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THE GEOBIOLOGY OF HAMELIN POOL



RESEARCH REPORTS OF THE
BAAS BECKING GEOBIOLOGICAL
LABORATORY'S SHARK BAY PROJECT

Compiled by
R V Burne & G Hunt

Contributions by
J Bauld, R V Burne, L A Chambers,
J Ferguson, I Johns, G Skyring, R Summons,
M R Walter & others



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Preface

Professor Laurens Gerhard Marinus Baas Becking (1895 - 1963) was a distinguished scientist whose pioneering work established the importance of microbial activity in influencing the physico-chemical properties of the natural environment. During the 1950s his research focussed attention on the potential of sulphate-reducing bacteria to form metal sulphide deposits at low temperatures. Working with a small group of colleagues he demonstrated that several sulphide minerals of economic interest could be synthesised in cultures of sulphate-reducing bacteria.

The success of this research, carried out with both BMR and CSIRO, encouraged the Australian Mineral Industries Research (AMIRA) to formally join with these organisations to facilitate Baas Becking's work, and later, following his death in 1963, to create a laboratory bearing his name.

The Baas Becking Geobiological Laboratory (BBGL) was formally established in 1964 "to investigate the biological and chemical processes associated with the formation of mineral deposits and with other geological phenomena". Up until 1976 much of the research involved laboratory studies on the biology and biochemistry associated with mineralization processes, but in 1977 a major research program commenced in Spencer Gulf, South Australia to apply the experience gained by the Laboratory to the *in situ* examination of modern sedimentary environments under the general project title "Sulphide Mineralisation in Carbonate-Rich Sediments". This research on the sulphur cycle in modern peritidal carbonate environments pioneered many aspects of modern sedimentary geobiology.

It became clear that this methodology could be also be applied to the study of the carbon cycle, and in 1982 the Laboratory broadened its approach to encompass geobiological research related to the genesis, accumulation and recovery of petroleum. Emphasis was placed on the study of microbially sourced hydrocarbon accumulations typical of late Proterozoic and lower Palaeozoic rocks. Several major Australian sedimentary basins preserve relatively undeformed sequences of these ancient rocks and, although they had been traditionally regarded as unprospective, significant discoveries in rocks of equivalent age in the USSR and Oman encouraged the BBGL to commence investigation of their hydrocarbon potential.

As part of this program, a major research project was initiated in Hamelin Pool, an embayment of Shark Bay, Western Australia. The area is remarkable from the point of view of environmental microbiology in that extensive tracts of the intertidal and subtidal zones of the hypersaline embayment are dominated by ecosystems comparable to those which flourished in shallow seas and lakes of the Proterozoic and Cambrian. The enormous expanse and wide variety of microbial mats constructed by benthic microbial communities in Hamelin Pool constitute the most significant assembly of phototrophic microbial ecosystems in the world. These include the first documented living examples of stromatolites with a morphological diversity and abundance comparable to those that inhabited Proterozoic seas. As such, they offer the only extensive living analogue for study of the nature and evolution of the Earth's biosphere up until the early Cambrian. Comprehensive research by Dr Brian Logan and colleagues from the Department of Geology, University of Western Australia between 1956 and 1975, followed by further investigations by the Geological Survey of Western Australia (led by Dr P E Playford) established the environmental and geoscientific framework within which BBGL research could be undertaken.

The Shark Bay Project was nearing completion when, in 1986, the BBGL was reviewed by a committee comprising Dr A D T Goode (BHP), Dr P J Cook (BMR), Dr B J J Embleton (CSIRO), Dr R W Henley (BMR), and Mr B M Thomas (Shell Australia). The Committee found that BBGL was undertaking work of a high scientific calibre but that its separate management structure had become redundant in view of the evolution that had occurred in both BMR and CSIRO. It recommended that it was now more appropriate for this work to be integrated with high priority mainstream research in BMR and CSIRO. It was recommended that BBGL cease to function in its present form from 30 June 1987 and its scientific skills be deployed to BMR and CSIRO research teams working in such priority areas as petroleum geology and geochemistry, water resources, biotechnology, sedimentology and ore deposit genesis. It was also recommended that modern sedimentary environment studies be pursued as part of BMR's wider responsibility to contribute to man's impact on the environment (e.g. coastal studies).

These recommendations were adopted, the BBGL was closed in July 1987, and staff were redeployed to other programs in CSIRO and BMR. This, coupled with the subsequent re-organisation of

BMR following the Wood's Review, has delayed the finalisation of aspects of the Hamelin Pool research program and the publication of results. Despite this, a great deal of information is currently available as the Laboratory provided regular documentation of its research in Quarterly and Annual Reports, and most of the major findings of the project have now been presented at scientific meetings and are available in the form of Conference Abstracts. Some papers have already appeared in the scientific literature, but the bulk of the research is still being prepared for publication, and will appear progressively over the next two years.

In the interim, this volume brings together the various progress reports on the Shark Bay project published in the Quarterly and Annuals Reports of the BBGL together with a bibliography of project publications to date by former members of the BBGL. Also included in the volume are abstracts of presentations about the project made to the 1985 Sponsors' Meeting, and a previously unpublished paper reviewing the significance of the BBGL work in Hamelin Pool which was presented to a Symposium on Shark Bay in Perth in 1986.

The contributions published here are reproduced as they originally appeared and without subsequent editorial revision. For example, the record of high levels of heavy metals in groundwaters in Nilemah Embayment is retained, although they were later found to have been due to contamination of samples. It must therefore be emphasised that these contributions, especially those from Quarterly Reports, were essentially written to communicate initial results emerging during the course of research, and in some cases opinions and conclusions have been subsequently revised.

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THE GEOLOGICAL SIGNIFICANCE OF HAMELIN POOL, SHARK BAY

M R Walter

Division of Continental Geology, Bureau of Mineral Resources,
Geology and Geophysics, Canberra

Hamelin Pool plays a special role in our understanding of the history of the Earth. Not only are there abundant stromatolites like those that have been forming on Earth for at least 3,500 million years, but more fundamentally, the ecosystem as a whole has many ancient features. For 3,000 million years before the evolution of animals and plants all aquatic environments on Earth were dominated by microorganisms (bacteria, cyanobacteria and later by microscopic algae) very similar to those that are now abundant in Hamelin Pool. These are the organisms that build the stromatolites and live in them, but many of them also colonise vast areas of the shallow marine (subtidal) environment in Hamelin Pool in places where there are no stromatolites. There is no place anywhere else on Earth where that biological record survives today with the diversity and abundance that it does in Hamelin Pool. So Hamelin Pool, to geologists, is an example of the way the Earth was for 3,000 million years not just in coastal environments or bays but on continental shelves as a whole and in lakes and anywhere where there was standing water. The analogy is not exact because there have been some major changes (for instance, there were no fish or other animals before 1000 million years ago), but it is sufficiently instructive that a great deal can be learnt about the early Earth by studying Hamelin Pool. This area is a window on the past, and a natural laboratory in which we can study processes that were very widespread on the early Earth.

Over the last 30 years major geological studies of Hamelin Pool have been conducted by the University of Western Australia and the Geological Survey of Western Australia. From 1980 to 1987 the Baas Becking Geobiological Laboratory (of the Bureau of Mineral Resources and CSIRO) undertook a program integrating geology, geochemistry and microbiology. It is that work that I will very briefly describe. The purpose of this was to investigate the processes of formation of particular types of oil accumulations and metal deposits. Such accumulations and deposits do not occur in Hamelin Pool, but the processes by which they form can be studied there. For instance, we have studied how organic matter accumulates in sediments. That is important because oil comes from organic-rich sediments which initially form at the Earth's surface and are then deeply buried and heated, driving off the hydrocarbons which comprise the oil. In addition, there are

opportunities to study the processes of formation of copper, lead and zinc ore deposits. Some of the groundwaters around Hamelin Pool are brines, much more saline than seawater, that are potentially very effective at leaching metals from rocks and transporting them through the sediments. In places, these waters encounter hydrogen sulfide produced by bacteria, and metals could be precipitated to form deposits that are comparable to ore deposits. The better we understand these processes, the more successful will be our exploration for metals and oil.

Ancient limestones and dolomites are interpreted by geologists primarily on the basis of modern examples that can be observed in the process of formation. The carbonate sediments of Shark Bay are one of the best known of these examples as a result of the detailed and extensive studies conducted there. These studies have had a major impact on the interpretation of ancient rocks.

Environment

The unique features of Hamelin Pool result firstly from the semi-arid climate of the region, where the potential rate of evaporation is ten times the annual rainfall, and secondly from the presence of the Faure Sill, which severely limits the rate at which normal seawater can replace that concentrated by evaporation in the Pool. These two features in combination cause the water in the Pool to be almost twice as saline as normal seawater. Many animals and aquatic plants cannot tolerate such high salinities and so are excluded from the Pool. In most of Hamelin Pool there are no seagrasses and few seaweeds, and there are none of the large marine snails that normally graze on bacteria and algae. As a result of this lack of competition and grazing, microorganisms that are normally rare are able to thrive. The bottom-dwelling microbes form several different mat-like communities that are distributed according to their environmental requirements and tolerances.

In order to understand the ecology and chemistry of the area it is necessary to have comprehensive records of the main environmental features. A considerable amount of information about the weather is available because a weather station was manned at the old Hamelin Post Office for many decades, most recently by John and Mehalah Sellenger. Despite this, we needed more information, so we developed and installed two automatic monitoring stations that collected the data listed below (table 1). Measurements were made every two hours for up to two and a half years, between September 1983 and April 1986.

	Ground Water Level	Tide	Solar Radiation	Rainfal	Air Temp	Water Temp	Wind Run	Wind Direction	Barometric Pressure
FLINT CLIFF	*	*	*	*	*	*	*		
NILEMAH	*							*	*

Table 1 The asterisks indicate which environmental characteristics were measured by automatic monitoring stations at the two sites listed.

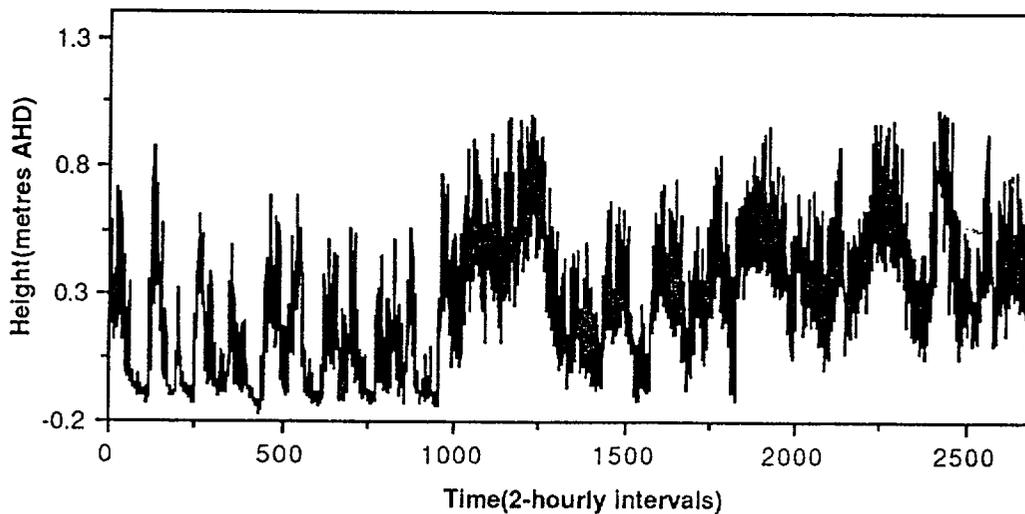
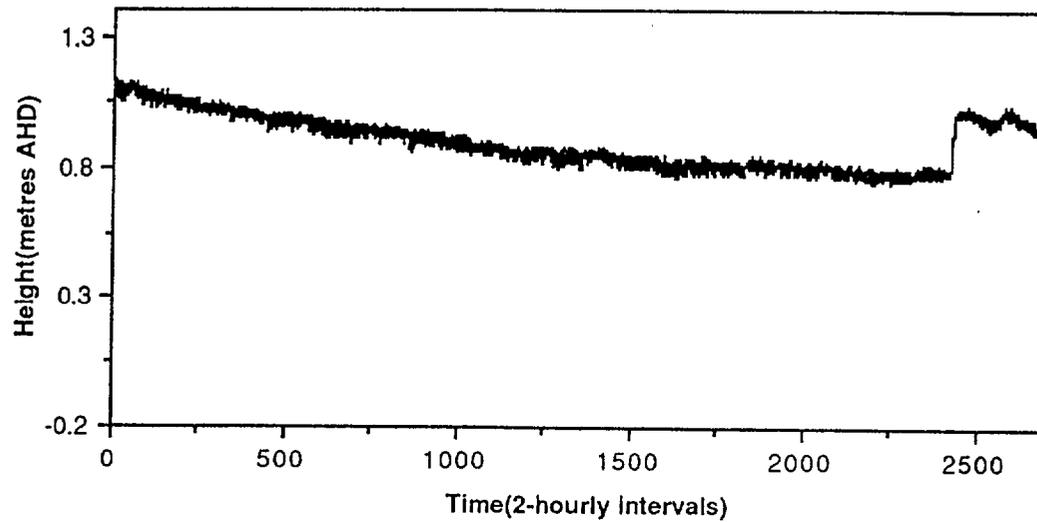


Figure 1 Two examples of data from the monitoring system in Nilemah Embayment. Both records start in November, 1984 and run for over 2500 hours, with readings every 2 hours. The vertical scales are heights in metres related to the standard "Australian Height Datum". The upper diagram shows groundwater levels at one site; the lower diagram shows tide heights.

Figure 1 shows examples of a little of the data collected. It shows tide heights for Nilemah Embayment and groundwater levels for one monitoring site near there for a period of 2500 hours (104 days) starting in November, 1984. The small fluctuations in groundwater

level were caused by changes in barometric pressure and the big increase on the right resulted from rain. Data such as these, when combined with the detailed topographic surveys carried out for us by the Australian Survey Office, provide the background that is essential for confident interpretation of the biology and chemistry of the Pool.

Fauna

The waters of the Pool have been thought of almost as a biological desert, but we have found quite diverse and abundant communities of organisms. Without attempting a census of all the organisms present we nonetheless have recognised 78 species of animals as listed below.

ANIMALS ON AND AMONG STROMATOLITES

	<u>Species</u>	<u>Size-Range</u>	<u>Food Source</u>
Dugong	1	~ 3,000 mm	sea grass
Fish	15	8 - 1,500 mm	fish crustaceans detritus in sand plankton
Sea Snakes	1	~ 1,000 mm	fish
Molluscs			
Bivalves (clams)	5	2 - 15 mm	suspended organic matter
Gastropods (snails)	5	1-2mm	cyanobacteria?
Crustaceans	5	0.5 - 35 mm	plankton and organic detritus
Annelids (worms)	2	0.5 - 5 mm	small animals suspended organic matter
Medusae	1	100 - 300 mm	suspended organic matter
Nematodes	30	< 1 mm	bacteria, algae, small animals
Foraminifera	10	< 1 mm	bacteria, organic detritus
Sponges	3	5 - 15 mm	suspended organic matter

In compiling this list we have been assisted by several specialists, including W L Nicholas and P De Deckker. Future studies of Hamelin Pool would benefit substantially from a comprehensive census of the animal populations. Conspicuous by their absence in this list are large animals that graze on bottom-dwelling microbes, especially large gastropods (sea-snails), and other types of grazers such as parrot fish, echinoids (sea urchins) and chitons.

Microbial mats

The rarity of grazing animals allows microbes to flourish and form the extensive mat-like structures and stromatolites for which Hamelin Pool is famous. Microbial mats are most widespread in the permanently submerged (subtidal) area of the Pool. The microbial community there is very different from that in the beach (intertidal) zone. It contains abundant microscopic algae with silica skeletons (diatoms) and microscopic green algae as well as the cyanobacteria ("blue-green algae") that form the intertidal mats. It includes a number of presently undescribed types of organisms. Living within the mats are abundant minute animals of many different kinds.

Here and there this complex community constructs columnar and dome-shaped stromatolites up to two metres high - these are true reefs, with all of the ecological complexity that this implies. Attached to them are sponges and several kinds of large algae (seaweeds), and living in and amongst them are prawns, sea-snakes, fish and many other types of animals. Dating using the radioisotope ^{14}C has shown that they have taken several thousand years to reach their present height. The largest (which presumably are the oldest) may have begun to form soon after the Faure Sill became established some 10,000 years ago, but they have not yet been dated. Calcium carbonate precipitates as a hard cement within the stromatolites almost as fast as they form, so they become rocks. The precipitation is very patchy and as a result they have a spongy, porous internal structure. This is of special interest because it is just such rocks that can form natural reservoirs for petroleum, and in fact there are known examples of ancient stromatolite reefs that contain petroleum. Research on the presently forming examples in Hamelin Pool has helped with exploration for reservoirs of this type, and will continue to do so.

When we first started research in the area we heard apochryphal stories about huge domal structures in the middle of the Pool. No such structures were ever found by us or appear on satellite images or aerial photographs, so perhaps we were having our legs pulled. But what is there is equally interesting. Some 200 square

kilometres in the southern half of the Pool are covered with black ooze up to 1.5 metres thick; this consists of carbonate mud with abundant microscopic siliceous skeletons of diatoms and up to 5% by weight of organic matter. It is a petroleum source rock in the process of formation. How it forms is still a matter of some controversy: some scientists (including myself) consider that it is debris eroded off the intertidal zone and adjacent shallow subtidal shelves during cyclones and other storms, and swept out into the Pool where it settles during quiet periods (cyclones pass within 100 kilometres of the Pool on average once every seven years). The ooze contains some unique organic chemicals of microbial origin different from any found in other areas of the Pool, so some proportion of the organic matter apparently comes from organisms that live in the ooze. The other point of view is that most of the organic matter comes from organisms that live in the ooze. Our research on the chemistry and microbiology of this deposit is continuing so we can gain a better understanding of its origin.

The intertidal microbial mats and the stromatolites they construct have been studied for many years, and it is these rather than the more extensively developed but less studied subtidal forms that most scientists think of when Hamelin Pool stromatolites are mentioned. Several different communities of cyanobacteria are prominent in the intertidal zone, with species forming "smooth", "pustular" and "tufted" mats being the most common (these names are based on the surface shapes of the mats). The distribution of each community depends primarily on its resistance to exposure to the atmosphere during low tides. For instance, the pustular mats can tolerate a great deal of exposure and so are able to colonise huge areas of the upper intertidal zone as in the Nilemah and Gladstone Embayments. These and the subtidal mats together cover about 1000 square kilometres forming what can be thought of as a huge factory generating organic matter.

Even though it is only microbes that produce the organic matter in this example, our measurements show that this can be a highly productive system, comparable with other more "advanced" marine ecosystems and with some grasslands and forests on land. This shows that microbial ecosystems have to be considered as major sources of organic matter in the past, and must be considered when we try to predict the distribution of source rocks for petroleum. In order to be able to predict such distributions we need to understand the controls on productivity, so that has been one of the emphases of our research in the Pool. The productivity of planktonic (floating) microbes in the Pool is very low, as a result of low levels of the essential nutrient, phosphorus, in the water.

Productivity is kept high in the mats through a very tightly coupled system in which both phosphorus and nitrogen are extracted from the water and recycled within the mat ecosystem.

Groundwater

Surrounding the Pool is a zone of intense chemical activity with processes driven by complex interactions of the effects of rainfall, tidal flooding, evaporation and microbial activity. We selected the four kilometre-wide flats of Nilemah Embayment (Fig. 2) as the site at which to study these processes. Rainfall, though sparse, is sufficient to produce a large accumulation of fresh and brackish water in the high red sand dunes that flank the embayment. This flows seawards through the sediments, constituting one of the inputs into the chemically active flats. Secondary reservoirs of rainwater occur in the low ridges of shell debris built during storms on the supratidal flats of the present and recent past (as was known to the Aborigines, who dug wells in the beach ridges). Tidal waters flood the flats and raise the level of the groundwater up to a kilometre inland from the intertidal zone. Evaporation on the barren flats is intense, so the groundwaters evolve to become concentrated brines with salinities reaching eight times that of seawater (Fig. 3).

