Oxygen and Sulfide

To determine diurnal changes in these mat communities both dark and light oxygen and sulfide profiles were determined using microelectrodes that had been prepared by Cohen as described by Revsbech et al. (1983). Details may be found in the Microelectrode Calibrations and Data Calculations section above. The application of these electrodes to sediments and microbial mats has been described by Jorgensen et al. (1983), Revsbech and Ward (1984), and by Jorgensen et al., 1979. Profiles from the sulfur spring were taken in situ, whereas those from the microbial mats at the salinas were taken on cores brought back to the laboratory. The cores were taken by hand using 1 1/2 inch diameter acrylic tubing. These cores were kept in water baths in their own pond water and at ambient temperatures of 29°C, and were continuously aerated. Light profiles were taken at a light intensity of 1150 microEinsteins per meter² per sec (µE m⁻² s⁻¹). In order to achieve very fine resolution when sampling these cores the microelectrodes were inserted into the mat with the use of micromanipulators (Stoelting Co.).

Anoxygenic Photosynthesis

To investigate the question of whether the microbial communities in the 42 per mil pond (A2) and at the marsh site were capable of anoxygenic photosynthesis using H₂S as an electron donor, the core was overlain with a known amount of pond water and then covered with paraffin oil after the light oxygen and sulfide profiles had already been taken. A known amount of sulfide was then inserted under the paraffin oil into the overlying water. The core was kept in the dark and continually monitored by sulfide and oxygen electrodes inserted at the depth of maximum photosynthetic activity before the paraffin was added. Once a steady sulfide reading was reached the light was switched on and the decrease in sulfide along with the increase in oxygen that occurred following illumination were monitored. After a steady-state oxygen concentration was reached the photosynthetic activity of the community was compared to that seen before the sulfide was added. Sulfide concentrations were increased until they became toxic to these microbial mats.
Figure IV-2. Oxygen, sulfide, and pH microelectrodes used by Cohen research group. For further details of the construction and use of these electrodes, see Revsbech and Ward (1984), and Revsbech, et al., (1983).
Oxygen Level Recovery

A core sample from the 150 per mil pond was studied. A light oxygen profile was taken (Fig. IV-3), the core then kept in the dark for approximately 2 hours, after which a dark O₂ profile was taken. After these baseline determinations were made the core was illuminated (1152 µE m⁻² s⁻¹ from an optic fiber lamp) and profiles were taken after 17, 34, and 63 minutes of illumination.

Results

Light/Dark Profiles of Oxygen and Sulfide and Photosynthetic Rates

Introduction to Results

Dark and light oxygen profiles taken and photosynthetic rates determined in the microbial mats from the different salinity ponds using an O₂ microelectrode (Figures IV-4, IV-5 and IV-6) show two distinct layers of oxygenic photosynthetic activity in the mats at the marsh site and in the 42 per mil pond. This activity can probably be ascribed to the presence of diatoms in the top layer and cyanobacteria in the lower layer. The 90 per mil and the 150 per mil pond light O₂ profiles (Figures IV-3 and IV-6) show a single peak of photosynthetic activity, due to the presence of diatoms and some cyanobacteria. The *Aphanothecia* sp. found in the 90 per mil pond were planktonic and therefore could not be responsible for this peak. The sediment of pond 4 (150 per mil) showed relatively poor mat development and the sediment was covered with a gypsum crust which accounts for data obtained from the O₂ profile. It was concluded that oxygenic photosynthetic activity decreases with increasing salinity.

Sulfide profiles were also taken from these mats both in the light and in the dark using a sulfide microelectrode. In almost all cases only trace amounts of sulfide were detectable. In the light, sulfide only appeared in deeper layers of the mat (in the marsh mat at about 0.5 mm in the 42 per mil site and at 1.75 mm). Only in the mat of the 150 per mil pond did sulfide occur in the light close to the surface (0.5 mm depth) in detectable levels (Figure IV-5, indicating that sulfate reduction rate at this site was high). In the dark nearly all mats looked reduced up to the surface. Hardly any oxygen was detectable after the cores had been incubated in the dark for 2 hours. However since there was no profound difference in sulfide profiles in light and dark, sulfate reduction is probably not limited by photosynthates.
Table IV-2. Summary of site oxygen profiles and photosynthetic rate profiles.
Figure IV-4. Marsh site 20 per eel salinity, light and dark oxygen profiles and rates of photosynthesis.