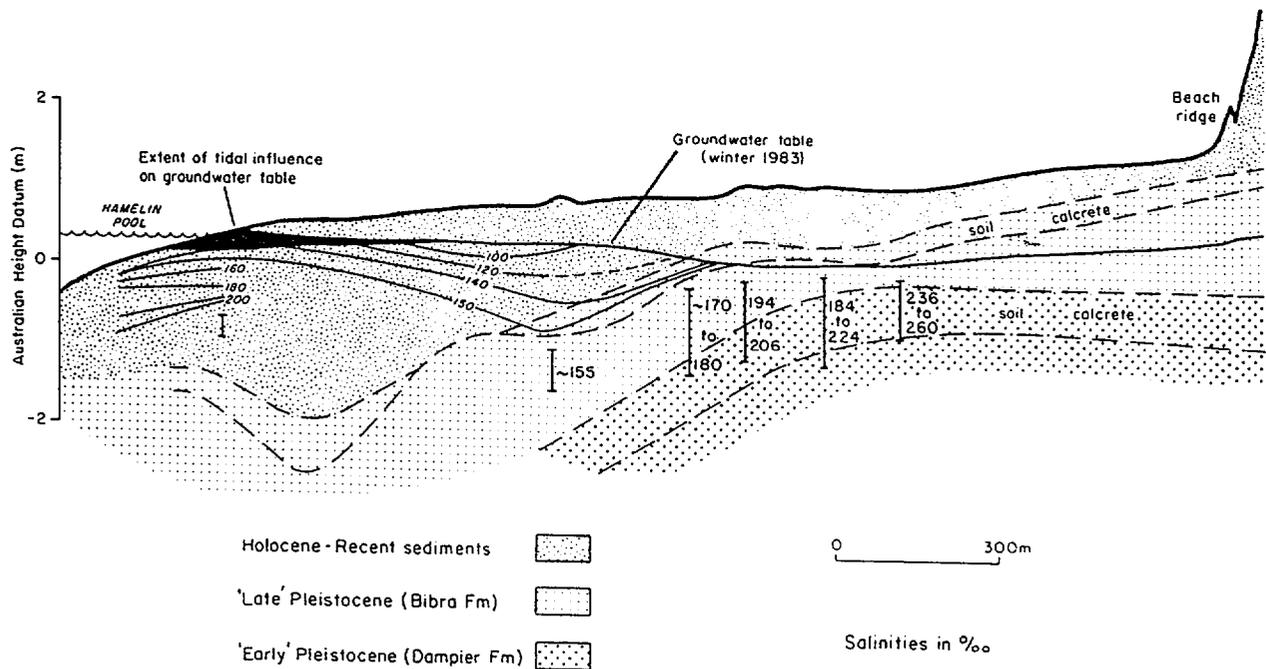
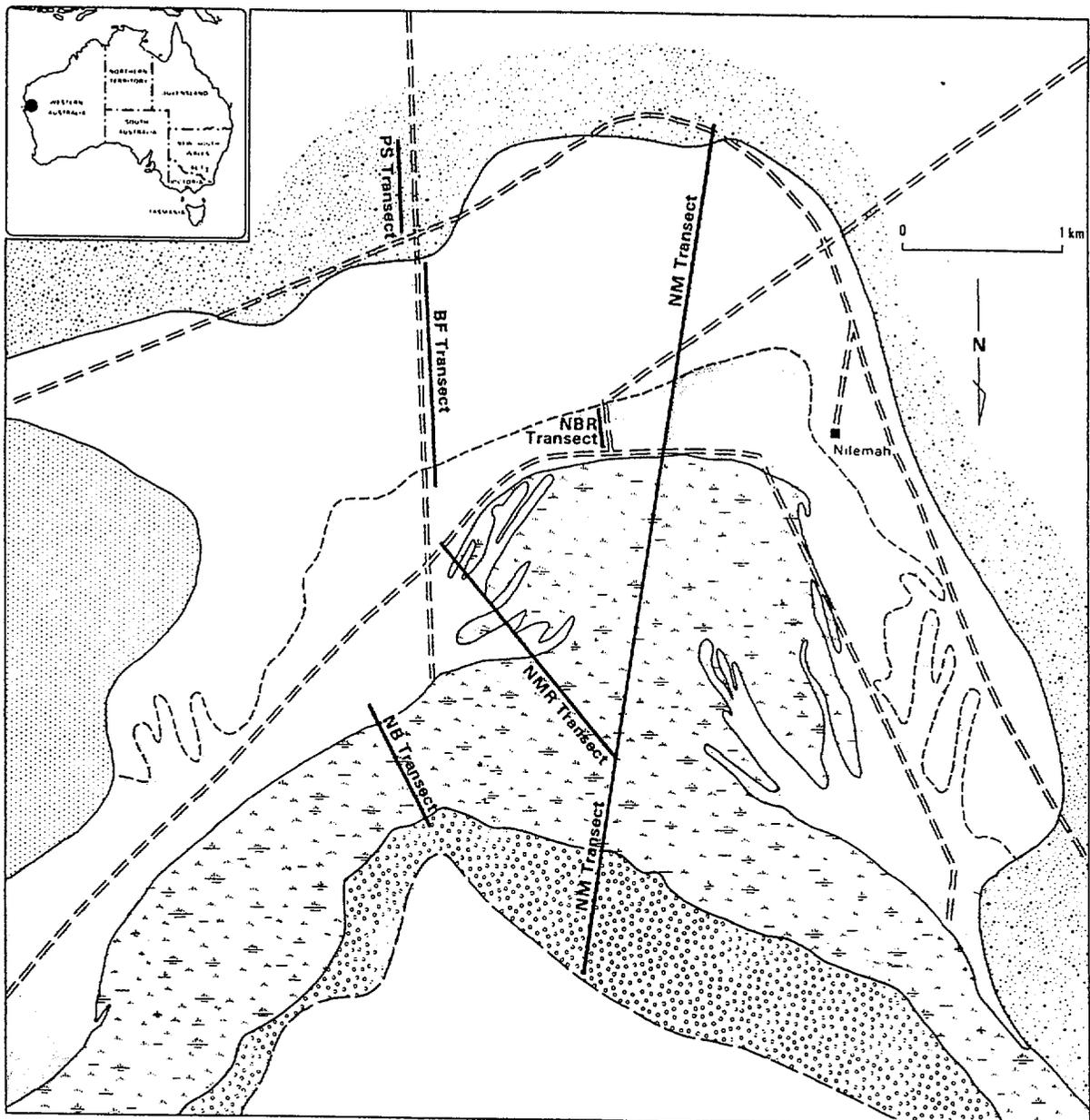


Figure 3. Subsurface section along part of transect NM shown in figure 2. The figure shows the distribution of the various types of sediments, the position of the groundwater table, and the salinity of the groundwater. The salinity is given in "parts per thousand" (for reference, normal seawater has a salinity of 35 parts per thousand).



19/G50-9/1

- | | |
|--|--|
|  Peron Sandstone |  Sublittoral platform |
|  Toolonga Calcilutite |  Tidal flats |
|  Beach ridges |  Back flat |

Figure 2. Map showing the geology and the locations of the groundwater study transects in Nilemah Embayment.

Living within these groundwaters are bacteria that are chemically very active. In the sediments of the back flats, bacteria oxidise the plant debris that accumulates in the soil, producing carbon dioxide which then reacts with dissolved calcium and magnesium

to precipitate the minerals, calcite and dolomite. Beneath the supratidal flats are bacteria that obtain the energy they need for growth by reducing the sulfate in seawater to sulfide. The sulfide reacts with iron in the groundwaters to produce iron sulfide minerals, and also strips all the dissolved oxygen out of the water. Across much of the four kilometre width of the flats the waters are sufficiently saline to precipitate calcium sulfate (gypsum). In places, this forms interlocking masses of large crystals that cement the sediment into gypsum rock. The concentrated brines are denser than even the highly saline seawater of the Pool, and they seem to flow through the sediments, apparently even reaching the centre of the Pool (the main evidence for this is that the sediments in the centre of the Pool contain brines more concentrated than the overlying seawater).

In some other areas around the shores, where there are not such extensive flats to act as sites of evaporation, rainwater which has dissolved calcium carbonate from the shells in the beach ridges emerges on the beaches and evaporates, reprecipitating the carbonate. This produces a thin, hard crust of "beachrock". Some of the carbonate reprecipitates within the ridges, cementing the shells to form the very porous rock (coquina) used locally for building. The beach ridges themselves are a remarkable phenomenon: they are constructed during storms by the washing inshore of huge quantities of shells overwhelmingly dominated by a single species of clam. The clam is known to live in small numbers in the Pool, but the source of the vast quantities found in the beach ridges is still something of a mystery.

Solar ponds

Lines of playa lakes ("birridas") occur in the swales in the dune fields adjacent to the Pool. The gypsum that fills these was probably introduced in wind-blown sea spray, as it has the same sulfur isotopic composition as that in the ocean. On the western side of Hamelin Pool one such line of lakes intersects the shoreline at a site where there is a group of small sinkholes on an extensive supratidal platform. These probably formed when a slight rise of sea-level flooded an old birrida and some of the gypsum dissolved, causing the ground to collapse. Groundwater seeps into the sinkholes and they are flooded during very high tides. The water in them evaporates to form a very dense brine which sinks to the bottom of the deeper pools. The brine is heated by the Sun, reaching temperatures of 35°C. Plant debris that accumulates in the pools rots, using the oxygen dissolved in the brines (making them "anaerobic"). The result is that the pools have layered water bodies, with cool, oxygenated, hypersaline water at the top,

underlain by hot, anaerobic, supersaline water. The chemical gradient between these waters allows the growth of several distinct microbial communities, distributed according to their tolerance to or use of oxygen. In microcosm this little ecosystem mimics the evolution of the Earth's earliest ecosystems, from those intolerant of oxygen through to those now widespread on the beaches of Hamelin Pool that live under our oxygen-rich atmosphere. In fact we, as air respiring animals, would not be here if it were not for cyanobacteria such as these, for it was they that first developed the capacity to produce oxygen from water, so releasing it to the atmosphere.

Hamelin Pool has become famous to scientists because of its stromatolites. These occur in greater abundance and diversity there than anywhere else on Earth. But they are just one manifestation of the rich and varied microbial communities that abound in and around the Pool. This is an ecosystem that can tell us much about the early Earth; it will reward those who study it for many years to come.

The research very briefly described here is that of the following staff of the Baas Beeking Geobiological Laboratory, and a number of collaborators in other organisations:

John Bauld - ecology of the microbial primary producers
Bob Burne - sedimentology of the stromatolites
Jim Ferguson - geochemistry of the sediments and waters
George Heys - fauna
Ian Johns - automatic monitoring of the environment
Lyn Plumb - geochemistry of the sediments and waters
Graham Skyring - ecology of the sulfate reducing bacteria
Roger Summons - organic geochemistry
Phil Trudinger - sulfur oxidising bacteria
Malcolm Walter - stromatolites

Acknowledgements

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BAAS BECKING GEOBIOLOGICAL LABORATORY ANNUAL REPORT, 1978

INTRODUCTION

The Baas Becking Geobiological Laboratory is a research organisation jointly sponsored by the Commonwealth Scientific and Industrial Research Organisation (CSIRO), the Bureau of Mineral Resources (BMR), and the mineral industry acting through the Australian Mineral Industries Research Association. The Laboratory was formed in 1965 with the aim of investigating, with economic as well as scientific objectives, the possibility that some large stratiform sulphide ore deposits, such as those at Mount Isa and McArthur River, were initially formed by low-temperature processes in sedimentary basins. A crucial factor in the establishment and continued operation of the Laboratory has been the support of the Australian Mineral Industry. It was largely at the instigation of H.F. King that mining companies were encouraged to join BMR and CSIRO in sponsoring geomicrobiological research. Throughout its lifetime the Laboratory has received, and depended on, financial contributions from AMIRA. Sponsoring companies and others have also collaborated with Laboratory personnel on a number of field-orientated studies and have provided invaluable logistical support, technical information, and research materials. The Laboratory, which currently employs eleven scientists from CSIRO and BMR, is one of the few in the world in which biologists, chemists, and geologists work together on geologically related problems.

During its first ten years of operation the Laboratory undertook studies on a number of mineralised areas and conducted investigations aimed at developing an understanding of the organisms and processes associated with mineralisation.

Highlights of this period were:

- . the experimental demonstration of the environmental conditions governing pyrite formation and of the importance of disulphide ions in this process.
- . the experimental reproduction of a range of textural features caused by post-depositional processes in ore deposits. In particular, a possible mechanism for the origin of microbanding in sedimentary deposits was established.

- . a description of the physical chemical conditions governing solubilities of base metals in brines.
- . the documentation of metal enrichments and of sulphate-reducing bacteria in volcano-sedimentary exhalative environments and evaporative inland lakes.
- . the characterisation, in biochemical and physiological terms, of sulphate-reducing bacteria from a variety of marine and freshwater environments
- . the elucidation of factors controlling sulphur isotope fractionation during chemical and bacterial sulphate reduction, and
- . the recognition of the importance of organisms and organic matter in the mobilisation and transport of metals.

The results of these investigations allowed the formulation of models of ore genesis on which the current research of the Laboratory is based. In particular, the conclusion was reached that, under certain specified conditions, biological sulphate reduction could have been a major source of sulphide in the formation of large base metal sulphide deposits.

Yet to be determined are the extent to which this process has, in fact, operated in the formation of major ore deposits, the specific nature of the conditions governing large-scale biogenic sulphide mineralisation, and the significance of the process to exploration strategy.

In 1976 the Laboratory commenced a five-year program in which the biological research is based on studies within a modern sedimentary environment. Concurrent research is being undertaken on the laboratory simulation of sedimentary systems, and on the characterisation of known orebodies.

Research on modern environments has been undertaken in the northern region of Spencer Gulf, South Australia, and has reached the stage where an integrated picture of the sedimentology, chemistry, and biology of this region is emerging. The environment exhibits a number of features which are analogous to those implicit in current models of sedimentary ore genesis. Minor studies were also made on the stromatolitic intertidal environments at Shark Bay, Western Australia.

In the laboratory, experimental sedimentary systems have been devised to simulate aspects of ore genesis which are not readily studied in the natural environment. In the current experiment, features of a metalliferous, organic-rich carbonate sediment are being examined.

Shark Bay, WA

During March, Shark Bay was visited in the company of M. J. Jackson, J. Kennard, M. D. Muir, and M. R. Walter of BMR. This environment is characterised by many sabkha-like features and a varied and extensive development of stromatolites. The excursion was led by Dr P. Playford of the Geological Survey of Western Australia.

Samples from 7 different stations within intertidal zones were taken for sulphate reduction rate assay. The results are given in Table 4, which also contains stable sulphur isotopic data and a brief description of the kinds of sediments studied. The rates in the organic-rich, thickly laminated sediments were generally very high. It was apparent that the organic matter contained in these sediments was derived from gelatinous material sloughed off from the extensive stand of intertidal and subtidal columnar stromatolites. The sloughing of the stromatolites was accentuated by the high tides and rough seas resulting from cyclonic conditions a few days prior to sampling.

It is possible that enormous quantities of organic matter dislodged from a large surface area of columnar stromatolites could be transported to deep or shallow basins by wind and tide action. In such organic-rich sediments, high rates of sulphate reduction could occur.

TABLE 4
SULPHATE REDUCTION RATES, SULPHATE CONTENTS, AND $\delta^{34}\text{S}/\text{‰}$ VALUES FOR SHARK BAY SEDIMENTS

STATION DESCRIPTION	SULPHATE REDUCTION RATES mmol m ⁻² d ⁻¹	μmol SULPHIDE g ⁻¹ SEDIMENT	PORE-WATER SULPHATE	$\delta^{34}\text{S}/\text{‰}$	ACID-LABILE SULPHIDE
1. Organic-rich thickly laminated black sediment	19*	88*			-14.5
2. Same as for 1 but apparently more recent	69	56	+27.7		-11.5
3. Same as for 1 but further seawards	14	34	+22.0		-11.9
4. Same as for 1 but different location	29	51			
5. Pustular mat sediment	0	0			
6. Smooth mat sediment	4.6	6	+20.7		-23.2
7. Sandy sediment between columnar stromatolites	4.9	4			

(* is the arithmetical average of at least 3 assays.)

SULPHUR ISOTOPES

L.A. Plumb

Sulphide resulting from bacterial sulphate reduction is considerably enriched in ^{32}S compared to the sulphate from which it arises, and the phenomenon has been used extensively in interpretations of isotope data from ancient sediments. This project is designed to establish what isotopic patterns may be expected in sulphide forming in sediments underlying present-day intertidal algal mats. Sulphur isotope analyses have been done on acid-labile sulphides and pore-water sulphates from cores taken at the same times and locations as the material being used to determine the rates of sulphate reduction and carbon dioxide fixation. The cores were sectioned horizontally to differentiate the black sulphidic bands which, between samplings, vary quite considerably in position (Fig. 5), possibly because of scouring, rapid sedimentation, or oxidation of sulphides. Variations due to sampling appear unlikely since sulphide concentrations calculated to a 5 cm depth all agree closely with results obtained, by a different analytical technique, during determinations of the rate of sulphate reduction.

$\delta^{34}\text{S}$ values for pore-water sulphate are little different from seawater sulphate ($+20.5\text{‰}$) except for one sample from Station 2 at Shark Bay (Table 4) which exhibits particularly high sulphate reduction rates. Sulphide values at Mambray Creek and Shark Bay range between -9 and -23‰ (Tables 2 and 4, Fig. 5), most values falling about -16‰ . This is an average fractionation of -35.5‰ relative to seawater sulphate, which is in the range of the higher fractionations obtained in experimental systems and which is usually associated with a low rate of sulphate reduction per cell. This may indicate that the high overall rates of sulphate reduction in Mambray Creek sediments (see p.12) are the results of high population of bacteria with relatively slow metabolic activity.

BAAS BECKING GEOBIOLOGICAL LABORATORY
ANNUAL REPORT, 1979

INTRODUCTION

The northeastern region of Spencer Gulf, South Australia, continued as the focal point of the Laboratory's modern environment program with comparative work being undertaken in coastal salt lakes of southern Eyre Peninsula; associated studies on Shark Bay, Western Australia, and the Ball Trough were completed. These field studies were augmented by laboratory experiments designed to assess the plausibility of models generated on the basis of field evidence.

Shark Bay, W.A.

During an excursion to Shark Bay in 1978, radioisotope experiments were carried out at Hamelin Pool in order to estimate the primary productivity of selected intertidal blue-green algal mats and of subtidal columnar stromatolites. The rates of primary productivity and mat pigment content are shown in Table 2.

TABLE 2.

PRIMARY PRODUCTIVITIES AND PIGMENT
CONTENT FOR ALGAL MATS IN HAMELIN
POOL, SHARK BAY.

MAT TYPE	PRIMARY PRODUCTIVITY		CHL <i>a</i> CONTENT ^a (±S.D.)	
	mg C m ⁻² h ⁻¹	mg C mg chl <i>a</i> ⁻¹ h ⁻¹	mg m ⁻²	mg g ⁻¹ protein
<u>Intertidal mats</u>				
Smooth (STN 6)	17	0.24	124(±23)	3.27(±0.88)
Tufted	85	0.16	714(±170)	18.60(±4.78)
Pustular (STN 5)	nd ^b	9.12	nd ^b	(1.80 ± (0.50))x10 ⁻³
<u>Subtidal mats^c</u>				
Colloform	113	2.25	92(±34)	2.35(±0.80)
Internal	nd ^b	1.00	nd ^b	(1.10(±0.41))x10 ⁻³

^a Chl *a* = Chlorophyll *a*, number of determinations = 8

^b nd = not determined

^c from subtidal stromatolite column

Colloform is surface mat; internal mat is of gelatinous, resilient consistency.

The high productivity of colloform mat ($113 \text{ mg C m}^{-2}\text{h}^{-1}$) reflects the relatively constant nature of the subtidal environment. Unlike colloform mats, the other two stratiform mats occur in the intertidal zone and, in consequence, may be subjected to considerable desiccation stress. Both primary productivity ($\text{mg C m}^{-2}\text{h}^{-1}$) and photosynthetic efficiency ($\text{mg C mg chl } a^{-1}\text{h}^{-1}$)* are lower than for colloform mat.

Tufted mat productivity ($85 \text{ mg C m}^{-2}\text{h}^{-1}$) was greater than that for smooth mat ($17 \text{ mg C m}^{-2}\text{h}^{-1}$) and reflects its presence in environments where water is retained longer than on smooth mat, which occurs on better drained sediment surfaces. The area of smooth mat sampled was probably exposed to prolonged desiccation before our excursion, since smooth mat in Spencer Gulf has much higher primary production rates.

* Chl *a* = Chlorophyll *a*, the primary photosynthetic pigment.

BAAS BECKING GEOBIOLOGICAL LABORATORY ANNUAL REPORT, 1982

INTRODUCTION

The carbon and sulphur cycles are inexorably linked. Their products in sediments are evaporites, carbonates, iron sulphide and organic matter - and ultimately, here and there, base-metal sulphide ores and petroleum accumulations. At high temperatures the links are purely chemical, but generally at the Earth's surface they are biochemical and, predominantly, microbial. The search for petroleum accumulations and sulphide ores is either empirical, or it is an attempt to resolve some local aspects of the carbon and sulphur cycles. This is obviously an immense simplification, but is no less true for that. These two geochemical cycles, their links, and their ultimate products, are the subjects of the Laboratory's current research program, which focusses on parts of this system of special relevance in Australia.

There is another reason for focussing our research on Proterozoic to Cambrian basins, and that is the occurrence here of distinctive Holocene coastal, lacustrine and desert sedimentary environments analagous in many ways to the palaeoenvironments recognised in basins that predate the Silurian origin of land plants. In Shark Bay, Spencer Gulf, the Coorong Lagoon area, and in various saline lakes, we have the opportunity to study the workings of the carbon and sulphur cycles, in ecosystems comparable to those of the Proterozoic and Cambrian, to search for distinctive signatures for significant processes, and to contribute to the theoretical and observational framework needed for the interpretation of Proterozoic and Cambrian Sequences. Many of these signatures are isotopic, and for that reason we have a growing set of projects on the isotope geochemistry of hydrogen, carbon, oxygen and sulphur in waters, sediments and rocks.

Sulphides In Tidal Channels, Shark Bay, Western Australia

Sulphur isotope distribution in algal laminated sediments from tidal channels at Shark Bay has been studied. The sampling sites are in tidal flats marginal to Lharidon Basin and Gladstone Embayment (see Fig. 3). The former site is subject to intermittent desiccation but at the other location this is unlikely since the channel has a direct connection with the South Gladstone Embayment. The sediments there were covered by 20 to 30 cm of water when samples were taken, while those at Lharidon basin were topped by halite crystals.

Sulphide concentrations and isotope values for both sediments are given in Tables 1 and 2. The range of values (-17.2 to -31.8) is equivalent to fractionations of 1.038 to 1.052 relative to seawater sulphate. This is not distinguishable from fractionations in other marine environments. Minute quantities of zinc-reducible sulphide (presumably pyrite) were found and its isotope distribution was generally ^{32}S -enriched compared to the acid labile sulphide. This relationship is common in sediments but has most often been explained in terms of the acid labile sulphide being produced most recently in a system closed to sulphate. The trend of increasing ^{32}S content with depth in these sediments argues against a closed system. The same type of pattern has been observed in sediments of the Santa Catalina Basin and the Bali Trough over much greater depths.

Isotope Studies in Shark Bay, Western Australia

Gypsum, groundwater sulphate and sulphides have been analysed for sulphur isotope distribution and are detailed in Table 3. The sulphate values show a strong marine influence in both Nilemah and Solar Ponds. Even birridas (salt lakes) 1-2 km from the present shoreline have gypsum that is of marine origin. Along the Nilemah transect (see Fig. 4) there is an indication of lighter (e.g. +18.5‰) continental sulphate in samples near the beach ridges. These samples also have lower salinities consistent with a continental origin. Fluctuation of the values across the supratidal plain may indicate a zone in which either continental or marine influence has dominated at different times. Deuterium and oxygen isotope analyses of the groundwaters are being undertaken and should help the interpretation. A different situation exists at Flagpole Landing where there is a noticeable groundwater seepage at the base of the dunes. The sulphate in this has a value of +17.9‰ and is thought to be influenced by the nearby flow of borewater in which sulphate is +13.6‰.

Dark coloured sediments below the water table in the Nilemah supratidal plain (Table 3, A4, B23, B28) were initially thought to be principally sulphide, but acidification yielded only minor

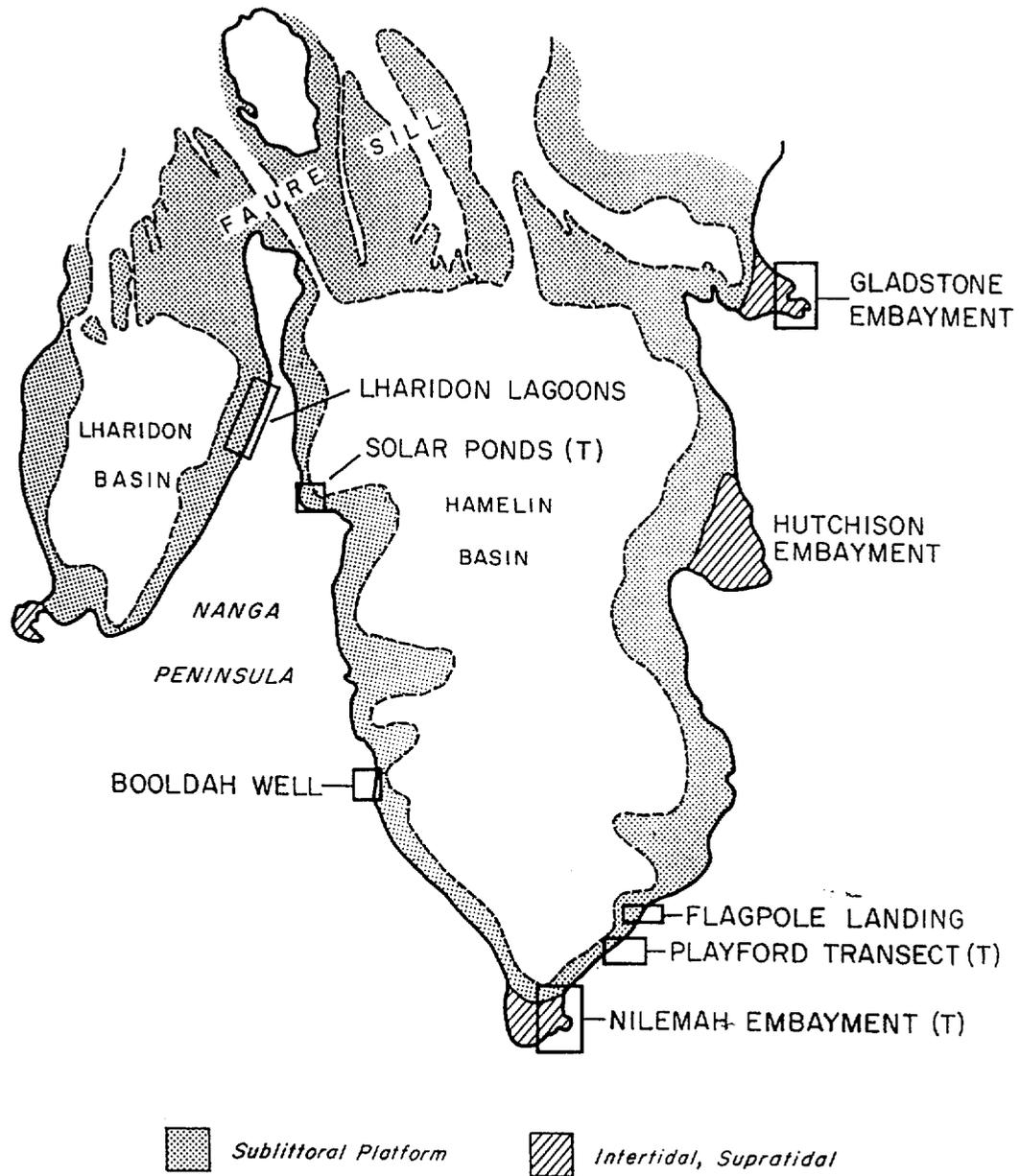


Fig. 3 Groundwater sampling locations at Hamelin Pool and Lharidon Basin. Transects were established at those locations marked with a (T).

TABLE 1.
SULPHIDE CONCENTRATIONS AND ISOTOPE
DISTRIBUTIONS IN SEDIMENTS IN TIDAL CHANNELS
AT SHARK BAY, W.A.

Depth Interval (cm)	ACID LABILE SULPHIDE			
	LHARIDON BIGHT		GLADSTONE EMBAYMENT	
	mg g ⁻¹ (dry wt)	δ ³⁴ S ‰	mg g ⁻¹ (dry wt)	δ ³⁴ S ‰
0 - 5	0.47	-17.2	2.40	-19.7
5 - 10	0.70	-19.0	0.93	-21.3
10 - 15	0.48	-24.1	0.15	-25.1
15 - 20	0.19	-23.4	0.14	-24.9
20 - 25	0.09	-25.3	0.20	-27.2
25 - 30	0.10	-25.1	0.06	-25.5
30 - 35	0.17	-27.6		
35 - 40	0.10	-32.0		
40 - 50	0.08	-29.4		

TABLE 2.
SULPHUR ISOTOPE DISTRIBUTION FOR ZINC-REDUCIBLE
SULPHIDE FROM SEDIMENTS IN TIDAL CHANNELS
AT LHARIDON BIGHT AND GLADSTONE EMBAYMENT,
SHARK BAY, W.A.

SITE	DEPTH INTERVAL (cm)	δ ³⁴ S ‰
Lharidon Bight	0 - 20	-25.4
	20 - 35	-27.7
	40 - 55	-28.8
Gladstone Embayment	0 - 10	-23.5
	10 - 15	-25.4
	20 - 25	
	25 - 31	-28.0

TABLE 3.
SULPHUR ISOTOPE DATA FOR GYPSUM,
GROUNDWATER SULPHATE, AND SULPHIDE SAMPLES
FROM SHARK BAY, W.A.

		GYPSUM	$\delta^{34}\text{S} \text{ ‰}$
Nilemah Transect		A 5	+22.3
		A 6	+22.2
Solar Pond			+22.4
Inland Birrida		1	+22.1
		2	+22.5
		3	+22.2
GROUNDWATER SULPHATE			
Nilemah Transect	B	20.14	+18.5
		21 (5)	+20.3
		22 - 6	+20.5
		22	+20.0
		22.15	+18.9
		23	+18.9
		23.33	+20.5
		24 -- 12	+19.9
		25	+20.0
		25 (5)	+20.9
Solar Pond	1		+21.8
	2		+22.0
	3		+21.6
Solar Pond Transect		31.6	+20.8
		33.16	+21.4
		24.47	+21.4
Playfords Transect			+23.4
Flagpole Landing			+17.9
Bore Water			+13.6
SULPHIDES			
Nilemah Transect	A2	Acid	-14.2
		Labile	
		Zinc	-17.2
Nilemah Transect	A4 B23 B28	Reducible	
		Acid	-26.6
		Labile	
		Zinc	-32.2
		Reducible	

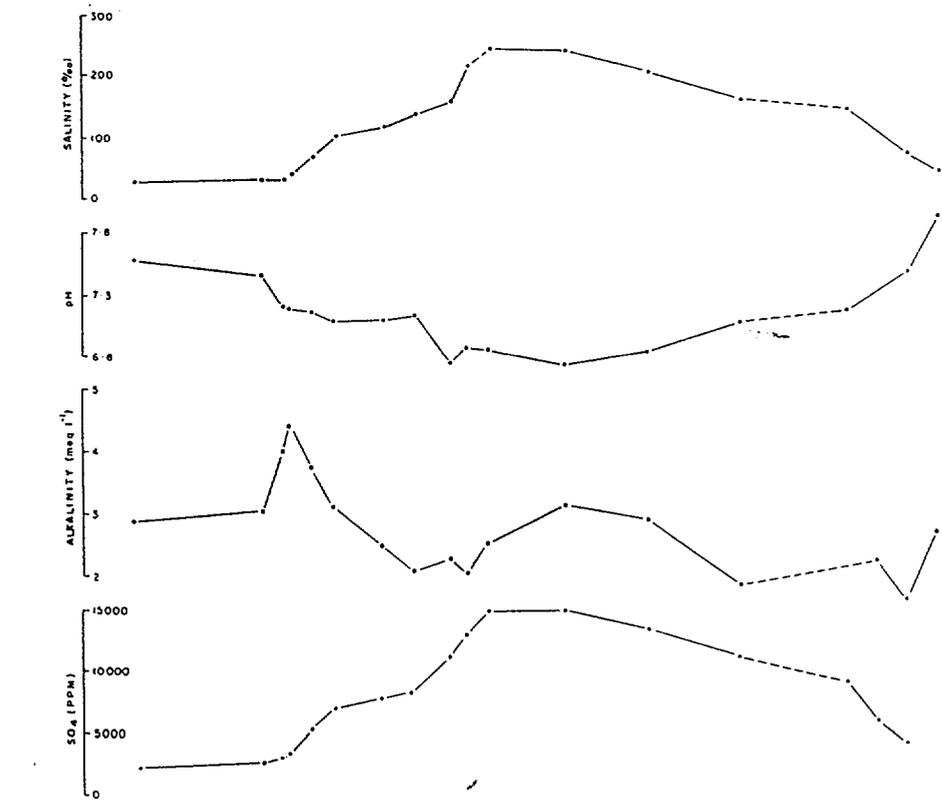
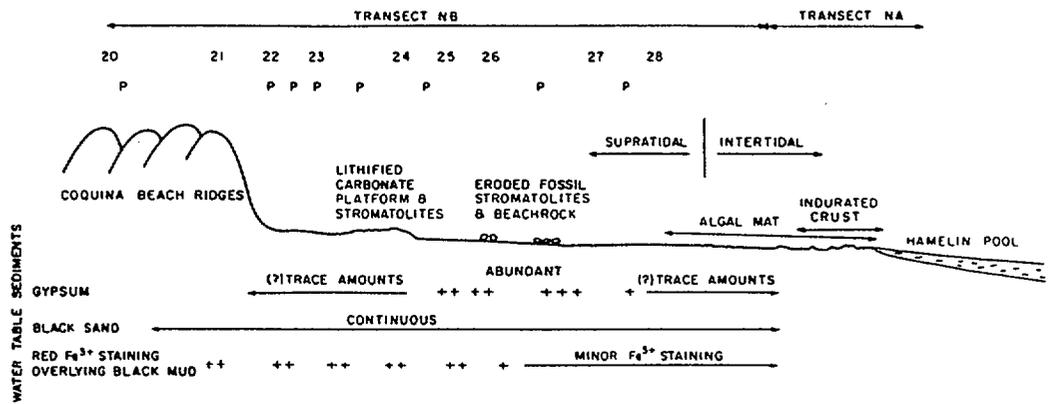


Fig. 4 Chemical composition of groundwaters in the peritidal zone of Nilemah Embayment.

quantities (6-7 $\mu\text{gS}^{\text{=}}/\text{g}$ wet sediment) and the black amorphous residue. In the low intertidal sediments (Nilemah Transect A2) however, sulphide concentrations were of the order 500 $\mu\text{gS}^{\text{=}}/\text{g}$ wet sediment. The sulphides from the supratidal sediments are more ^{32}S -enriched than the more abundant intertidal material (-26.6 and -32.2 versus -14.2 and -17.2). Relative to seawater sulphate, these values represent the upper and lower ranges of fractionation in marine environments.

GROUNWATERS IN A SEMI-ARID COASTAL HOLOCENE CARBONATE ENVIRONMENT AT HAMELIN POOL AND LCHARIDON BIGHT, WESTERN AUSTRALIA

R.V. Burne, James Ferguson, D. Fitzsimmons, L.A. Plumb, M. Thomas

Coastal areas around Hamelin Pool and Lharidon Bight contain three main types of groundwater: (i) marine brines formed from the hypersaline seawater of Hamelin Pool and Lharidon Bight, (ii) continental groundwater, which occurs partly as freshwater lenses within Pleistocene sands and coquina beach ridge, (iii) artesian groundwater, which discharges from bore holes drilled to the artesian aquifer system underlying the near-surface sands.

Much of the variation of the hydrological regime around Hamelin Pool at Lharidon Bight is related to the local topography of the coastal areas, which produces intertidal/supratidal zones varying in breadth from about 100 m at the Playford site south of Flagpole Landing, through about 300 m at Flagpole Landing, to several km in Nilemah, Gladstone and Hutchison Embayments.

Continental groundwater in the coastal areas occurs as freshwater lenses in the coquina beach ridges and also as considerably more saline waters in the underlying Pleistocene sands. These saline waters could be part of a regional groundwater system or they may have formed by downwards percolation of freshwater from the overlying beach ridges. Possible exceptions to this type of groundwater regime occur at Flagpole Landing and Gladstone Embayment. At Flagpole Landing groundwater discharging from the base of the coquina dunes onto the supratidal flats may contain artesian water from an inland borehole. At Gladstone Embayment there may be extensive groundwater drainage into the high supratidal zone and saline flats immediately landward. Also, the supratidal sediments in this area are predominantly stiff, impermeable clays, in contrast to the highly permeable carbonate sands and silts common in other coastal areas.

TABLE 4.
CHEMICAL PARAMETERS OF SEAWATER AND LOW-SALINITY METEORIC AND ARTESIAN GROUNDWATERS,
FROM HAMELIN POOL

Location	Probable Origin	S [°] /∞	pH	Alkalinity (meq. l ⁻¹)	Ca/Cl	Sr/Cl	Weight ratios x 10 ²			
							Na/Cl	K/Cl	Mg/Cl	SO ₄ /Cl
Well in coquina beach ridge (Booldah Well)	Meteoric	11	8.49	5.9	7.8	0.87	73	5.0	6.8	17
Borehole, Hamelin Station	Artesian	5	6.70	4.1	6.1	0.10	75	3.4	7.7	24
Hamelin Pool, Nearshore Surface water	Marine	78*	8.06	3.0	2.1	0.043	58	2.1	6.3	14

* Salinities 55 - 70[°]/∞ are typical

TABLE 5.
CHEMICAL PARAMETERS AND PROBABLE ORIGINS OF GROUNDWATER SURVEY SAMPLES FROM
HAMELIN POOL AND LHARIDON BIGHT

Location	Probable Origin	S ^o /∞	pH	Alkalinity (meq. l ⁻¹)	Ca/Cl	Sr/Cl	Weight ratios x 10 ²			SO ₄ /Cl
							Na/Cl	K/Cl	Mg/Cl	
Saline water beneath Coquina dunes, Nilemah Embayment (NB 20.14)	Meteoric component	33	7.58	2.9	2.8	0.18	56	2.2	5.7	12
Water from beneath lithified crust at base of dunes, Petit Lagoon (LBN)	Meteoric component	30	7.81	2.2	2.7	0.06	59	2.1	6.2	14
Water from base of dunes at Playford site (PA11)	Possible meteoric component	60	7.23	4.8	2.3	0.05	62	2.1	6.3	14
Water from base of dunes on Solar Ponds Transect (BH 31.16)	Possible meteoric component	73	7.35	2.8	2.0	0.05	59	2.1	5.9	12
Water from beneath lithified pavement at landward edge of supratidal zone, Nanga Lagoon (LBS1)	Marine	58	7.68	1.7	2.1	0.04	61	2.1	6.3	14
Water from area of high discharge at base of dunes, Flagpole Landing	Meteoric and artesian	30	7.62	3.2	3.2	0.18	64	2.6	6.0	23
Near-shore, surface seawater, Hamelin Pool	Marine	78	8.06	3.0	2.1	0.04	58	2.1	6.3	14

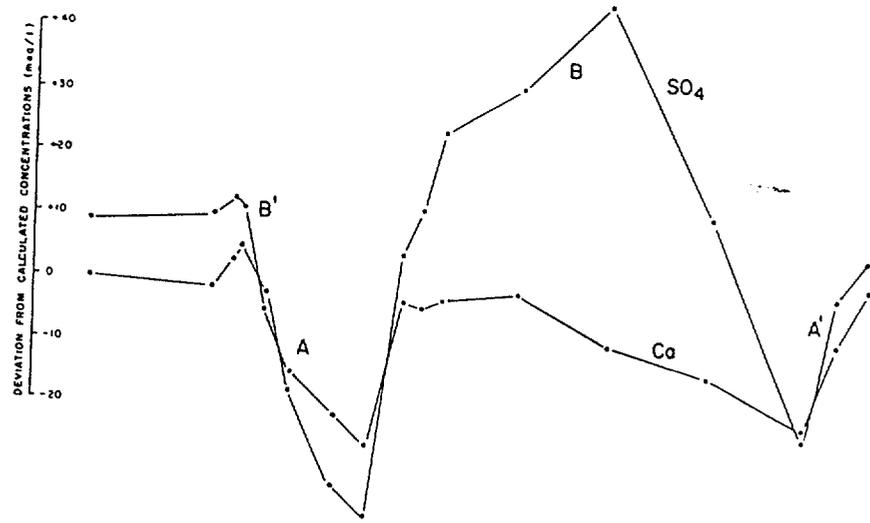
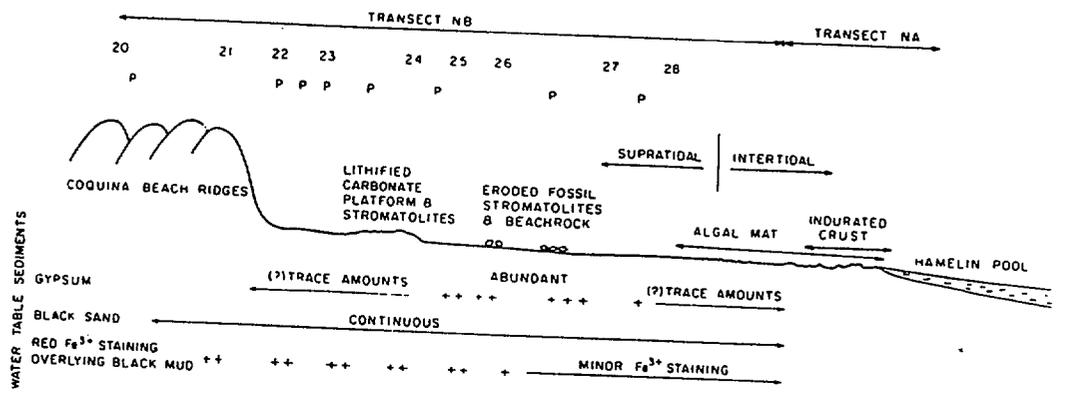


Fig. 5 Deviations of Ca and SO₄ concentrations from those predicted for evaporated seawater with gypsum precipitation commencing at salinity 4.0 x SW.

To obtain an indication of the chemical diversity of the groundwaters in the Hamelin Pool and Lharidon Embayment coastal areas, groundwater survey samples were collected at a number of locations and a tentative assessment of their origins was made on the basis of chemical data. The information is summarised in Tables 4 and 5. Clearly the artesian water from the Hamelin Station borehole and the dune water from Booldah Well are mainly non-marine water. Continental-water influence is also evident in the landward margin of the supratidal zone at Petit Lagoon ($S = 30\text{‰}$) and at Flagpole Landing ($S = 30\text{‰}$), and over a zone extending from near the middle of the supratidal zone to beneath the beach ridges at Nilemah Embayment. Water from beneath the dunes at Nilemah Embayment has high Ca/Cl and Sr/Cl ratios and is the least saline of groundwaters along a transect extending to Hamelin Pool. The origins of the groundwater at the base of the dunes at the Playford site are not clear. The Sr/Cl ratios of the waters are about 20% higher than that of Hamelin Pool seawater, but a difference of this magnitude may not be significant. The origins of the water in the Solar Ponds and at Flagpole Landing are discussed elsewhere in this report.

At Nilemah Embayment a combination of broad intertidal and supratidal flats and marine and continental groundwater input has allowed the two groundwater types to evolve through a number of chemical stages before they meet and mix near the middle of the supratidal zone. When seawater is concentrated by evaporation a small quantity of aragonite is precipitated and then at salinities of about $4 \times SW$, gypsum starts to precipitate. This sequence occurs in surface seawater samples evaporating in tidal ponds in the Hamelin Pool and Lharidon Bight and, in these areas, gypsum precipitation starts at salinities close to the predicted value. The calcium and sulphate concentrations in the incoming continental groundwaters at Nilemah are sufficiently close to those of normal seawater for their predicted gypsum precipitation point to be close to that of normal seawater. However, when the actual calcium and sulphate concentrations in groundwaters along the Nilemah transect are compared to those predicted for evaporating seawater, it becomes apparent that there are major discrepancies (see Fig. 5).

These discrepancies are of two types: (i) areas along the transect where calcium and sulphate are lost from the waters in nearly equivalent proportions, but the $a_{Ca^{2+}} \times a_{SO_4^{2-}}$ duct is below that necessary for saturation with respect to gypsum ($A + A'$, Fig. 5) and (ii) areas where the waters have acquired excess sulphate but not an equivalent excess of calcium ($B + B'$). At present the processes

involved are not definitely known, but possible explanations can be given.

The broad area of high sulphate concentrations at B¹ corresponds approximately to the area where the sediments contain large quantities of gypsum. Presumably, the high sulphate concentrations result from dissolution of sedimentary gypsum when the waters became temporarily undersaturated with respect to gypsum because of an influx of tidal or continental floodwater. The lack of an equivalent increase in calcium may result from the precipitation of aragonite. However, precipitation of the amount of aragonite involved seems to require that the carbonate alkalinity available in concentrated Hamelin Pool seawater be supplemented by alkalinity generated within the sediments by, for example, bacterial sulphate reduction. The approximately equivalent decrease of calcium and sulphate in zones A and A¹ suggests that gypsum has precipitated from the groundwaters and marine brines at these locations. Most likely the water chemistry reflects a period when the incoming groundwaters were more saline. This period could have been followed by an influx of lower salinity, continental water or by normal seawater which, at the time of sampling, had not had time to reequilibrate with gypsum in the sediments. In interstitial waters of sabkhas of the Persian Gulf, gypsum precipitates at about 3.4 x SW salinity, which is lower than the value of 4 found for the surface marine brines of Hamelin Pool and Lharidon Bight, but is higher than the lowest value of about 2.5 x SW at which calcium and sulphate concentrations start to decrease in the Nilemah groundwaters.

IRON AND THE FIXATION OF SULPHIDES IN MODERN SEDIMENTS

P.A. Trudinger

In earlier studies in this Laboratory we concluded that rates of bacterial sulphate reduction in many modern sedimentary environments are of the same order as those of sulphide deposition calculated for a number of base-metal sulphide deposits (Trudinger, P.A., Lambert, I.B. and Skyring, G.W., 1972, *Econ. Geol.*, 67:1114-27). Such deposits include the Kupferschiefer (Mansfeld), Roan Antelope, McArthur (HYC) and Mour't Isa.

This conclusion is supported by recent determinations of sulphate reduction rates in the intertidal sediments of Spencer Gulf (see Baas Becking Report, 1980) and in several shallow water coastal sediments studied by overseas scientists.

A survey of the literature, however, reveals that most unconsolidated detrital and bioclastic reducing sediments contain only low concentrations of fixed sulphide: maximum values are generally below 1.5 -2% S and mean values are below 1.0% S (see Fig. 8). These concentrations compare reasonably well with those of relatively low-grade ores like Kupferschiefer (average 3% S) and Roan Antelope (average 1.1% S), but are an order of magnitude below those of high-grade ores such as the McArthur HYC (14% S) and Mt Isa (12% S) deposits.