Figure IV-5. Oxygen profile and photosynthesis of 42 per eel pond.
Figure IV-6. Profiles of 90 per mil salinity pond. Light and dark oxygen profiles and photosynthesis rates.
Figure IV-3. Profile of 145 per aii salinity pond. Light and dark oxygen profiles and light hydrogen sulfide profile. Collected at 23°, pH 8.4, and run at 28.5°C.
42 Per Mil Pond

Several light oxygen profiles were taken at the 42 per mil site (Fig. IV-5). These profiles show that the O₂ maximum is reached between 0.4 and 0.5 mm, and has a value of about 160 uM O₂.

90 Per Mil Site

The light O₂ profile showed relatively constant concentrations of about 154 umol O₂/min from the surface down to a depth of about 900 µm. Below this depth the oxygen concentration decreased quickly reaching a zero reading at 1.5 mm.

150 Per Mil Site

The light oxygen profile for the 150 per mil site shows a drop in oxygen concentration from the high surface value of 57 umol O₂/min, and an apparent second peak concentration of 55 umol O₂/min at 5000 µm depth (Fig. IV-5).

Quantum Yield (µM O₂/µE)

The initial slope of a photosynthesis vs intensity plot is a function of the light photosynthetic reaction, and, according to Parsons, et al. (1972), is not usually influenced by other factors. Due to the nature of the sampling procedure, we did not actually derive the quantum yield (µM O₂/µE) but rather a value directly related to it (µM O₂/m²/µE). Our calculations show that the greatest quantum yield (or efficiency) was found at 500 µm depth (Table IV-3). This is the same depth at which the maximum photosynthetic rates were found. The next highest yield was at 750 µm. Going to 1000 µm there was a fairly sharp drop in yield (from 0.024 to 0.017 µM O₂/m²/µE), and by 1250 µm there was essentially zero yield at low light intensities. The values at the surface and 250 µm depth were about the same as that at 1000 µm (Table IV-4).

To determine these yields we measured incident light intensity and the amount of light that could be detected through a 1.5 mm slice of the mat. Using these two points, and assuming a linear relationship for simplicity, the intensities at the intermediate depths were estimated.

Anoxygenic Photosynthesis Results

We attempted to establish the occurrence of anoxygenic photosynthesis in the microbial mat of the 42 per mil pond. When the light was switched on after small amounts of sulfide (100 µM) were added to the mat the sulfide concentration decreased and the oxygen concentration increased accordingly. Large amounts of sulfide (1 mM) seemed to inhibit H₂ production under
these conditions it took much longer for oxygen concentration to build up again. At low sulfide concentrations oxygenic and anoxygenic photosynthesis seemed to occur simultaneously, while at high concentrations only anoxygenic photosynthesis took place. No accurate measurements were possible, but a rough estimate of the anoxygenic photosynthetic activity is 5-10 micromoles sulfide per minute. Since no control measurement was possible, we are not sure whether the decrease in sulfide concentration was due to anoxygenic photosynthesis by cyanobacteria or to sulfide oxidation by Thiobacillus-like organisms.

Photosynthetic activity in the mat of the 42 per mil pond was not inhibited by light intensities up to 1150 µE m⁻² s⁻¹ (Figure IV-7). Inhibition occurred only at a depth of 2 mm (a conclusion based on only one point). Therefore the fact that the top layer of the mat was less photosynthetically active than the deeper layers cannot be ascribed to inhibition by high light intensity unless the light intensity encountered in the normal habitat is much higher. The mat reaches a maximum photosynthetic activity at the highest light intensity. With increasing depth the light intensity decreased (the light intensity values given in the graph are those measured at the surface of the mat and no light penetration could be detected through a 2 mm slice of the mat). Conclusions cannot be drawn from this experiment.

O₂ Level Recovery Experiment Results

Our results indicate that 2 hours was not enough time to achieve a baseline dark profile since the first recovery profile taken (after roughly 2 1/2 hours dark and 17 minutes light) showed lower O₂ levels than the "dark" profile. Nevertheless, recovery profile trends were seen. Surface O₂ concentrations dropped from 57 to about 50 µM but never below this level. In contrast, at 0.1 mm depth concentrations fell from 56 to 34 µM O₂. At 0.2 mm depth the O₂ level was probably even lower as the dark profiles show sharp decreases with depth in this range.