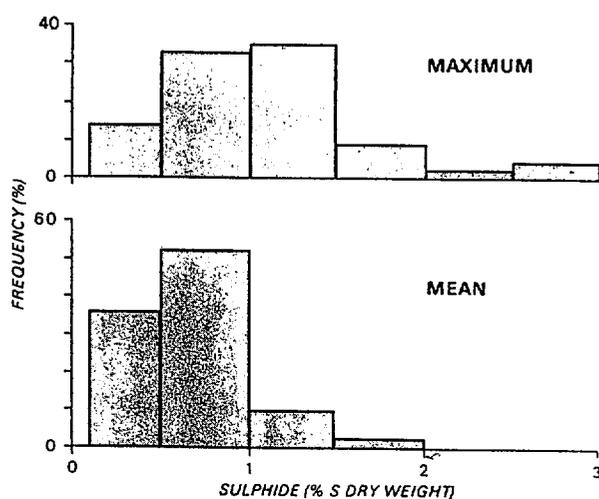


Fig. 8 Frequency plots of mean and maximum values for fixed sulphide in unconsolidated, reduced marine sediments (sediments containing an average of less than 0.1% sulphide not included).
Data from: black Sea, Baltic Sea, Great Bay Estuary, NH, Gulf of California, Californian offshore basins, Cariaco Trench, Pacific Ocean, Long Island Sound, Limfjorden, Solar Lake, Pedernales, Venezuela, Indian Ocean and Moroccan Basin.

A major limitation on the fixation of biogenic sulphide in sediments is the supply of reactable metals. Nevertheless, there are a few reports that potentially reactable iron (acid extractable) exceeds the amount fixed as sulphide even in sediments (e.g. Black Sea) that are permanently overlain by hydrogen sulphide-containing waters. A considerable excess of acid-reactable iron over fixed sulphide was found in all but one of 15 samples from the reduced sediments of Gladstone Embayment, Shark Bay, W.A. Fe/S values ranged from 1.2 to 13.6 with an average of 5.4 and a standard deviation of 2.9.

Studies have been undertaken to determine the total amount of hydrogen sulphide-reactable iron in sediments by exposing samples to an atmosphere of hydrogen sulphide for various times. Preliminary results with material from Spencer Gulf and Shark Bay indicate that, within the active zone of sulphate reduction, the amount of potentially hydrogen sulphide-reactable iron exceeds that actually fixed as sulphide in situ.

We will be undertaking further work to determine the reasons for the non-reactability of iron in the in situ system.

SULPHATE REDUCTION RATES IN SEDIMENTS FROM HAMELIN POOL, GLADSTONE EMBAYMENT AND NILEMAH EMBAYMENT, WESTERN AUSTRALIA

L.A. Plumb, M.H. Reed, G.W. Skyring

Sulphate reduction rates in cyanobacterial mat-associated sediments of the hypersaline environments in Hamelin Pool were similar to those found in cyanobacterial sediments from Spencer Gulf, S.A. In some intertidal locations on the shores of Hamelin Pool, there are deposits of sediments which, when forming, contain a large quantity of organic material that was dislodged from intertidal and subtidal columnar stromatolites by tidal waters. These sediments are characterised by high sulphate reduction rates and $\delta^{34}\text{S}$ ratios that suggest a partially closed system with respect to sulphate.

In November, 1980, sediments of the latter kind were found in the area now known as Playford's Transect and in the same area as that studied by Bauld in 1979. These black, reducing sediments extended landwards of the high tide line and were covered by loosely packed shelly material of a prograding beach ridge. The sulphate reduction rates in the black sediments were 7.7 ± 3.9 mmol $\text{m}^{-2}\text{d}^{-1}$ or 285 ± 169 mmol $\text{g}^{-1}\text{d}^{-1}$ ($n = 12$), lower than those previously found (0.5 to 2.0 mmol $\text{g}^{-2}\text{d}^{-1}$) in similar sediments. With respect to sulphate reduction rates in marine environments, these are quite high. The sulphide concentration was 59 ± 28 $\mu\text{mol g}^{-1}$ which was similar to those found previously (34 to 88 $\mu\text{mol g}^{-1}$).

Sulphate reduction rates were also determined for laminated carbonate sediment from Gladstone Embayment. The sediments were colonised by cyanobacterial mat and were covered by tidal waters. The sulphate reduction rates, sulphide and sulphate concentrations, and a brief description of the 0-20 cm layer are

given in Table 8. The sulphate reduction rates were highest in the 0-1 cm layer; below 5 cm the rates were very low. There was, however, a slightly higher sulphate reduction rate in the black laminated layer between 10 and 11 cm. Although these cyanobacterial mat-associated sediments from Gladstone Embayment were not exactly analogous to those in Solar Lake, the pattern of sulphate reduction with respect to depth was very similar.

Sulphate reduction rates were also determined for sediments taken along surveyed transects at Nilemah Embayment. The rates were generally very low except for those found in the unconsolidated sediments at Station 2, Transect A. These rates (2 to 9 mmol m⁻²d⁻¹) were similar to those in sediments at Playford's transect. These, and previous studies in Hamelin Pool, indicate that in these stromatolite environments there is translocation of large quantities of organic stromatolite debris. In areas where this organic material collects and becomes part of the sediment, high sulphate reduction rates are observed.

TABLE 8.
SULPHATE REDUCTION RATES AND OTHER CHARACTERISTICS OF
CYANOBACTERIAL MAT ASSOCIATED SEDIMENTS OF
GLADSTONE EMBAYMENT, W.A.

Sediment type	layer cm	Sulphate concentration in porewater mM	Sulphide concentration $\mu\text{mol g}^{-1}$	Sulphate reduction rates $\text{nmol g}^{-1}\text{d}^{-1}$.
cyanobacterial mat, black	0-1	89	49	1880
black	1-1.5	87	45	292
grey	1.5-3.0	89	24	96
black	3-4	87	32	79
black	4-5	89	93	157
black	5-5.5	98	44	88
grey	5.5-7	81	49	20
black	7-8	78	26	3
black and grey	8-9.5	84	20	2
black and grey laminated	10-11	84	19	150
"	11-12	107	13	3
"	12-13	103	13	4
shell fragments, grey laminated	13-15	95	9	2
black and grey laminated	15-17	95	4	0
grey laminated	17-18	95	6	3
black laminated	18-20	101	25	3

BAAS BECKING GEOBIOLOGICAL LABORATORY
ANNUAL REPORT, 1983 (PUBLISHED 1984)

INTRODUCTION

Three projects that became fully established during 1983 are studies of petroleum source rocks in the Cambrian of the Officer Basin, lead-zinc deposits in the Devonian reefs of the Canning Basin, and the microbial ecology, geochemistry and sedimentology of Hamelin Pool, Shark Bay.

Hamelin Pool is a misnomer for a marine barred basin, 60km long by 20-30km wide, forming the eastern lobe of Shark Bay in Western Australia. It is the best analogue available anywhere for the microbially dominated carbonate depositional systems that were widespread during Proterozoic and early Palaeozoic times. The sedimentology of the Pool is well known as a result of many years of research of Dr Brian Logan and his students from the University of Western Australia, but relatively little is known about its geochemistry and microbiology. We are in the process of determining the factors that control the production and preservation of both organic matter and sulphide minerals in this area, and have recognised and are delineating organic-rich facies. Our development of an electronic remote monitoring system is enabling the long-term monitoring of the zone of interaction between the sea and groundwaters, and the same system is being used to provide comprehensive records of tides and significant features of the weather; all the information is available in Canberra via satellite and telex links. This will provide a data base against which to interpret observations and experiments made during field visits. The research in Hamelin Pool is designed to interact with our studies of ancient stromatolitic carbonate-evaporite sequences such as that of the Bitter Springs Formation of the Amadeus Basin, where we are studying palaeoenvironments and the sources and distribution of organic matter.

During the latter part of the year the laboratory jointly sponsored a 3-month visit to Australia by Dr Judith McKenzie of the Geological Institute of the Swiss Federal Institute of Technology. The other sponsors were the Research School of Earth Sciences, ANU, and Comalco. Dr McKenzie is a geochemist with very extensive experience in the application of stable isotope techniques in sedimentology. While here, she visited Shark Bay and South Australian carbonate lakes and lagoons with various members of our staff, and discussed our work in those areas.

In July, Dr J. Bauld commenced a nine-month period of research at two laboratories in the US, supported, in part by NSF and NASA grants to the host laboratories, and by the Ian Potter Foundation. At UCLA, laboratory work commenced on an investigation of the preservation and decomposition of cyano-bacterial sheaths, using Lyngbya species from the Shark Bay mats. At Indiana University, a strain of the phototrophic bacterium Chromatium vinosum, also isolated from Shark Bay was used to investigate the heterotrophic capabilities of such phototrophs.

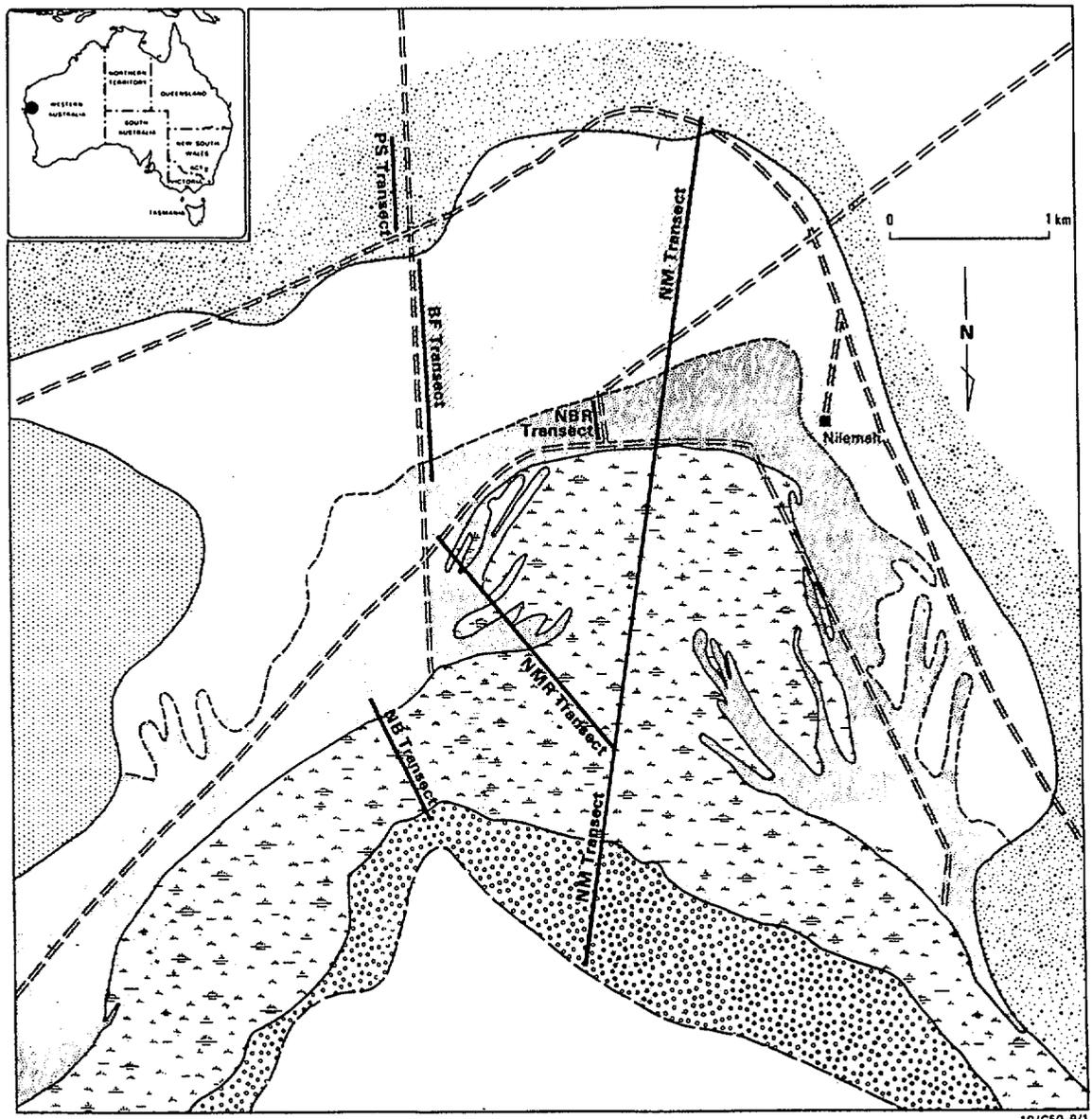
HYDROLOGY OF PERITIDAL ZONES, NILEMAH EMBAYMENT WESTERN AUSTRALIA

James Ferguson, L.A. Plumb, B. Simeonovic, I.C. Reichstein

The association of stromatolitic carbonate sequences with both basemetal and hydrocarbon prospective basins has directed research to the Holocene and Pleistocene carbonate environment in Shark Bay. Some diagnostic features of the models for ancient environments are linked with groundwater and early diagenetic processes, and these aspects are being studied in the peritidal zones of Nilemah Embayment. Figure 3 shows the transects established in Nilemah Embayment in relation to major geomorphic subdivisions. A consequence of the geological history of Nilemah Embayment is a range of sediment types from fine-grained silt with low permeability to coarse permeable coquina beach ridges. Such variation contributes to a complex hydrological environment and influences the evolution of the groundwaters and, ultimately the diagenetic processes. At Nilemah Embayment there are examples of carbonate lithification in the low intertidal zone and dolomite and calcrete may be forming in the present-day hydrological regime in Pleistocene marine sequences. The project aims to characterise these processes in relation to the groundwater hydrology as an aid in palaeoenvironmental interpretation.

The hydrological regime of the tidal flats has been studied by using piezometers (Transect NM), and measuring salinities and oxygen isotope distributions. (Extension of this approach to the back flats is planned).

Piezometric measurements were made during winter, when tides were relatively high and the groundwater table in the supratidal zone was low, following a period of drought. Consequently, the tide height regularly exceeded the height of the groundwater table at distances up to about 1500 m inland from the intertidal zone, which would favour landwards movement of seawater.



19/G50-9/1

- | | | | |
|---|----------------------|---|----------------------|
|  | Perron Sandstone |  | Sublittoral platform |
|  | Toolonga Calcilutite |  | Tidal flats |
|  | Beach ridges |  | Back flat |

FIGURE 3: Transects established at Nilemah Embayment, Shark Bay, W.A.

In fact, short-term differences in groundwater level were restricted to about 500 metres inland by limitations caused by the hydraulic conductivity of the sediments. During the two-week sampling period the height of the tides gradually increased, which caused a progressive change in the height and shape of the tidally controlled water surface in the study zone (Fig. 4). The landward limit of tidally induced water-table fluctuations coincides with the zone of sub-surface carbonate lithification, which suggests a genetic relationship. A further indication of this is the sharp increase in salinity with depth in the intertidal zone (Fig. 5): this is consistent with a possible meteoric-seawater mixing system. It is also interesting to note the relationship along the transect between the salinity of surface porewater and small incipient beach ridges, which support some vegetation (Fig. 6). There appear to be freshwater lenses which are not greatly influenced by short-term climatic effects (Fig. 6, salinity after recent rain following drought conditions). The oxygen isotope distribution shows a general increase in ^{18}O from beach ridge to sea and an overprinting influence of fresh meteoric water associated with the incipient beach ridges.

Fig. 7 gives the relationship between $\delta^{18}\text{O}$ and salinity for the waters of NM transect compared to some seawater brines. There appears to be considerable continental influence with only the three most seaward samples showing significant marine influence. Samples from the incipient beach ridges show reversals to lower values.

PRODUCTION AND FATE OF ORGANIC CARBON IN CYANOBACTERIAL MATS

L.A. Plumb, J. Bauld, D.T. Ho, I.C. Reichstein

The dependence of bacterial sulphate reduction and other heterotrophic processes on cyanobacterial primary productivity is indicated by observations that photosynthetically active mat supports higher sulphate reduction rates than does inactive mat, and that the most rapid sulphate reduction rates occur immediately below the living cyanobacterial mat. It is in this context that the partitioning of photosynthetically fixed CO_2 -carbon between cyanobacterial biomass (Particulate Organic Carbon = POC) and soluble, excreted compounds (Dissolved Organic Carbon = DOC) assumes considerable significance. While utilisation of POC is delayed because of the requirement for decomposition and solution before it can become available as substrate, DOC provides a potential source of immediately available organic carbon for heterotrophic uptake.

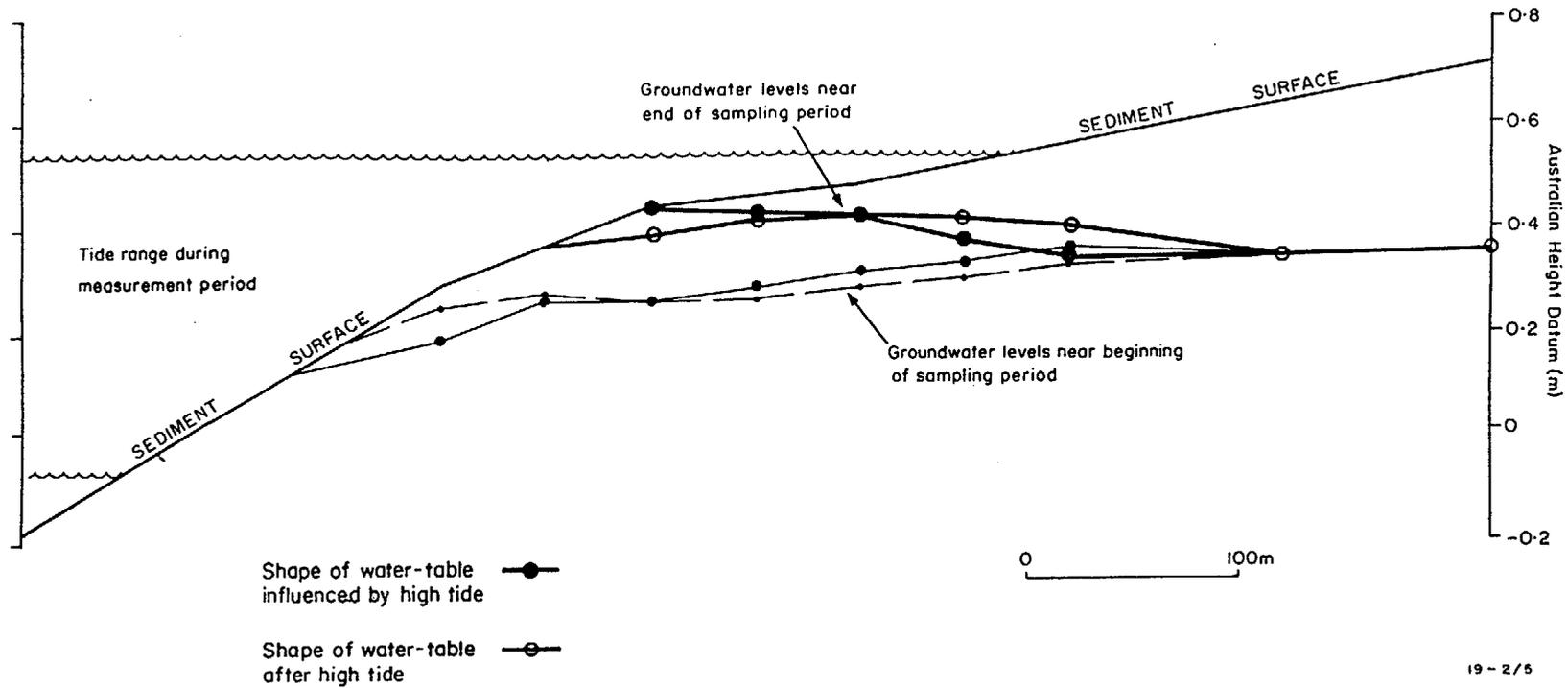


FIGURE 4: Response of groundwater table in the intertidal zone to tidal fluctuations Nilemah Embayment Winter 1983.

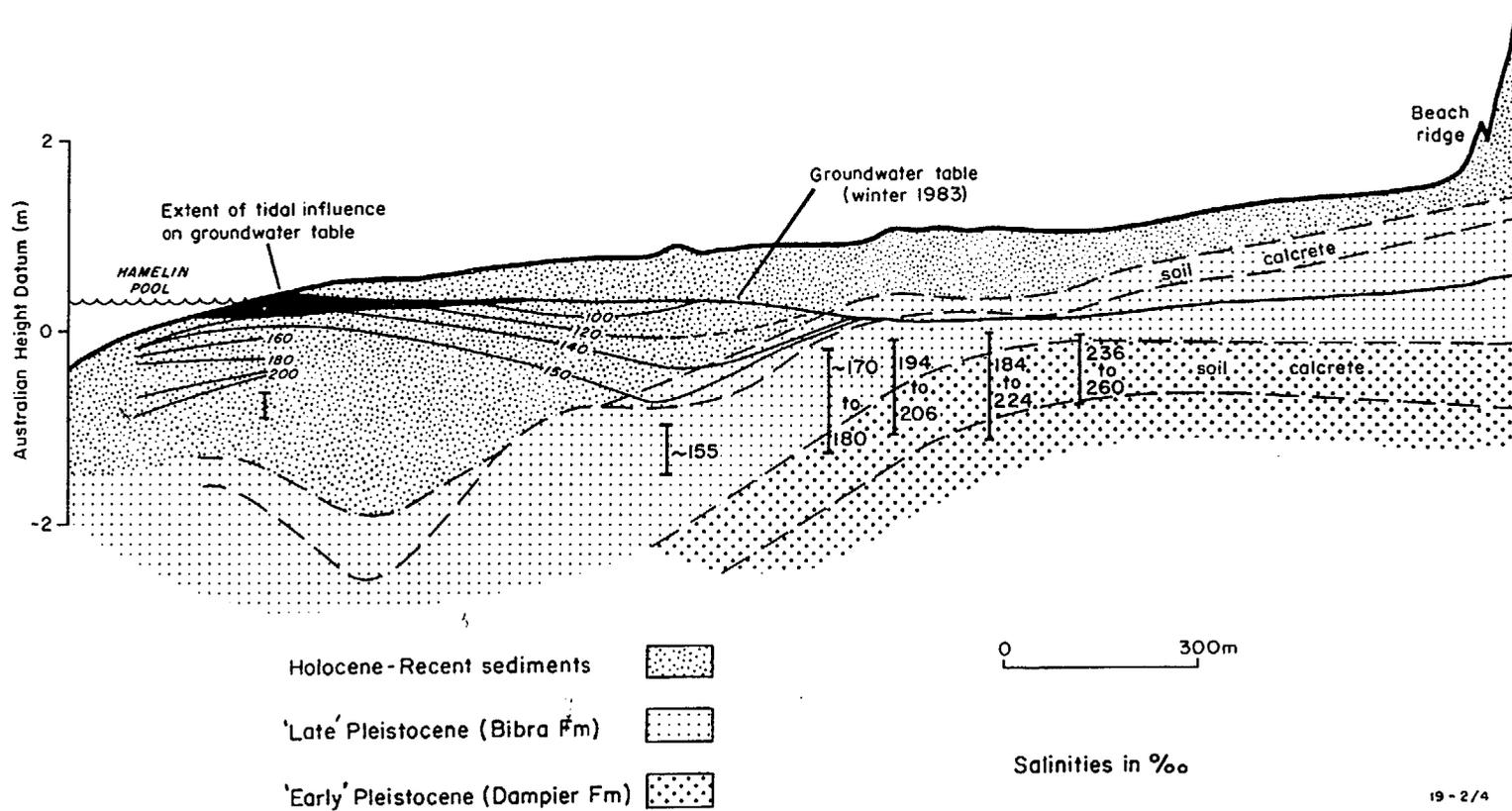


FIGURE 5: Groundwater level and salinity profile across the intertidal and supratidal zones. Nilemah Embayment Winter 1983.

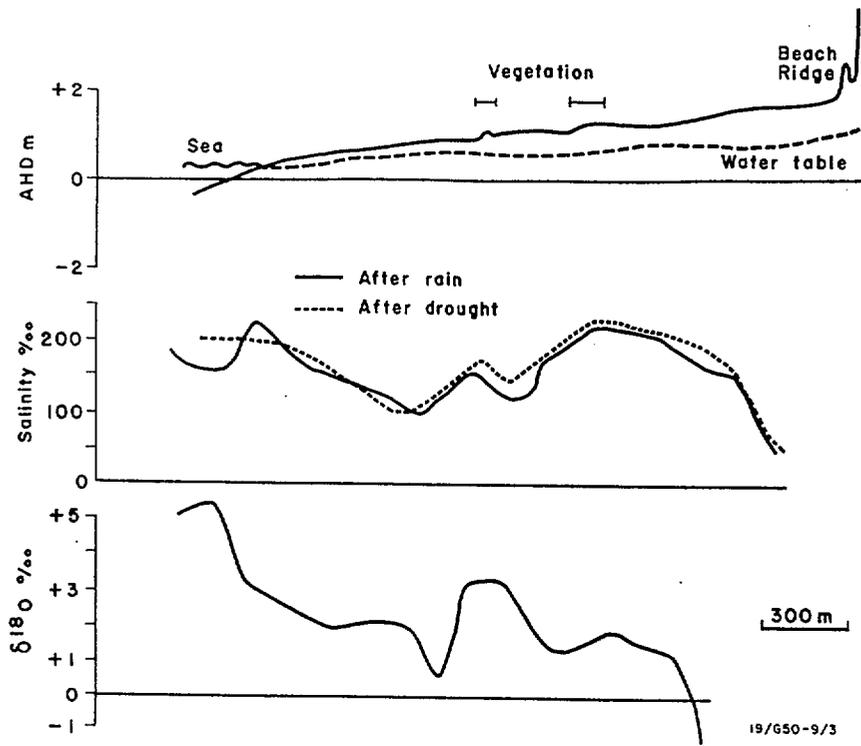


FIGURE 6: Salinity and oxygen isotopes NM transect.

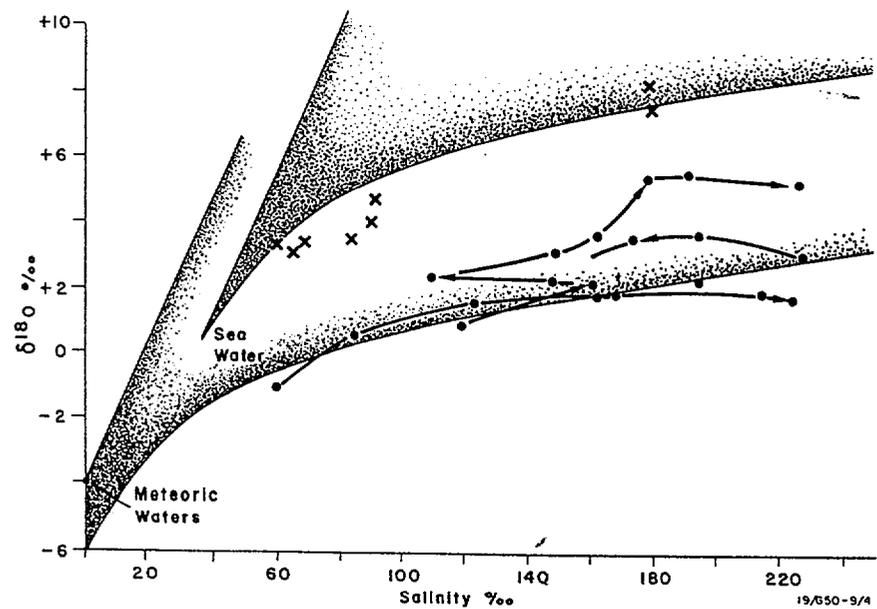


FIGURE 7: $\delta^{18}\text{O}$ vs salinity for Hamelin Pool groundwaters. Shaded areas represent possible ranges for groundwaters evolving by evaporation from either meteoric water or seawater. Waters of lower seawater derivation (x). Waters along NM transect (.). Arrows indicate sequential samples from beach ridge towards the sea.

Environmental factors affecting POC and DOC production and the detection of components of DOC suitable as substrates for sulphate-reducing bacteria have been reported earlier. The final phase of this project has used radioactive labelling, gas chromatography and specific inhibition of metabolic activities to assess pool sizes and turnover rates for acetate, propionate and butyrate.

Since its inception, this project has been supported by a Marine Science and Technologies (MST) Grant (formerly AMSTAC).

SULPHATE REDUCTION IN HOLOCENE ENVIRONMENTS

G.W. Skyring, S. Dibb

The object of these studies is to provide basic information for development of models for the production and preservation of organic matter and metal sulphides in ancient sediments.

1. Intertidal sediment, Hamelin Pool, Shark Bay WA.

Preliminary studies have been carried out on the relationship between sulphate reduction and other biogeochemical factors in an intertidal sediment in Shark Bay. A shallow intertidal pool with smooth cyanobacterial mat colonising the surface of the sediment was chosen. Chemical and physical changes in the porewaters and overlying waters, and sulphate-reduction rates in the sediments, were monitored for several hours. Unfortunately, long-term monitoring was prevented by the occurrence of unexpected and excessively high tides.

Results: The results obtained so far are given in Tables 7 and 8.

The pH of the surface waters appeared to fall continually until flooding occurred with tidal waters. The pool had an average depth of 7.5cm and evaporation did not appear to be a significant factor over the 2-3 hour experimental period. Active photosynthesis by the thin cyanobacterial mat would be expected to raise the pH. Lowering of the pH could be effected by one or more of the following processes:

- oxidation of sulphide and ammonia to sulphuric and nitric acids, respectively;

TABLE 7: SOME CHEMICAL AND PHYSICAL PROPERTIES OF SURFACE WATER AND POREWATERS OF A POOL IN THE INTERTIDAL ZONE, PLAYFORD'S TRANSECT, HAMELIN POOL (31/5/83 and 1/6/83).

Time	Sulphate mM	NH ₄ ⁺ μM	pH ⁽¹⁾	Salinity ‰	Temp, °C	Sulphate reduc. rate ⁽²⁾ (n mol m ⁻¹ hr ⁻¹)
Pool Water						
11.00	73	0	8.02		25.8	
12.45	59 ⁽³⁾	0	7.96		27.2	
13.45	66	0	8.11 ⁽⁴⁾		28.8	
Sediment porewater						
13.00	69	29	7.41 ⁽⁵⁾	70	24.0	27.6 (662)
15.15	59 ⁽⁶⁾	44 ⁽⁷⁾		68	24.0	17.3 (415)

Notes

1. The pH was measured with respect to an electrode standardised in an 2X.ASW*-Tris HCl (0.005 molal) (Hansson, I.; 1973, Deep Sea Research, 20, 479-491). The pH data on these concentrated sea waters may be subject to some change pending a more thorough examination. However, it is clear that standardisation of electrodes must be made in buffers of appropriate salinities. The temperature coefficient for Hamelin Pool water at 68‰ salinity was 0.0129 pH units per °C.
2. Sulphate reduction rates were measured on the sediments only. A ³⁵SO₄ method was used. Results were given with respect to the porewater. Entries are the average of 3 determinations. Entries in brackets are daily rates.
3. & 6. The sulphate concentrations in this experimental series appeared unusually variable. Similar values were noted in 1980 however. This will be investigated further.
4. Up to this time the pool was isolated, and as time progressed, the pH of the surface water (average 9 cm in depth) decreased. Then tidal waters at pH 8.24 flooded in rapidly and pH of the pond water rose to 8.11.
5. The pH measured on the following day was pH 7.69 during a period of continuous flooding with tidal waters.
6. Gassing the porewaters with O₂-free N₂ resulted in a loss of 90% of the ammonia.
7. Phosphate and sulphide were below detection levels in both surface and porewaters. The average of six sulphide determinations for the sediment was 6.5 μmol S⁻¹.

*ASW = Artificial Sea Water

TABLE 8: SOME CHEMICAL AND PHYSICAL PROPERTIES OF POREWATERS FROM THE BLACK MUDS OF THE HIGH INTERTIDAL REGION OF HAMELIN POOL.⁽¹⁾

Date	Sulphate mM	Sulphide mM ⁽²⁾	NH ₄ ⁺ μM	pH	Alkalinity ⁽³⁾ meq l ⁻¹	Salinity ‰
30/5/83	70	—	31	7.29	4.650	68
2/6/83	70	1.00 ⁽⁴⁾	135	7.26	7.530	68

(1) The average sulphate reduction rate from six replicates was 197 μmol l⁻¹ day⁻¹ with respect to the porewater.

(2) The average sulphide concentration of the sediment was 23.4 μmol g⁻¹.

(3) Calculated according to the formula

$$TA = \frac{1000}{V_a} V_a N - \frac{1000}{V_s} (V_s + V_a) a_H / f; \text{ where}$$

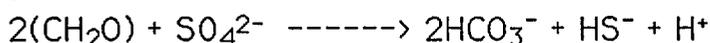
TA = total alkalinity, vs sample volume, V_a = volume of standard acid, N = acid normality, a_H = 10^{-pH} and f = an empirical constant.

A value of 0.77 was used for f. For Hamelin Pool, a value of 3.498 was obtained for total alkalinity.

(4) After filtering through a 0.45μ millipore the sulphide concentration decreased to 0.86 mM.

- respiration of CO₂ by the heterotrophic population of microorganisms;
- diffusion of the sediment porewaters, which have a considerably lower pH (See Table 7).

Note: L.R. Gardner, 1973 (Geochim. Cosmochim. Acta. 37, 53-68), computed several models for sulphate reduction in marine carbonate sediments. Each of his models predicted a fall in pH, a rise in alkalinity, and, of course, a rise in HS⁻ (dependent on the presence of iron). With Fe₂O₃ present, sulphate reduction may cause precipitation of CaCO₃ at pH 7.55 or lower but, with an Fe-free CaCO₃ sediment, sulphate reduction results in the dissolution of CaCO₃. The molar ratio between alkalinity and sulphate reduced in a closed system is generally 2:1, according to the following equation:



Gardner's models predicted an asymptotic pH value of 6.93, but this could be raised to pH 7.7-7.9 to include the effects of ammonia. It is probable that the lower pH and higher alkalinities of the porewaters in Hamelin Pool black sediments (with respect to that of surface water) are due to the activities of the sulphate-reducing bacteria.

On the basis of the present data, the sulphide in the porewaters of the black sediments would have been produced in about 5 days by the sulphate reducers, and the total alkalinity (corrected for sulphide, ammonia and borate) would be produced in 7 days. However more data are required to confirm these trends.

The estimation of pyrite-S as sulphide and the possibility of rapid pyrite formation:

Dr. R. A. Howarth and his colleagues at Woods Hole, Massachusetts Marine Biological Laboratory have suggested, in a series of recent papers, that pyrite may be formed more rapidly in some organic-rich marine environments than previously encountered. (See Howarth and Marino 1984, Microbial Mats : Stromatolites. Eds. Y. Cohen, R.W. Castenholz and H.D. Halvorson. Alan R. Liss Inc. NY.). Samples from the intertidal black sediments at Hamelin Pool were examined for rapid pyrite formation by determining the incorporation of ³⁵S²⁻ from ³⁵SO₄²⁻ into pyrite. This required the direct determination of pyrite-S in the presence of sulphate and organic-S (as cyanobacterial mat).

A number of trial experiments were done with authentic pyrite. Granulated tin as the reductant in boiling 20% SnCl₂ in 10N HCl for 3 hours gave the highest recoveries of 83 to 90% of the S. In

the presence of 1.0g Na₂³⁵SO₄ (≈ 7mmoles), a distillation period of 4 hours resulted in the reduction of 0.10% of the sulphate. The reduction of ³⁵SO₄²⁻ was not catalysed by the presence of authentic pyrite, zinc sulphide, cysteine or cyanobacterial sediment.

On the basis of these experiments, Hamelin Pool sediments from the intertidal zone along Playford's transect appear to contain only very small quantities of Sn-reducible (pyrite) S (7 to 26μmolg⁻¹). From the data of the sulphate reduction experiments, there appeared no clear indication of the rapid incorporation of ³⁵S²⁻ into the 'pyrite' component of the sediment. However, it was evident from these preliminary experiments that methodology will have to be refined to provide unequivocal evidence as to whether or not rapid 'pyrite' formation occurs in these sediments.

2. Sulphate reduction in sediments colonised by cyanobacterial mats

In previous studies (Skyring et al., 1983, Aust. J. Mar. Freshwater Res. 34, 359-374) we showed that the zone of most active sulphate reduction in the intertidal sediments of Spencer Gulf was in sediments contiguous with the mat or maybe within the mat itself. Similar results were observed for the cyanobacterial sediments of Hamelin Pool, Shark Bay. On the basis of these studies, a double chamber was constructed to measure more precisely the temporal relationship between the rate of photosynthesis of the cyanobacteria on the top side of the mat and the rates of sulphate reduction on the bottom side of the mat. The chamber allows liquid to flow over and under a disc of cyanobacterial mat: chemical changes in the flowing liquid can then be monitored.

Preliminary work with this apparatus has shown the following:

1. Photosynthesis within a disc of cyanobacterial mat (4.9 cm² x 1 mm) causes a measurable rise in the pH of seawater flowing over it. At very slow rates of flow (ca. 5 ml hour⁻¹), changes of up to 0.17 of a pH unit were measured. Even at fast flow rates (ca. 0.8 to 1 ml min⁻¹) rises of 0.07 to 0.11 of a pH unit were measured. The effects of light were also repeatable with the same mat disc (Figure 13).
2. Under conditions of constant illumination and constant flow, steadystate photosynthesis could be obtained. This was evident from the fact that the pH of the seawater flowing from the mat was maintained at a constant level after the initial rise (Figure 14).

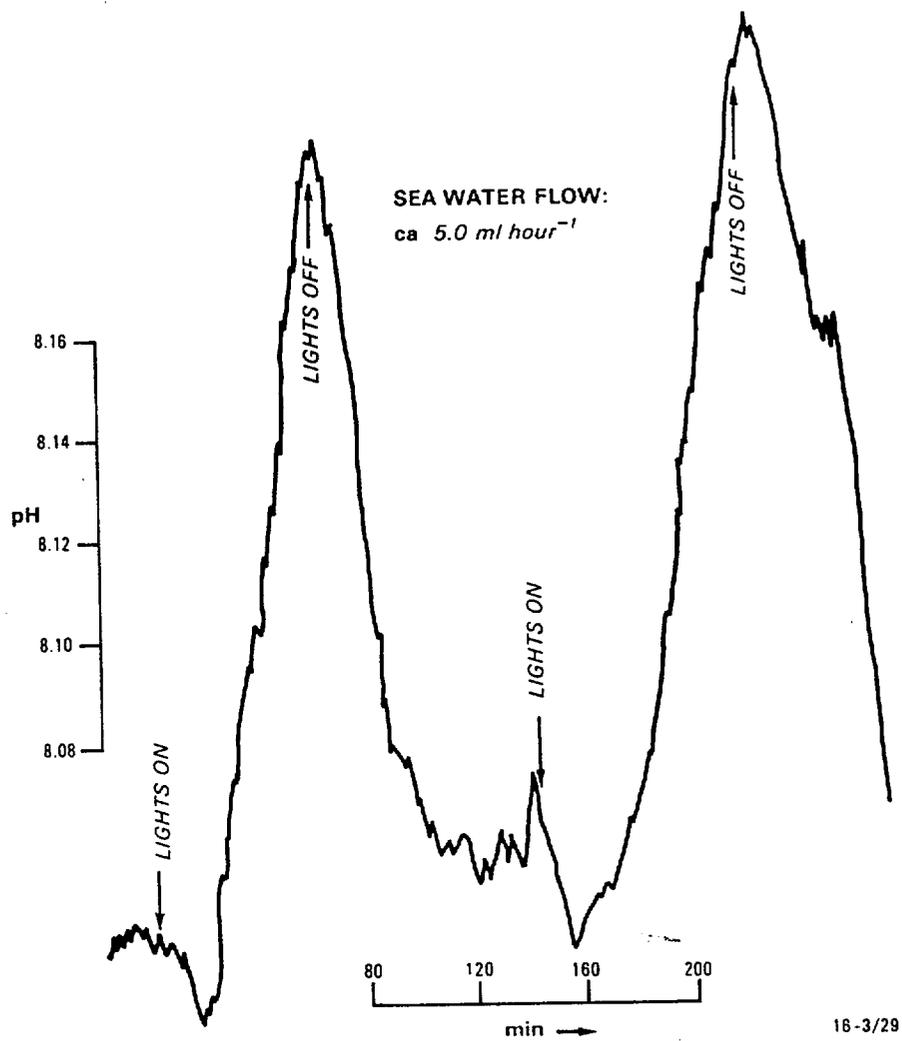


FIGURE 13: Changes in the pH of seawater flowing over Spencer Gulf mat.

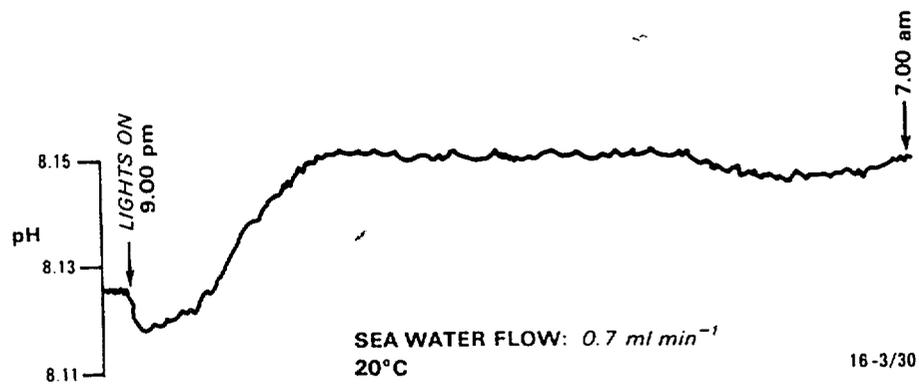


FIGURE 14: "Steady state" photosynthesis in Spencer Gulf mats—shown by continuous pH measurements.

3. When the flow rates of seawater through the top and bottom chambers were the same, the rate of change of pH was faster in the top chamber than the bottom chamber.
4. When flow of seawater through the bottom chamber was stopped, sulphide accumulated. Points 3 and 4 indicate that the metabolism of organisms on the top and bottom side of the mat can be measured separately.
5. The pH of the seawater flowing over non-illuminated mat was lower (ca. pH 8.04 to pH 8.07) than the pH of the seawater in the reservoir (pH 8.23). This was presumably the result of respiration and appeared to proceed during illumination. Respiration should also be measurable with this system.
6. A single piece of mat responded to illumination at various lux (not measured) after three weeks continuous operation, during which several variations in flow of seawater were examined. (Note: The pH values reported here are not absolute).

These preliminary results indicate that the chamber should be adaptable to a more precise measurement of the stoichiometry of and temporal relationships between C and S metabolism in cyanobacterial mats than has been previously possible.

BAAS BECKING GEOBIOLOGICAL LABORATORY ANNUAL REPORT, 1984

INTRODUCTION

Five years ago the Laboratory commenced a research program on Proterozoic and Cambrian petroleum. Parts of the program were slow to start because of delays in appointing key staff, but we have now made substantial progress. As with all of our research we have endeavoured to approach the problems from many different directions, with as much interdisciplinary interaction as we can achieve. From the beginning we have recognised that the processes and ecosystems we are studying were significant not only in Cambrian and older times, but also were operative throughout the Phanerozoic, particularly in hypersaline environments, so the significance of the research is not limited to the interpretation of Proterozoic and Cambrian sequences. Concurrent with this program has been another on the "Mississippi valley-type" lead-zinc deposits in Devonian reefs of the Lennard Shelf, Western Australia. This has included experimental work on processes of sulphate reduction, including the possibility of bacterial reduction as part of ore deposition, as well as a wide range of petrographic, geochemical and fluid inclusion studies of the deposits and their host rocks. Our research on the microbial enhancement of oil recovery draws on experience gained in both our other programs, and contributes to them, in that it is concerned with the microbiology, geochemistry and fluid mechanics of basinal fluids. All three research programs are planned for completion in 1987. All three involve extensive cooperation with industry and are supported by industry funding.

Some of the highlights of the 1984 research are:

- The discovery of an extensive sulphidic, relatively organic-rich sediment in southern Hamelin Pool. This has yet to be mapped, but seems to cover some 100 km².
- Elucidation of the effect of salinity and other factors on the preservation of organic matter in sediments. High salinities affect some bacterial processes, including sulphate reduction, retarding the degradation of organic matter in anaerobic environments.

BIOGEOCHEMISTRY OF HOLOCENE ENVIRONMENTS

Objective: To develop an integrated biological, chemical and geological understanding of those modern environments that are

most significant for interpreting key ancient environments, including those associated with low-temperature ore deposits and petroleum accumulations; to elucidate the roles of major groups of organisms in the geochemical cycles of major elements.

HOLOCENE CARBONATE ENVIRONMENT, SHARK BAY (WA)

J. Ferguson, G.W. Skyring, J. Bauld, G. Bickford, R.V. Burne, G.R. Heys, D. Ho, F.S. Lupton, L.A. Plumb, I. Reichstein, B. Simeonovic, R. Summons, S. Dibb, M.R. Walter

Organic Geochemistry:

Organic matter in the oxic surface sediments of Hamelin Pool is generally in low abundance (1-2% T.O.C.). The exception is a moderately rich deposit at the southern end of the basin plain (5% T.O.C.). The major sources for this organic matter as judged by biomarker distribution, are the subtidal benthic microbial communities. The biomarkers present include a suite of pentacyclic triterpenoids, derived from bacteria, and several highly branched C₂₀ (Fig. 1, I) and C₂₅ (Fig. 1, II), isoprenoid hydrocarbons. These isoprenoids decrease in concentration from the surface community (benthos) to the underlying sediment and then continue to decrease with depth within the sediment column. This pattern suggests that they are produced by the benthic microbes and are not the products of subsurface diagenesis.