Thus this core shows a double peak profile with sharp O₂ concentration gradients in the upper half millimeter. After 34 minutes in the light this double peak profile is replaced by a smooth profile gently decreasing from the surface to about 0.2 mm depth and more rapidly decreasing after that to a baseline value of 3 µM at 0.6 mm depth. The shape of the profile remained basically the same on further illumination with concentrations increasing all through the profile but still reaching a baseline of 3 µM O₂ by 0.6 mm. An hour of illumination was not enough time to allow the core oxygen profile to fully recover to the original light profile values.
Table IV-3. Summary of photosynthesis rate and depth data versus salinity (all determined at incident light intensity of 1150 μE m⁻² sec⁻¹).

<table>
<thead>
<tr>
<th>Ponds</th>
<th>Salinity</th>
<th>20 per mil</th>
<th>42 per mil</th>
<th>90 per mil</th>
</tr>
</thead>
<tbody>
<tr>
<td>maxima photosynthetic rate (μmol O₂/m²)</td>
<td>225</td>
<td>80</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>depth of maxima photosynthetic rate (microns)</td>
<td>500</td>
<td>400</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>sum total photosynthetic rate in top 1 cm (μmol O₂/m²)</td>
<td>864</td>
<td>more than 229</td>
<td>213</td>
<td></td>
</tr>
</tbody>
</table>

Table IV-4. Quantum yield estimates and Iₓ where Iₓ is an indirect measure of the intensity at light saturation.

<table>
<thead>
<tr>
<th>Depth</th>
<th>&quot;quantum yield&quot;</th>
<th>Iₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μmol O₂ m² μE⁻¹</td>
<td>μE m⁻² sec⁻¹</td>
</tr>
<tr>
<td>5</td>
<td>0.014</td>
<td>346</td>
</tr>
<tr>
<td>250</td>
<td>0.016</td>
<td>367</td>
</tr>
<tr>
<td>500</td>
<td>0.015</td>
<td>189</td>
</tr>
<tr>
<td>750</td>
<td>0.024</td>
<td>227</td>
</tr>
<tr>
<td>1000</td>
<td>0.017</td>
<td>244</td>
</tr>
<tr>
<td>1250</td>
<td>0</td>
<td>158</td>
</tr>
</tbody>
</table>

where Iₓ is an indirect measure of the intensity at light saturation.
**Figure IV-7.** Light saturation curves for core from 42 per oil pond.
Discussion

Discussion of Oxygen Profiles and Photosynthetic Rates

The light oxygen profiles show similar characteristics at all sites examined: a zone in the upper portion of their profiles where O$_2$ content is fairly constant. The width of this zone varies slightly for the three lower salinity sites, being 1.0 mm at the mat, approximately 1.2 mm at the 42 per mil pond, and 0.9 mm at the 90 per mil pond. This zone is only 0.5 mm wide at the 150 per mil site. Though the profiles are fairly homogenous in their upper sections (Figures IV-3-6 or Table IV-2) the marsh (20 per mil) and the 42 per mil profiles do show some evidence for two zones of peak oxygenic photosynthetic activity. Microscopic examination of the 42 per mil mats showed both abundant diatoms and cyanobacteria, and it is likely that the apparent double peak of activity, which may be an artifact, is due to the presence of diatoms at the surface and cyanobacteria in a subsurface layer. The marsh site had cyanobacteria and diatoms; *Beggiatoa* was also very abundant. *Oscillatoria* sp. were by far the dominant photosynthetic species. The presence of abundant *Beggiatoa* is indicative of a shallow oxygen/sulfide interface which could easily shift position. Activity at the 90 per mil site peaked at 0.25 mm, probably due to pinnate diatoms since they are most abundant at this position. No photosynthetic rate determinations were made at the 150 per mil pond which was dominated by *Aphanothecel* oxygen concentrations, however, were low.

Since there were distinct areas of peak activity in profiles which showed much uniformity in the upper zones it is probable that bioturbation is a significant modifier of profiles in these mats. The shapes of these profiles support an interpretation of the presence of bioturbation rather than diffusion alone as the mechanism modifying the profiles. Bioturbation was quite evident at the 42 per mil site where tube-building polychetes (annelid worms) were abundant. Because of their high salinity tolerances, it is likely that polychetes and/or nematodes were the bioturbating agents at the marsh, whereas nematodes alone were probably the main agent at the 90 and 150 per mil sites. Prorocentrum, ciliates, and motile chlorophytes, found at all sites, could also be contributing to the bioturbation. The photic zone in all cases is less than 2 mm thick in these mats. In general the width of this zone decreases with increasing salinity (see photosynthetic rate profiles).