Anaerobic Microbial Processes in Peritidal and Subtidal Sediments of Hamelin Pool, (Shark Bay, W.A.)

Measurements of sulphate reduction rates and anaerobic hydrogenase activities in various environments dominated by phototrophic cyanobacteria and diatoms were continued during 1984. Major studies were concerned with the Nilemah Transect (p. 22, 24-26 BBGL Annual Report 1983), Playfords Transect (p. 15, BBGL, Annual Report 1981) and 9 stations located in the basin of Hamelin Pool (Fig. 2). Complementary to the rates of microbial processes, the geochemical properties of sediments and pore-waters which are the result of microbial activity or which are known to affect microorganisms were determined.

Peritidal Environments

Core samples were taken along the Nilemah Transect NM to coincide with the following: supratidal sediments where there was a subsurface reduced zone, sediments colonized by crenulate and pustular cyanobacterial mat, sediments colonized by tufted cyanobacterial mat, sediments colonized by smooth cyanobacterial mat.

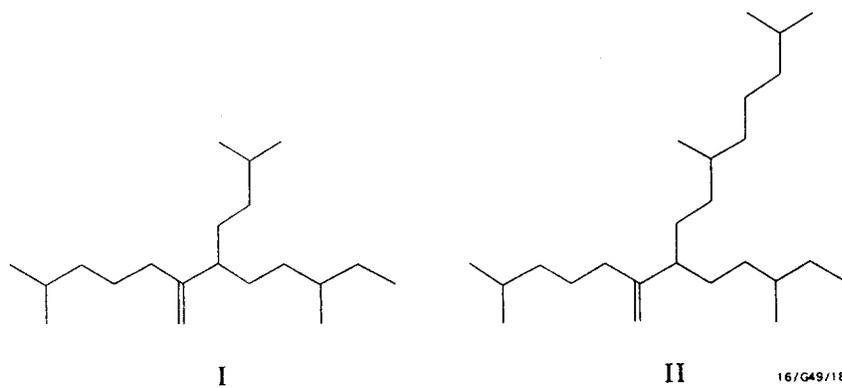


Fig. 1 Structures of C20(I) and C25(II) isoprenoid hydrocarbon from Hamelin Pool.

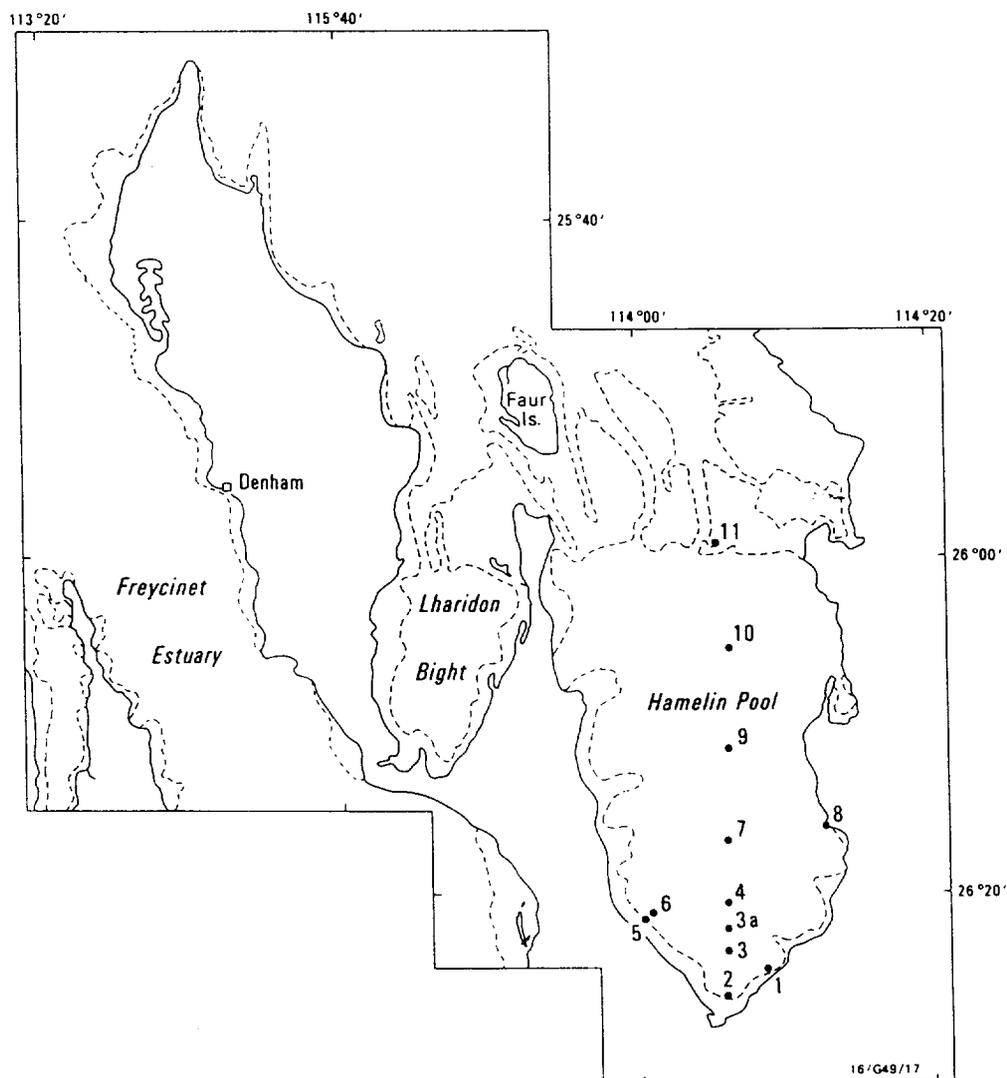


Fig. 2 Map of Hamelin Pool (Shark Bay) showing sample sites.

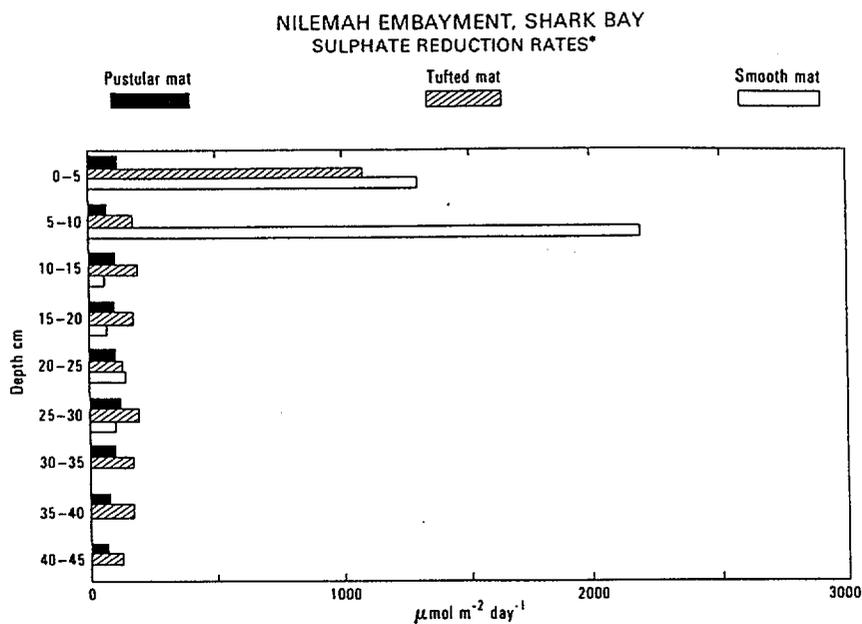


Fig. 3 Sulphate reduction rates in sediments associated with three types of cyanobacterial mat, Shark Bay.

* The rates were calculated from acid volatile sulphide and tin-reducible sulphur.

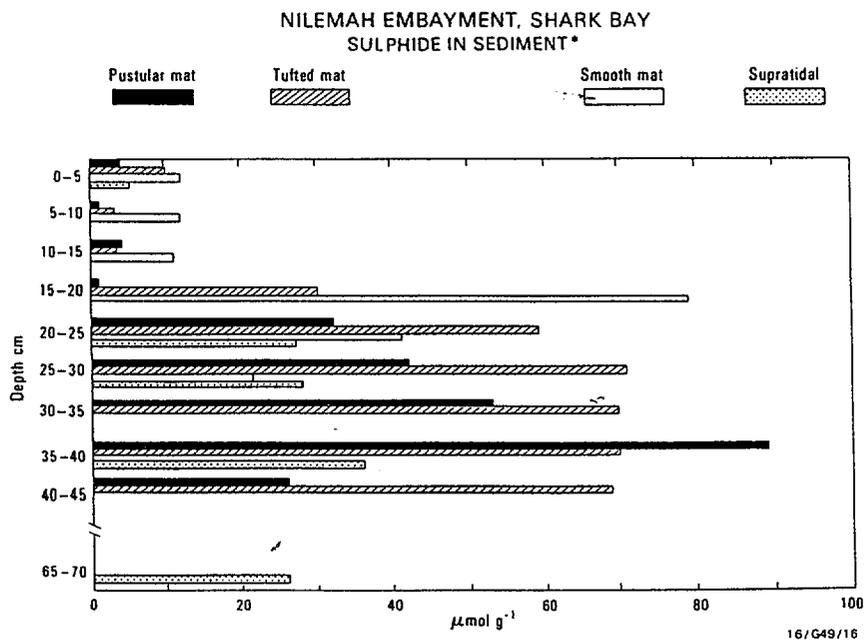


Fig. 4 Sulphide concentrations in sediments from the supratidal zone and those associated with three types of cyanobacterial mat, Shark Bay.

* The sulphide concentrations are given as the sum of the acid volatile sulphide and tin-reducible sulphur (presumably pyrite) fractions.

Sulphate reduction rates were determined in the sediments of the reduced zone of the supratidal environment and in 5 cm layers of the cores taken from the sediments colonized by cyanobacterial mats (Fig. 3). Sulphate reduction could not be detected in the supratidal sediments taken from the 30-35 cm and 45-50 cm layers. However the estimate for the 45-50 cm layer was just above background and the data may be indicative of a very low sulphate reduction rate. Sulphate reduction rates in the sediments colonized by mats were highest in smooth mat sediments. Rates in the tufted mat were lower than those in the smooth mat. As has been observed previously, sulphate reduction was not detectable in the pustular mat. Similar patterns were observed for microbial hydrogenase activity in these mat environments. Sulphate reduction rates in sediments below 10 cm were very low or undetectable. However, there did appear to be low but detectable rates in the sediments beneath the tufted mat. There were also appreciable amounts of tin-reducible sulphide (presumably pyrite) in these sediments below 10 to 20 cm (Fig. 4). What environmental conditions prevail to maintain conditions which result in the preservation of the "pyrite" in the subsurface layers are not yet known. Low but detectable hydrogenase activity was measured in subsurface sediments and this is indicative of microbial activity.

During the period from June to November 1983, a deposit of decaying organic sludge, around 50 x 10 m in extent, collected about 150 m west of Playford's Transect. Table 1 shows analyses of samples of this black sediment at various stages of diagenesis. Figure 5 is a diagrammatic representation of this environment. It is evident from the chemical properties of the porewaters, the acid-volatile sulphide (AVS) concentrations of the sediments and the relatively high sulphate reduction rates, that anaerobic processes were very active in these sediments. Alkalinities were the highest measured in this series. This is another indication that the sulphate reducers were very active in these sediments.

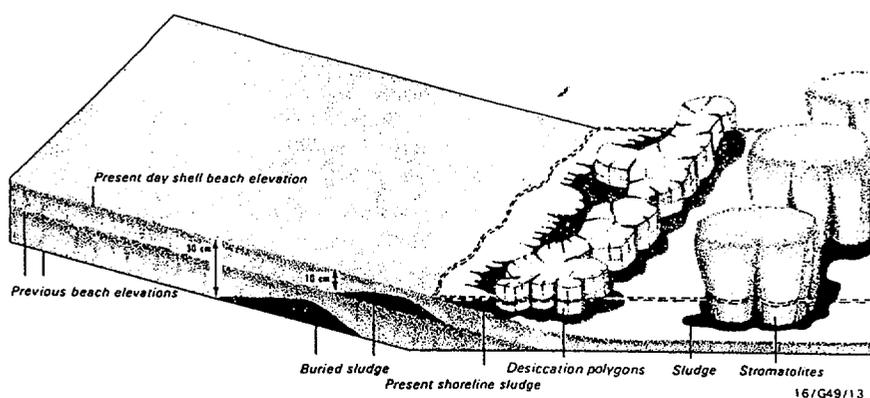


Fig. 5 A diagrammatic representation of the prograding shoreline at Playford's transect where organic sediments supporting active sulphate reduction are being buried by the prograding beach shells.

Table 1. Porewater and sediment analyses, Playford's Transect, November 1984

	Porewater						Sediment				
	%o	pH	SO ₄ ⁼ mM	S ⁼ mM	NH ₄ ⁺ mM	ALK meq l ⁻¹	Sulphide		Sulphate Reduction Rate		
							AVS μmol g ⁻¹	TRS μmol g ⁻¹	AVS mmol m ⁻²	TRS day ⁻¹	
Desiccation											
Polygons*	70	7.74	29	1.5	54	22	13	51	50	7.4	
Sludge	65	7.59	38	2.2	29	9	15	37	15	4.0	
Buried 10 cm	56	—	15	3.4	62	—	11	46	124	1.4	
Buried 30 cm	44	7.85	33	0.07	17	7	4	10	12	5.7	
Shoreline Sludge	121	7.66	70	0.9	5.9	11	17	35	12	4.8	

* These are brief descriptions of the varieties of black sediment in the intertidal areas of Playford's transect. The polygon material results from the desiccation and cracking of organic sludge which is stranded during low tides. The sediment consolidates and provides a barrier which prevents newly settled organic sludge from being carried back into Hamelin Pool with tidal water.

Figure 5 is a simplified representation of the sedimentary environment at this location of Playford's Transect.

Footnotes: Column Codes

%o	Salinity in ppt as NaCl
pH	These data have not been corrected for the effect of salt
SO ₄ ⁼	Sulphate concentration, mM
S ⁼	Sulphide concentration, mM
NH ₄ ⁺	Ammonia concentration, mM
AVS	Acid volatile sulphide
TRS	Tin-reducible sulphide

Subtidal Environments

Small cores were taken from a subtidal stromatolite off Flagpole Landing (p. 15 BBGL Annual Report 1981), and sulphate reduction rates and hydrogenase activities were determined in the soft gelatinous sediment covering the stromatolite and in the hard porous carbonate matrix of the stromatolite. Rates were also measured in sediments from the base of the stromatolite and from sediment slightly removed from the stromatolite. However, despite the fact that the carbonate matrix contained Sn-reducible sulphur (TRS), sulphate reduction was not detected. Similar patterns for microbial hydrogenase activity were observed in each of these environments.

There was a grey mottled appearance to the stromatolite matrix; the pigmenting material was not soluble in acid, but it was degraded by boiling with Sn and HCl, and sulphide was recovered during the digestion. It is presumed that the grey mottling was due to pyrite, a product of sulphate reduction. Gas from the stromatolite was 19.95% oxygen, 79.8% nitrogen and 0.3% CO₂; similar to that of air except that the CO₂ was about 8 times that found in air. These studies will be continued to determine if

sulphate reduction occurs at very low rates in the carbonate matrix of stromatolites.

The locations in Hamelin Pool where vibrocores were obtained are given in Figure 2.

Sulphate Reduction Rates in Sediments Above 10 cm Depth

Sediments from Stations 4 and 9 had the highest sulphate reduction rates at 12 and 19 mmol m⁻² day⁻¹ respectively. Moderate rates (0.7 and 1.0 mmol m⁻² day⁻¹) were determined for sediments from Stations 2 and 7, respectively and the rates for sediments from Stations 3 and 6 were very low (≤ 1 mmol m⁻² day⁻¹).

Sulphate Reduction Rates in Sediments Below 10 cm Depth

It was not feasible to determine the sulphate reduction rates for every 5 cm layer from all cores. The strategy adopted was to sample from the 5 cm layers at the top and bottom of the recognizably different sediment types. Black sediments and those which were apparently organic-rich were also sampled irrespective of their position in the sedimentary column. Previous work showed that sulphate reduction rates in subsurface sediments were likely to be low. Therefore, long incubation periods (up to 14 days) under nitrogen were used. For Station 2; although the sediments contained small quantities of acid-volatile sulphide (AVS (ca. 0.5 $\mu\text{mol g}^{-1}$)) and tin reducible sulphide (TRS, 29 to 52 $\mu\text{mol g}^{-1}$) (presumably pyrite-S), sulphate reduction was not detectable. Station 3 gave similar results to Station 2, but there appeared to be some sulphate reduction occurring at very low rates. The TRS in these sediments varied from 50 to 260 $\mu\text{mol g}^{-1}$. Station 4 represents a newly discovered (by R. V. Burne and R. Summons) and fairly extensive deposit of organic-rich black to grey mud about 40cm thick, overlying a buff to grey sandy sediment. About 80% of sulphate reduction occurred in the upper 10 cm. However there did appear to be a minor peak of activity between 20 and 30 cm and this may coincide with a different sediment type. Below 40 cm, sulphate reduction was barely detectable (Fig. 6). The sulphide concentrations are given in Fig. 7. Station 6: The sulphate reduction rates for Station 6 were barely detectable, even in the 0-5 cm layer. This was surprising, since the porewaters contained sulphide (up to 1 mM) and ammonia (from 0.5 to 0.8 mM) down to 120 cm and there were appreciable concentrations of TRS (10 to 180 $\mu\text{mol g}^{-1}$). Sulphate reduction at Stations 7 and 9 was not detectable below 10 cm. However, the sediments were, grey and contained small quantities of TRS (7 to 22 $\mu\text{mol g}^{-1}$).

For a brief discussion of rapid pyrite formation see the BBGL Annual Report, 1983, p. 36. As an example, sulphide concentrations of the Hamelin Pool sediments from Station 4 are given in Figure 7. There was a positive correlation between the sulphate reduction rates calculated from the AVS and TRS, respectively, in the sediment from the stations in Hamelin Pool. However, there was an inverse relationship between the AVS and the incorporation of ^{35}S into TRS (Fig. 8). From the results of various experiments, the limit of detection with respect to the TRS fraction is about $300 \mu\text{mol m}^{-2}$ or $4 \mu\text{mol g}^{-1}$. This is because some of the sulphate in the sample is reduced during reflux distillation with tin and hydrochloric acid.

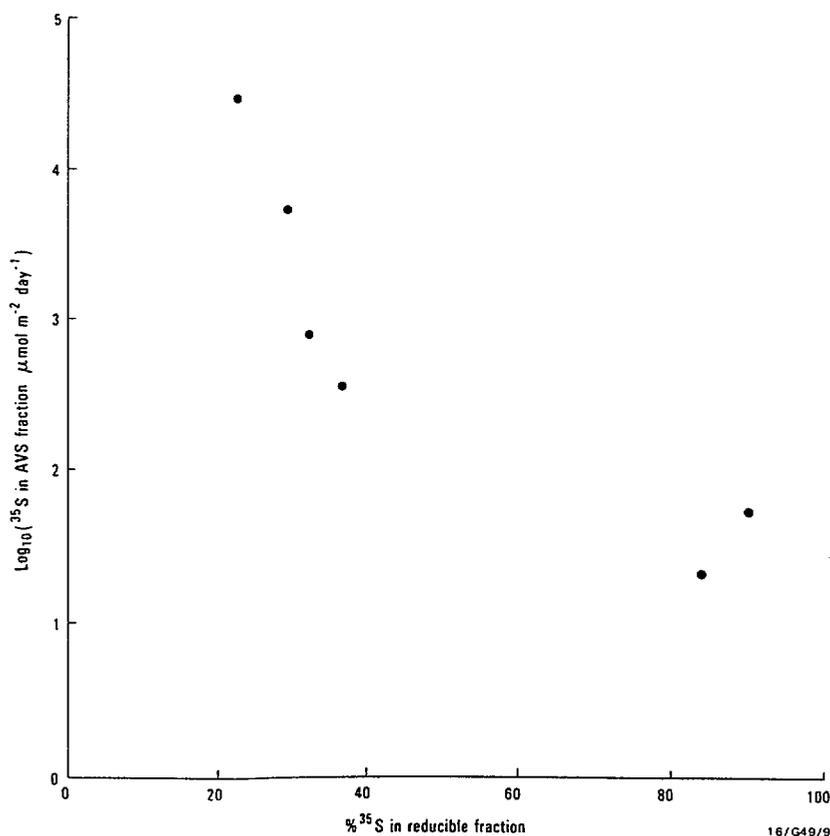


Fig. 8 Relationships between the sulphate reduction rates (as AVS) and the % of S appearing in the tin-reducible fraction; data from the 0-5 cm layer from Hamelin Pool stations 2, 3, 4, 6, 7 and 9.

Over the wide range of sulphate reduction rates which were determined in sediments of the Hamelin Pool environment, there was a positive but complex correlation between the rates and the concentration of organic matter. Hydrogenase activity correlated more simply and significantly with the acid-soluble organic-C concentration. Thus soluble organic-C may be a better indicator of "available" organic carbon than is total organic-C (Fig. 9).

One of the reasons for examining subtidal sediments from various parts of Hamelin Pool was to search for locations where organic matter and sulphide are preserved. Sediments from Station 4, down to 40 cm, were sulphidic and gelatinous. However, high organic carbon concentrations were characteristic of the upper 10 cm only. Subsurface sediments from Stations 3, 6, and 9 also had organic-C concentrations in excess of 1% down to 40 cm. From the present work it seems that sulphate reduction is very low when the acid-insoluble C is about 1% or less, even if this situation occurs in surface sediments such as at Stations 3, 6, and 7. Although sulphate reduction rates were undetectable in most subsurface sediments, it is not possible to conclude that it had ceased. Clearly some process must be responsible for the formation of TRS, which increases with depth at all locations, and the most likely cause is sulphate reduction. For example, the very low rates of reduction found for Station 3 would be interpreted as zero if taken individually. However, there did appear to be a trend for slightly higher sulphate reduction rates in the 100-145 cm layer, and this corresponded with slightly higher organic carbon contents. On the other hand, the sulphide in Station 3 sediments may have formed not as a result of in situ reduction, but as a result of lateral movement of waters from areas where sulphate reduction occurred at faster rates.

Hypersalinity and Anaerobic Microbial Processes

It was found in enrichment growth media that increasing salinity inhibited both the acidogenic activity of fermentative bacteria and the sulphidogenic activity of sulphate-reducing bacteria from Hamelin Pool sediment. The effect of salinity on hydrogenase activity as measured by tritium incorporation indicated that sulphidogenic bacteria may be relatively more inhibited than fermentative bacteria. Glucose enrichment of Hamelin Pool intertidal sediment stimulated sulphidogenesis at salinities lower than 210‰, but not at greater salinities (Fig. 10). Likewise, fatty acids accumulated in glucose-enriched sediment with a salinity of 210‰, but not at lower salinities (Fig. 11). The significance of these results regarding the preservation of organic matter in hypersaline sediments is: (1) fermentative processes are relatively less sensitive to saturating salinity than sulphidogenic processes; (2) low molecular weight organic compounds can accumulate and possibly be preserved at high salinities; and (3) at very high salinities, the anaerobic diagenesis of organic matter is severely retarded.

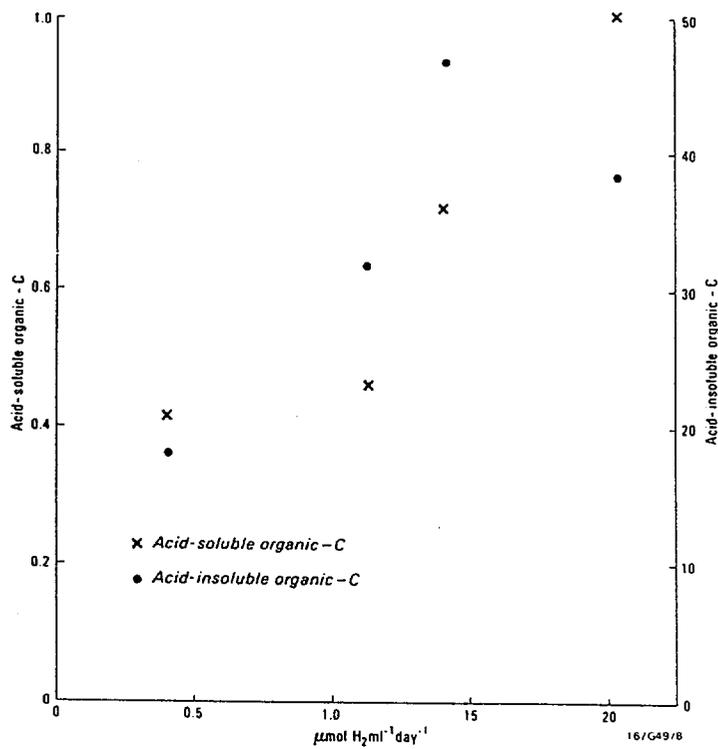


Fig. 9 Relationships between hydrogenase activity and organic carbon in Hamelin Pool sediments from Station 4.

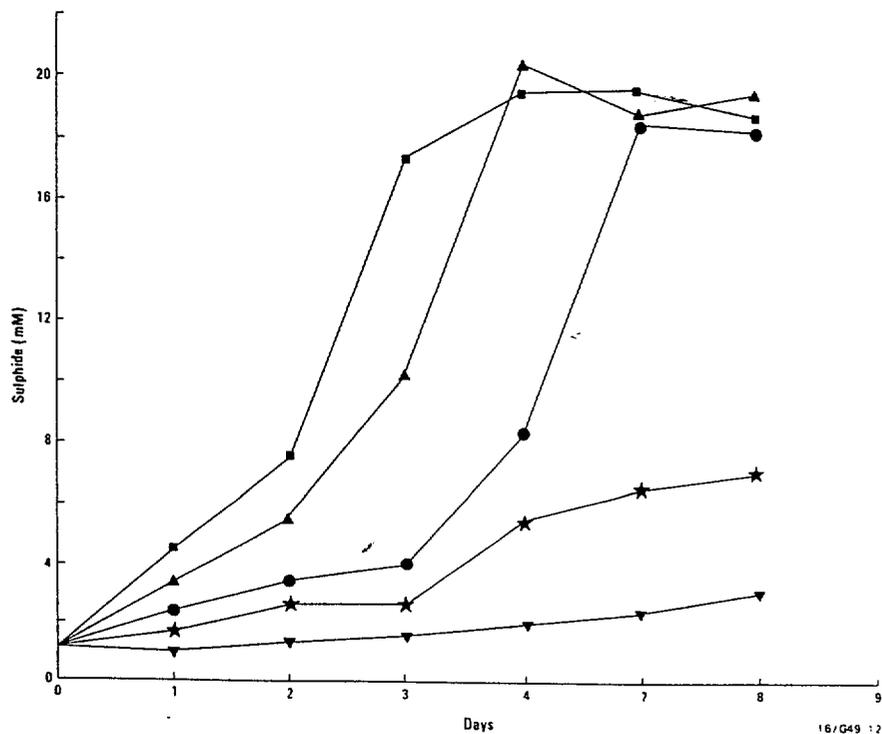


Fig. 10 The effect of salinity on sulphate reduction (plotted as sulphide production) in Hamelin Pool sediment slurries enriched with 10 mM glucose.

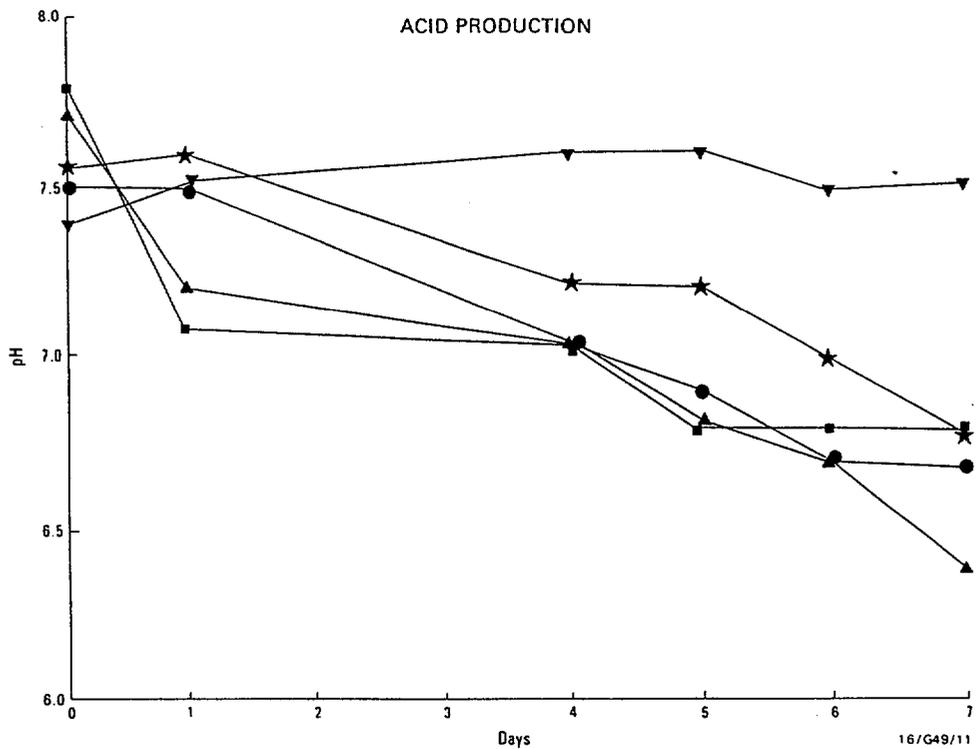


Fig. 11 The effect of salinity on acid production in Hamelin Pool sediment slurries enriched with 10 mM glucose.

Genetic Models of Stratiform Cu(Pb-Zn) Deposits

Genetic models of stratiform Cu(Pb-Zn) deposits have been assessed and modifications suggested on the basis of data from metal-poor but otherwise appropriate redbed-associated, hypersaline, marginal marine environments at Shark Bay and Spencer Gulf. In these marginal marine environments, low permeability Pleistocene marine carbonates underlie and form playa lakes immediately landward of more permeable Holocene marine carbonates. The Holocene carbonates form broad tidal flats, where organic matter and sulphide are produced mainly in the intertidal and adjacent subtidal zones. Consequently, the most favourable mechanism for the formation of high concentrations of metal sulphides involves a significant lateral component of groundwater flow through both the redbed and marine sediments, minimum precipitation of metal sulphides in the supratidal zone, and major precipitation in the intertidal and subtidal zones. This model would be most appropriate in explaining the formation of ore deposits such as the Mufilira Cu deposits in Zambia, where the host marine (or lacustrine) sediments grade laterally into redbeds and are underlain by a considerable thickness of argillaceous, impermeable marine or non-marine sediments, which would inhibit upwards groundwater movement. This lateral flow mechanism is complementary to genetic models in which evaporation from the

capillary zone or the upwards hydraulic potential caused by basinal compaction drives the ore-forming fluids vertically through organic-rich sulphidic supratidal sediments. The latter mechanism would be favoured by an environmental setting in which the metal sulphides were deposited in marine carbonates which were sufficiently fine-grained to favour the preservation of organic matter and which were deposited during first marine transgressions over permeable redbeds.

Within the general framework of these genetic models there are a number of specific processes, some of which have been identified and studied in the Spencer Gulf and Shark Bay environments. The following processes could be individually effective and in combination they could interact to produce a metal sulphide deposit with some of the major characteristics of existing ore deposits: (1) oxidizing, neutral to acid, saline near-surface groundwaters flowing through the redbed sediments from recharge areas at the landward margin of the coastal plain to marginal marine environments under the influence of a relatively high hydraulic head; (2) in the deeper parts of the redbeds (~20 m), dissolution of metalliferous iron oxide coatings under the influence of Fe(III)-reducing bacteria producing metalliferous Fe(II)-rich slightly acid, saline waters of near neutral Eh; (3) entrainment of these waters in the near-surface systems, where confining effects of clay lenses direct groundwater flow to deeper (20 m) parts of the aquifer system; (4) emergence of the metalliferous, Fe(II) rich waters into oxidizing carbonate-free areas of the redbeds; oxidation and hydrolysis of dissolved iron, producing acidic (pH 4) metalliferous waters low in Fe(II); (5) reaction of the acidic waters with carbonates (calcrete) as the waters enter near-surface environments, precipitating the remaining Fe(II) and producing saline, oxidizing, near-neutral metalliferous groundwaters, low in dissolved iron; (6) evaporative increases in salinity of the metalliferous waters when they flow into playa lakes formed at the landward margin of the marine environment by isolation of older marine units by arcuate beach ridges; (7) lateral flow of the metalliferous brines from the playa systems through older marine sediments into the overlying Holocene supratidal sediments; (8) minor removal of metals from solution in supratidal flats by reaction of copper with pyrite and major, but localized precipitation of metal sulphides in ponds where rates of bacterial sulphate reduction are high; (9) limited precipitation of metals in the high intertidal zone, where areas of high bacterial sulphate reduction rates beneath cyanobacterial mats are separated from brine systems by oxidizing sediments; (10) major precipitation of metals in the low intertidal zone and

adjacent areas of the littoral shelf by interaction of metalliferous brines with biogenic sulphide produced by sulphate-reducing bacteria during the diagenesis of diatomaceous mats; and (11) significant, but lesser metal sulphide precipitation in seaward areas of the littoral shelf and adjacent basinal plain environments as the metalliferous brines mix with seawater and the remaining metal precipitates with biogenic sulphide associated with a surface diatomaceous ooze.

Over all, the modern environment investigations support the contention that bacterial sulphate reduction could have provided the sulphide in some ore deposits. The evidence is strongest for those situations where the metalliferous ore-forming fluids can react directly with very shallow (generally significantly less than 0.5 m) near-surface environments, where bacterial sulphate reduction is sustained by organic matter derived from living ecosystems or surface accumulation of detrital organic matter. In these situations, rates of sulphide production are more than adequate to form deposits similar to the Kupferschiefer of Germany and Poland and the Roan Antelope Cu deposits of Zambia. In deeper peritidal environments, where the spatial association with the main sources of organic matter is not close, sulphate reduction rates are marginal to inadequate. The rates of sulphate reduction in the supratidal zone are low, because organic matter is not preserved in these areas. The extent to which this observation can be generalized is not clear, because the factors which control the preservation of organic matter in tidal flats have not been defined. Marine carbonate sediments of modern sabkhas are fine grained, which should increase the chances of the preservation of organic matter and the generation of relatively high rates of sulphate reduction.

The proposition that high metal concentrations can be produced in low-temperature shallow groundwater systems has not been adequately tested, because the redbed sediments in the modern environments are mature and have very low contents of readily mobilized metals. Evidence that the near-surface waters could *transport* significant quantities of metals is otherwise strong. Conditions necessary for the *mobilization* of metals from the sediments may be more readily developed in deep parts of the redbed sequence. Although groundwaters at depths of 20 m can be incorporated into the near-surface systems, more plausible mechanisms for mobilization of these deeper waters include entrainment of waters moving up-dip as a result of basin compaction, the existence of convection cells above basin-margin intrusives, and/or ascent of deep fluids along faults.

If Fe(II)-rich metalliferous deeper waters could be mobilized into the near-surface, seawards-flowing groundwater systems, then there are mechanisms by which they could readily evolve into iron-free metalliferous brines, which could flow almost unhindered across the marginal marine playa and tidal flats to intertidal and subtidal environments. There, metal sulphides could be deposited in a zoning pattern similar to that in some existing ore bodies where the metals are concentrated at the basin margins and zoned vertically and laterally in order of the solubility products of the metal sulphides.

During the year, Professor Noel James of Memorial University spent several months in the Laboratory working on aspects of the sedimentology of Shark Bay.

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Hydrology and hydrogeochemistry of the Nilemah Embayment, Shark Bay

Nilemah Embayment is a Holocene carbonate tidal flat bordering a wide coastal plain of aeolian Pliocene-Pleistocene red dunes and underlying red sandstones. Like the Persian Gulf sabkhas, the tidal flat adjoins a restricted hypersaline marine environment (Hamelin Pool), but the combination of semi-arid climate with relatively high topographic variation in the peritidal zone, and the presence of adjacent and underlying Pleistocene marine carbonate clays has produced a distinctive groundwater regime and related diagenetic mineral assemblage.

The Pleistocene marine carbonate clays at Nilemah both underlie and extend landwards of the Holocene sediments, forming an extensive playa environment between the tidal flats and the adjoining coastal plain. This playa inhibits flow of regional groundwaters into the peritidal zone both by reducing the hydraulic gradient and by forming a low permeability barrier between the redbeds and the Holocene marine carbonates. This low regional input accentuates the influence of rainfall and runoff in recharge of the Holocene peritidal groundwaters.

Rainfall recharge of this type has both general and localized effects on the groundwater systems. Generally, rainfall helps maintain a landward to seaward hydraulic gradient across the tidal flats. When input from this source decreases significantly, as occurs under drought conditions, the gradient may be reversed,

BAAS BECKING GEOBIOLOGICAL LABORATORY
ANNUAL REPORT, 1985

INTRODUCTION

During 1985 the various aspects of the Shark Bay research program reached an advanced stage. We now have extensive information on the regional distribution of buried organic matter and its chemistry. Each benthic microbial community is characterised by a distinctive suite of organic geochemical biomarkers, such that ancient examples of such communities and environments could now be recognised by geochemical techniques. The biomarker suites are as distinctive as the sediments. The distribution and rates of bacterial sulfate reduction are now known on a regional basis, so that sulfide production can be related to major environments. One particularly significant interpretation is that sulfide generated in the extensive tidal and supratidal flats may be carried through the sediments in heavy brines to the extensive deposit of carbonaceous sediments on the basin floor. Such lateral movement of sulfidic brines is of significance for models of ore genesis in sabkha-like systems.

Our sedimentological studies have led to a revision of the interpretation of facies relationships in Hamelin Pool. The lithified intertidal stromatolites have been shown to be subtidal stromatolites stranded by falling sea level. This will lead to a revision of many present interpretations of these and older stromatolites. We have also shown that the subtidal stromatolites are built by and are host to diverse communities of cyanobacteria, diatoms, green and brown algae, sponges, foraminifera, nematodes, fish, annelids and other organisms, communities comparable with those in marine stromatolites (including thrombolites) of Palaeozoic age. The subtidal stromatolites of Hamelin Pool form much more appropriate analogues for Palaeozoic and Proterozoic marine stromatolites than do the more usually compared intertidal forms.

We have found abundant microbially produced limestones in many lakes in Australia. The extent of the influence of benthic microorganisms in limestone formation seems to have been underestimated previously. The lakes have salinities ranging from half that of seawater to hypersaline. Close comparisons can be made between these lacustrine stromatolites and many Phanerozoic examples. Detailed studies in Lake Eliza have defined the factors controlling the preservation of organic matter in sulfate-rich environments.

with a resultant tendency for groundwater to flow landwards. Locally, there are major differences in the amount of rainfall recharge and its effect on the salinity of the groundwaters. These differences reflect the juxtaposition of major sediment accumulations, such as beach ridges, and areas where tidal currents have eroded the sediment surface. Two results of the interaction of rainfall recharge with the high topographic variation are the formation of groundwater mounds on the water table in areas of high recharge, and the development of low salinity areas where sediment accumulations restrict evaporation. In contrast, the eroded areas produce highly saline brines which, partly under the influence of a density gradient, move seawards through low intertidal and adjacent subtidal environments.

The groundwaters in the Nilemah playa and peritidal environments could be derived from three sources – groundwater from the redbed aquifers, local rainfall, and seawater – each of which may have a distinctive chemical and isotopic composition. Rainfall in this semi-arid region is highly variable in hydrogen and oxygen isotopic composition. Winter rainfall plots on a regression line with a slope close to the expected theoretical value and a "deuterium excess" higher than the world-wide average, but characteristic of oceanic vapour sources. Near-shore seawater in Hamelin Pool, which floods the tidal flats, is hypersaline and in very restricted lagoons reaches a $\delta^{18}\text{O}$ value of about 7.5‰ , which is higher than expected for arid or semi-arid environments.

Groundwaters emanating from redbed sediments are relatively saline (45‰). Their major ion composition is dominated by Ca^{2+} , Na^+ , SO_4^{2-} and Cl^- , and, like their minor ion composition, is similar to that of seawater. However, they can be distinguished from marine water because their $\delta^{34}\text{S}$ values of dissolved sulfate are low, their $^{87}\text{Sr}/^{86}\text{Sr}$ values high and their D/H and $^{18}\text{O}/^{16}\text{O}$ ratios low. This distinction becomes blurred by evaporation and addition of dissolved salts, which modify the redbed waters as they flow beneath the playa. As a result of these processes, salinities increase to about 220‰ , and $\delta^{18}\text{O}$ values rise from about -2 to $+3\text{‰}$.

The playa groundwaters are meteoric in origin and are essentially redbed waters overprinted by the effects of recharge by local rainfall. This water does not appear to make a major contribution to the peritidal groundwaters, which are recharged by rainfall, runoff and seawater. As a result the peritidal groundwaters have a seawater-like major ion and $\delta^{34}\text{S}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ geochemistry, but a D/H and $^{18}\text{O}/^{16}\text{O}$ composition reflecting a substantial meteoric

water contribution. Like the groundwaters in the playa, the peritidal waters are subject to evaporation as they flow seawards and salinities increase from 50 to $>200\text{‰}$ and $\delta^{18}\text{O}$ values from -2 to $+7\text{‰}$. When they reach the intertidal and subtidal zones they mix extensively with seawater in the near-surface zone of the sediments.

Diagenetic effects in the Holocene marine sediments at Nilemah Embayment are limited in comparison to those in tidal flats at Spencer Gulf in South Australia, and sabkhas at Abu Dhabi in the Persian Gulf. The high Fe and Mn concentrations and intensive aragonite cementation which are features of sites of non-marine groundwater discharge at Spencer Gulf do not occur in the vicinity of Nilemah, at least partly because the hydrological regime does not favour entrainment of deeper waters by the seawards-flowing near-surface waters. Significant quantities of dolomite and a wide spectrum of evaporite minerals, such as halite or magnesite, which are characteristic of the sabkhas, are not present at Nilemah. Dolomitization may be limited by the small quantities of fine-grained aragonite which are present in otherwise chemically favourable groundwater environments, and the formation of evaporite minerals is limited by the relatively low maximum salinity (up to 290‰) reached by the groundwaters. Gypsum does precipitate at Nilemah and there is considerable cementation of carbonates in beach ridges, where aragonite converts to calcite, and in the intertidal and subtidal zone, where micritic aragonite precipitates.

Sulfate reduction in anoxic sediments in Nilemah Embayment, Shark Bay

An objective of the Holocene environments program is to identify sites for modelling sulfide ore formation. There is an extensive volume of subsurface sediment in the supratidal and intertidal zones of Nilemah Embayment at the southern end of Hamelin Pool. It is grey and contains around 0.4% pyrite, its porewaters have a low Eh and contain small amounts of sulphide and ammonia (Fig. 1). Sampling this sediment was difficult because it was so porous that porewater was not easily contained during collection of the core. However, sulfate reduction was not detected by any of the following procedures: (i) rapid sampling and incubation of samples with radioactive sulfate for long periods under high purity nitrogen, (ii) addition of sulfide to maintain a low Eh during the preparation and incubation of the samples, (iii) addition of acetate and lactate, known to be readily oxidized by sulfate-reducing bacteria; (iv) careful determination of zero controls and statistical variations to facilitate the detection of very low

sulfate reduction rates. It is possible that the pyrite, sulfide and ammonia associated with these sediments were produced in situ during some earlier but recent and seasonal event, and the ammonia and sulfide preserved in the relatively static layer of highly saline water which saturates these sediments. Sulfate reduction of 2-3 nmol g⁻¹ day⁻¹ in other sediments from Hamelin Pool and Lake Eliza were at the lower limit of detection. Thus, if sulfate reduction occurs in the grey sub-surface sediments at Nilemah Embayment, the average daily rate is probably <3 nmol g⁻¹ day⁻¹. Analysis of porewaters from the subsurface sediments along transect NM indicates that the effects of anaerobic microbial metabolism become more evident from landward to seaward (Table 1).

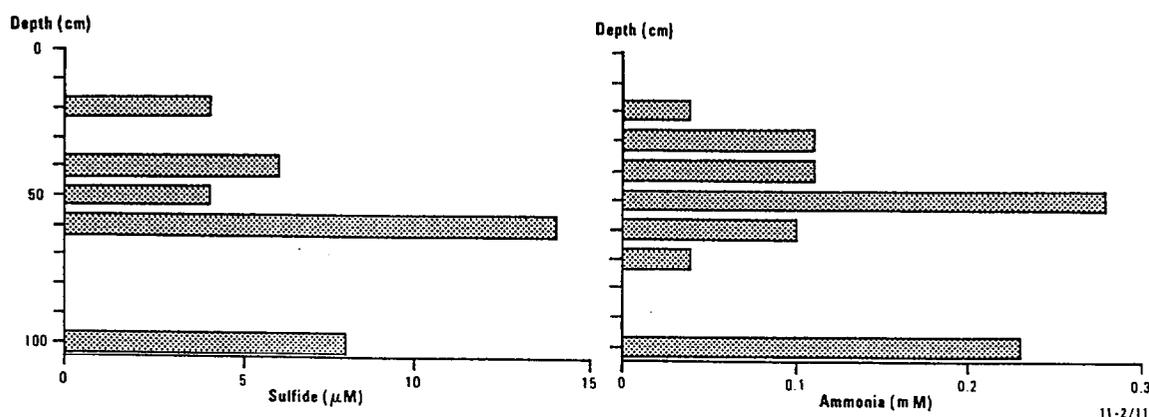


Figure 1. Sulfide and ammonia concentrations in porewaters from sediments of transect NM (at NM22.5, Winter, 1985).