The depth of the maximum rate of photosynthetic activity tends to shift closer to the surface with increasing salinity. Both peak photosynthetic rates and $O_2$ production in the top 1 mm of these cores decreased with increasing salinity. Rates of production fell sharply from the marsh site (20 per mil) to the 42 per mil site. Between 42 per mil and 90 per mil the productivity showed a much more gradual decrease. Though there are no photosynthetic rate data for the highest salinity pond.

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Figure IV-8. Photosynthesis at various depths of the sediment core and calculation of $I_k$ values at the 42 per mil site.
the fact that its peak concentration profile was only 57 uM
O₂ as compared to 150-170 uM at the other sites,
suggests that another sharp drop in productivity occurs in going
to this high salinity.

Sulfide Profiles

The sulfide profiles showed sulfide concentration below
expected values, indeed below the resolution capabilities of our
microelectrodes. The only exception was the profile of the 150
per mil site, where relatively high concentrations were found.

The light marsh profile shows essentially no free sulfide
until a depth of 1.75 mm, where the concentration sharply
increases, leveling off at 3.5 mm. The final concentration at
this depth was approximately 30 uM. A dark profile taken 2
hours after incubation showed surface concentrations of about 30
uM (or about what the steady base level was in the light
core) with concentration increasing slightly with depth and
leveling off by a depth of 2.75 mm (Fig. IV-12). The 42 per mil
sediment core (Fig. IV-12) light sulfide profile showed only a
gradual increase in concentration between 3 and 10 mm. By 10 mm
the concentration was probably still under 10 uM. A profile
taken after 4 hours in the dark showed sulfide increasing much
more quickly, beginning marked change about 0.25 mm to reach an
approximate stable concentration (probably about 10 uM) at
2.5 mm. After 4 hours in the dark the 42 per mil core had some
*Segiatoa* scattered on its surface, verifying the profile's
finding of a sulfide sink at the surface and indicating that this
was the location of the oxygen/sulfide interface. In contrast,
the marsh cores were completely covered by *Segiatoa* after
only about 20 minutes in the dark and by 2 hours had gone totally
anoxic. No profiles were done for the 90 per mil site. The 150
per mil light sulfide profile shows a gradual though erratic
increase in sulfide concentration with depth. The maximum
concentration seen in this core was 150 uM H₂S at 9.5
mm (Fig. IV-3).

Comparative Analyses

The 150 per mil pond showed the highest sulphide
concentrations (though in the upper 7 mm it appears quite similar
to the marsh site), followed by the marsh, and then the 42 per
mil pond. There is no direct correlation between the observed
sulfide profiles and the salinity gradient. Either there is no
correlation or the correlation is overshadowed by other factors.
All three sites have available sulfate and since sulfate
reduction rates depend on sulfate concentration (Martens and
Berner, 1974), differences in concentrations of sulfate at the
sites do not explain the differences in the profiles. One line of
explanation for the profiles is that the activity of the
sulfate-reducing bacteria differs at each site because of
substrate availability, sedimentation rate, or some other factor
or factors. However, the 150 per mil and the marsh site probably

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OF POOR QUALITY
Figure IV-9. Photosynthesis rates at the various depths of sediment core at various light intensities (the 42 per mil pond).
Recovery

Figure IV-10. Changing oxygen profiles upon transfer from dark to light (145 per sq m pond).
Figure IV-11. Marsh site sulfide profiles in the light (1500 \(\mu E\ m^{-2}\ \text{sec}^{-1}\)) and dark. Values are given in mV since, being smaller than 50 \(\mu M\), they were all below the linear range of the sulfide electrode. \(pH = 8.83\).
Figure IV-12. Sulfide profiles in the light (1500 μE m⁻² sec⁻¹) and the dark (42 per mil pond).
represent two extremes: the marsh site, open to mixing with bay waters, is surrounded by dense vegetation while the 150 per mil site is isolated at the end of a series of connected saline ponds with no surrounding vegetation growing on the evaporite, mineral-laden soil (abundant *Aphanothec* are present in the water column).

Another line of explanation for the anomalously low sulfide concentrations at the 42 per mil site is the existence of a sulfide "sink," such as ferrous iron, that does not operate at the other sites. Ferrous iron reacting with sulfide may form iron monosulfides and eventually pyrite. Roger François found significant pyrite formation in the sediments of the 42 per mil pond, the highest rates of formation being in the top centimeter. Other experiments by the Klug group indicate high rates of sulfate reduction; sulfide must be taken up in some way since very little free sulfide was measured. The 42 per mil pond is located immediately adjacent to the spillway pond whereas the 150 per mil pond is removed from direct sea water contact (Fig. IV-1). Thus the 42 per mil pond may receive iron via its closer contact with the bay water.