Table 1. Some chemical and physical properties of porewaters from the reduced subsurface sediments of Nilemah Embayment, TRANSECT NM (STATIONS 2 to 33) and Hamelin Pool (STATIONS HP 2 to 4)

Station	Supratidal Zone					Intertidal Zone			Subtidal Zone			Hamelin Pool Water	
	2	5	7	15/16	19	21	27	30/31	33	HP2	HP3	HP4	
Depth (cm)	180	140	120	106	100	105	25	60	80	80	100	100	0
Salinity ‰	98	188	228	139	161	168	142	118	108	99	79	66	68
Eh* (mV)	238	252	184	78	158	110	22	-23	-7	ND	ND	ND	370
Sulfide (µM)	0	6.4	3.7?	17	8	8	44	89	212	47 ^a	59 ^a	—	0
Ammonia (µM)	0	9	9	12	0	0	45	45	63	96	170	139	0

* EH vs a standard redox solution at 440 mV.

^a Probably low because porewater samples were prepared from vibrocores: some oxidation probably occurred during separation of the porewater and sediment.

Because of the important biogeochemical implications of this extensive anoxic ecosystem with respect to sulfide preservation and metal precipitation in sabkha-like environments, subsequent investigations will be directed to resolving the spatial and temporal relationships between sulfide formation and its preservation.

Sulfate reduction in a solar pond

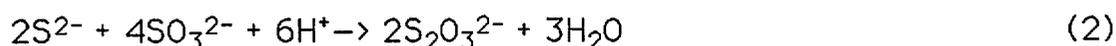
A solar pond on the western shore of Hamelin Pool is representative of one of the many environments where anaerobic microbial processes are predominant in sediments. The temperature of the bottom waters is around 15°C higher than that of the surface waters in this ecosystem. Sulfate reduction in the sediment is greatest in the surface layers and decreases rapidly with depth. Below 5 cm, acid-volatile sulfide decreases, and tin-reducible sulfide increases with depth. However, contrary to expectations, the salinity of the porewater decreases from 143‰ in the upper 5 cm to 29‰ in the 35-40 cm layer. Because Hamelin Pool water is 68‰, the lower salinity water is probably of terrestrial origin. The coincidence of the concentration depth profiles of salt and sulfate indicates that the sulfate distribution is due to dilution of the saline porewater with incoming ground water and not to sulfate reduction. These data indicate that the pond is being replenished with low-salinity water from the bottom (Figure 2). Such a system may have a high potential as an ore-forming environment because of the possibility of metals being transported to an active sulfate reduction site.

Sulfur cycling in Hamelin Pool sediments

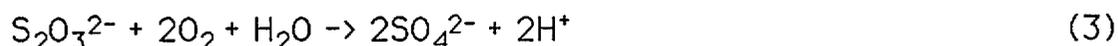
In coastal marine sediments, sulfide is produced by bacterial sulfate reduction in anoxic layers. If the supply of metals is adequate, sulfide may be fixed as metal sulfide and eventually transformed to minerals such as pyrite.

In most sediments, however, the bulk of the sulfide produced is reoxidized to sulfate. If the anoxic zone coincides with the photic zone, this oxidation can be effected by anaerobic, sulfide-oxidizing photosynthetic bacteria. Nevertheless, in most situations it is likely that sulfide diffuses to the aerobic zone, where, according to several literature reports, it is oxidized by a combination of chemical and biological processes.

First, chemical oxidation produces sulfite, which reacts with residual sulfide to form thiosulfate (Equations 1 and 2).



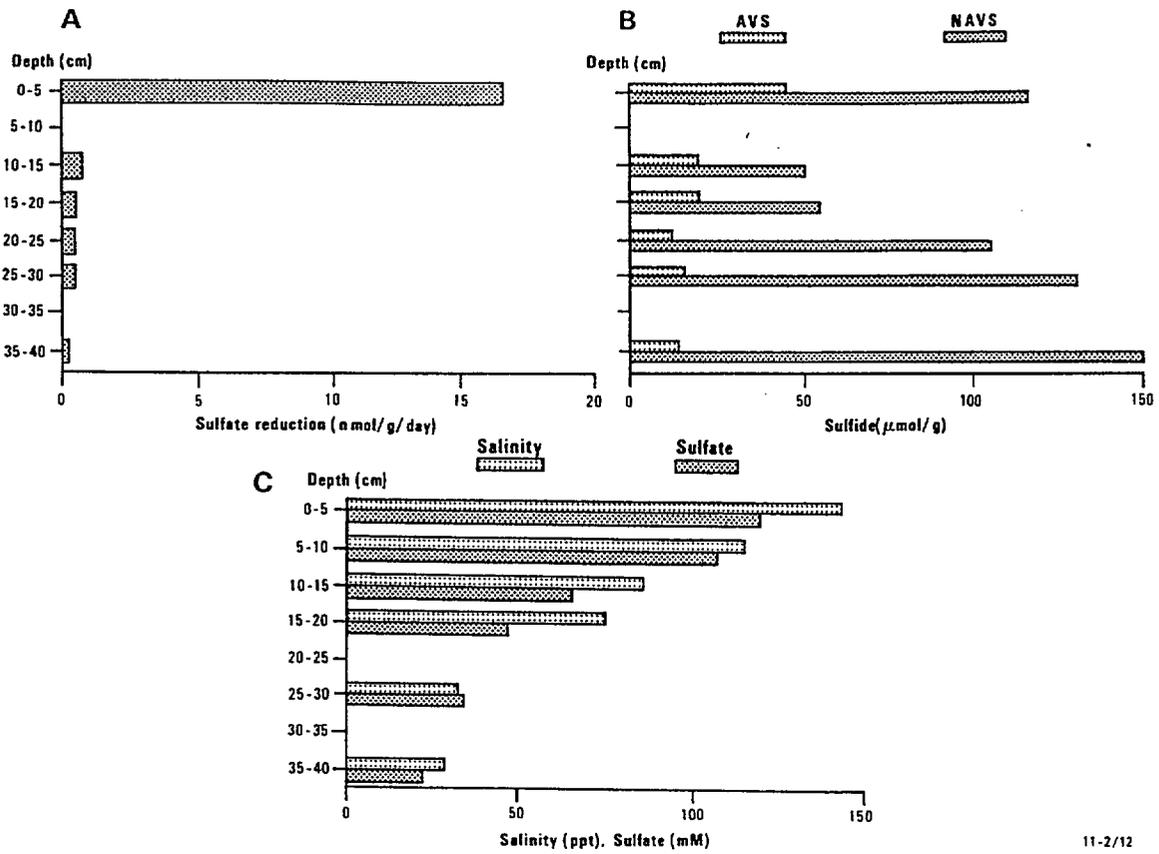
Thiosulfate is then oxidized to sulfate by bacteria (Equation 3).



From both intertidal and subtidal sediments of Hamelin Pool, Shark Bay, we have isolated bacteria that effect the complete oxidation of thiosulfate to sulfate, and the rates at which enrichment cultures develop indicate that the bacteria are actively involved in sulfide turnover in these sediments.

The bacteria are strict autotrophs, that is they are unable to utilize organic compounds, but derive their cellular carbon from carbon dioxide. Optimal growth occurs near neutral pH and a salt concentration of about 60‰, which is close to the salinity of Hamelin Pool water. The organisms have been tentatively assigned to the genus *Thiobacillus*, but they differ from the majority of neutrophilic thiobacilli in being unable to produce or oxidize polythionates ($\text{S}_n\text{O}_6^{2-}$).

The bacteria are to be examined for the presence of the distinctive hydrocarbon biomarkers that have been found in Hamelin Pool sediments.



11-2/12

Figure 2. Sulfate reduction rate, sulfide concentration and porewater salinity and sulfate in the solar pond sediments

AVS : Acid volatile sulfide
 NAVS: Non-acid volatile sulfide

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ORGANIC GEOCHEMICAL STUDIES IN HAMELIN POOL

R. SUMMONS

ABSTRACT

Organic matter in surface sediment of Hamelin Pool is generally in low abundance (1-2% T.O.C.). The exception is a moderately organic-rich deposit at the southern end of the basin plain (~5% T.O.C.). On the sublittoral platform the T.O.C. values decrease rapidly down the sediment column. Organic matter is present at depth in cores from the basin plain.

The major source of Hamelin Pool organic matter is considered to be subtidal benthic microbial communities. These communities show interesting variations in biotic composition and are generally

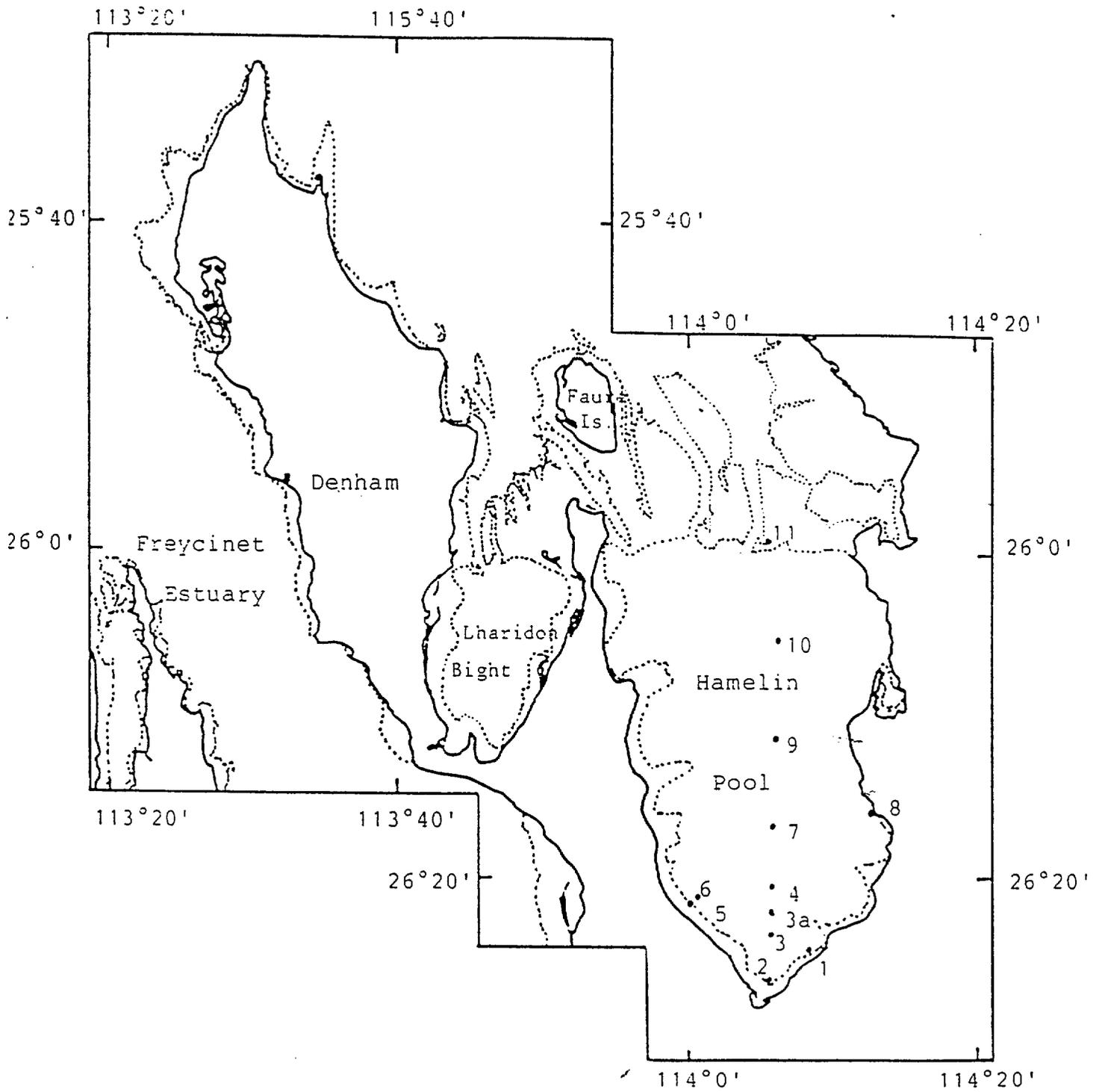


Figure 13 Map of Shark Bay showing sample sites

dominated by diatoms with some cyanobacteria. The organic rich deposit in the southern end of the basin plain contains diatoms not previously recognised in this basin. As well, a live community of Fragum was observed.

Hydrocarbon biomarker patterns show consistent positive correlations with depth and with T.O.C. Benthic mat communities which can be visually distinguished by their microbial components can also be differentiated by their very distinctive hydrocarbon distributions. Biomarker profiles indicate a large component of heterotrophic bacteria in the benthic communities.

This work is a joint contribution from the laboratory and in particular John Bauld, Bob Burne, Bob Dunlop and Vanessa Grey and Malcolm Walter.

Figure 13 Map of Shark Bay showing sample sites
branched acyclic isoprenoid hcs diagram
branched acyclic isoprenoid hcs sb diagram

HAMELIN POOL, SHARK BAY, AND COASTAL LAGOONS AS MODELS FOR STUDIES OF PROTEROZOIC AND YOUNGER SOURCE AND RESERVOIR ROCKS.

R V BURNE

Algal and bacterial dominated environments are of particular geological significance as the sites of primary production and degradative modification of organic matter that produces rich Type I and II kerogens. In addition, many Proterozoic and Phanerozoic limestones appear to have been deposited in environments strongly influenced by algal and bacterial eco-systems. The decline in the relative importance of microbial systems with the evolution of higher life forms through the Phanerozoic is well documented, and microbial systems dominate today only in specialised environments such as carbonate tidal flats, saline lakes, and hot springs. These are not direct analogues of ancient holomarine microbial environments. They nevertheless provide vital information for the interpreting of ancient sequences.

Intermittently exposed cyanobacterial mats are found in intertidal zones and along seasonally exposed lake margins. A number of factors influence their distribution, the most important probably being frequency and duration of inundation. They are important

producers of organic carbon, but the intermittent exposure typical of their environment assists the diagenetic destruction of the organic material. Conditions favourable for the preservation of organic carbon in mat deposits are encountered in Lake Eliza, where the mat sediments occur along a saline groundwater seepage zone. The positive head of water together with the porous but impermeable mat sediments provide an interstitial environment that inhibits complete degradation of the organic material.

Subaqueous environments provide a setting more favourable for the preservation of organic matter. In the southern basin of Hamelin Pool a benthic organic mat comprising diatoms, cyanobacteria, as well as other organisms exists in 5m of water at salinities of about 68‰. Despite an active fauna of shrimp and fish organic material is preserved beneath this mat to a depth of 20cm.

Microbial communities play a vital part in the formation of lithified stromatolites in several lakes as well as in Hamelin Pool. Mineralogies range from gypsum through monohydrocalcite, calcite, and aragonite to protodolomite. Textures vary from laminated, through thrombolitic to travertine. Morphologies also show great variety, with club-shaped forms in the high energy oolitic environments of Hamelin Pool, large mound structures in the relatively quiet deeper waters of Lake Inneston, and small columnar colonies in the shallow marginal waters of Slerford Mere.

Studies of these present day systems, undertaken in co-operation with J. Bauld and R. Summons, are providing information of direct significance for the interpretation of Proterozoic and younger source and reservoir rocks.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
JULY, 1978

BRIEF EXCURSION TO SHARK BAY, WESTERN AUSTRALIA.

During March, Drs. Burne, Bauld and Skyring, with two micropalaeontologists (M. Muir and M.R. Walter) and two geologists (M.J. Jackson and J.M. Kennard) from the Bureau of Mineral Resources, paid a visit to Shark Bay, an environment characterized by many sabkha-like features and a varied and extensive development of stromatolites. The excursion was led by Dr. P. Playford of the Geological Survey of Western Australia. One purpose of the visit was to evaluate Shark Bay as a potential environment for future studies by the Laboratory. The visit also provided the opportunity for further integration of the research interests of the Baas Becking and BMR personnel.

During the excursion to Shark Bay ^{14}C - radioisotope experiments were carried out at Hamelin Pool to estimate the primary productivity of selected algal mat types and some components of subtidal stromatolites.

Some of the algal mats are similar to the intertidal mats in Spencer Gulf. Others, including permanently subtidal stromatolites, are found only in Hamelin Pool. Laboratory processing and data computation will be completed soon.

Thirty samples from 10 different stations on the shores of Hamelin Pool were taken for sulphate reduction rate assay. These assays are almost complete and preliminary results indicate that in the organic-rich black sediments sulphate reduction rates are high. In sediments associated with pustular algal mats, sulphate reduction rates are low. Some of the thick organic-rich sediments have been formed by the co-sedimentation of large quantities of gelatinous organic debris sloughed-off the columnar stromatolites growing further off-shore. Sediments from selected areas of algal mat have been analysed for sulphur isotope abundance. $\delta^{34}\text{S}$ values range from -9 to 24 ‰ for sulphides and $+20.7$ ‰ (sea water) to $+28$ ‰ for pore water sulphates. The area appearing superficially to be the most similar to Mambray Creek mat, exhibited the greatest fractionation in sulphides (-24 ‰).

Scanning Electron Microscopy (SEM) and X-ray dispersion analyses are being used to study the structure of the algal mat and

associated sediments. The location of iron, which is the major fixative for sulfide in these sediments, is of particular importance. Observations on freeze dried, embedded and polished sections of the mat indicate that the major portion of the iron is present between, and not within, the silica and calcium carbonate grains and in many instances appears to be associated with organic debris. Iron is often co-incident with sulphur indicating that it is probably in the form of iron sulfides.

BAAS BECKING GEOBIOLOGICAL LABORATORY
 QUARTERLY REPORT
 OCTOBER, 1978

SHARK BAY, WESTERN AUSTRALIA.

As outlined in the July Quarterly Report a visit to Shark Bay was undertaken to evaluate this area as a potential environment for future studies. The sulphate reduction rates, determined for various algal mat-associated sediments at Shark Bay have now been calculated. These results are given in Table 4. As previously reported the rates in the thick organic rich sediments were generally very high. The sulphide contents of these organic rich sediments were also high. The rates obtained in the smooth algal mat were similar to those obtained in many samples of smooth algal mat at Spencer Gulf. Pustular mat did not appear to support active sulphate reduction probably because the sediment below the algal mat appeared loosely packed and well aerated thus inhibiting the activity of the sulphate-reducing bacteria which are strictly anaerobic.

TABLE 4. SULPHATE REDUCTION RATES AND SULPHIDE CONTENTS FOR SHARK BAY SEDIMENTS

STATION DESCRIPTION (mmol m ⁻² d ⁻¹)	SULPHATE REDUCTION RATES. g ⁻¹ SEDIMENT	mmol SULPHIDE
1. Organic-rich thickly laminated black sediment	19	88
2. Same as for 1 but apparently more recent	69	56
3. Same as for 1 but further seawards	14	34
4. Same as for 1 but different location	29	51
5. Pustular mat sediment	0	0
6. Smooth mat sediment	4.6	6
7. Sandy sediment between columnar stromatolites	4.9	4

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
APRIL, 1979

Staff: J. Bauld, L.A. Plumb, G.W. Skyring, P.A. Trudinger, I.A. Johns, M.H. Reed, H.M. Thomas.

1. Studies on aspects of the carbon cycle

Shark Bay

During an excursion to Shark Bay in 1978 (see Quarterly Reports: July 1978, p. 4; October 1978, p.7), radioisotope experiments were carried out at Hamelin Pool in order to estimate the primary productivity (photosynthetic CO₂-fixation) of selected intertidal blue-green algal mats and of subtidal columnar stromatolites. Data associated with these experiments are shown in Tables 1 and 2.

Table 1 gives the rates of primary productivity measured during in situ experiments, together with mat pigment content, accretion rates (Logan et. al., 1974) and sulfate-reduction rates (Oct. Quart. Rept. Table 4). Table 2 gives the results of chemical analyses of seawater collected from our experimental area. Primary productivity rates for the flat stratiform mats (smooth, tufted and colloform) are expressed per unit area. Unfortunately, the topography of the other mats precludes this and their productivities are standardized to chlorophyll *a* content (chlorophyll *a* is a pigment in the algae which traps the light energy utilized to fix CO₂ and form organic carbon).

The high productivity of colloform mat (113 mgC m⁻²h⁻¹) reflects the relatively constant nature of the subtidal environment. The photosynthetic efficiency (primary productivity per unit chlorophyll *a*) of colloform mat is about an order of magnitude greater than for the other stratiform mats.

Unlike colloform mats, the other two stratiform mats occur in the intertidal zone and, in consequence, may be subjected to considerable desiccation stress. Both primary productivity (mgC m⁻²h⁻¹) and photosynthetic efficiency (mgC mgC h⁻¹ a⁻¹ h⁻¹) are lower than for colloform mat. Both of these mat types, smooth and tufted, also occur in the intertidal zone of the Spencer Gulf study area.

TABLE 1. PRIMARY PRODUCTIVITIES AND PIGMENT CONTENT FOR ALGAL MATS IN
HAMELIN POOL, SHARK BAY.
Experimental area 2.8 km southwest of Flagpole Landing.

MAT TYPE	PRIMARY PRODUCTIVITY		SULFATE REDUCTION ^{***}	MEASURED ACCRETION RATE ^{****}	*CHL <i>a</i> CONTENT ($\bar{x} \pm s$, n=8)	
	mgC m ⁻² h ⁻¹	mgC mgchl <i>a</i> ⁻¹ h ⁻¹	m mol m ⁻² d ⁻¹	(mm y ⁻¹)	mg m ⁻²	mg g ⁻¹
<u>Intertidal mats</u>						
Smooth (STN 6) 17		0.24	4.6	≤ 10	124 ± 23	3.27 ± 0.88
Tufted 85		0.16	nd	≤ 10	714 ± 170	18.60 ± 4.78
Pustular (STN 5) nd		9.12	undetectable	2	nd	(1.80 ± 0.50) × 10 ⁻³
<u>Subtidal mats</u> ^{**}						
Colloform 113		2.25	nd	probable <1	92 ± 34	2.34 ± 0.80
Internal nd		1.00	nd	nd	nd	(1.10 ± 0.41) × 10 ⁻³

nd not determined

* chl*a* = chlorophyll *a*

** from subtidal stromatolite column.
Colloform is surface mat: inter-
nal mat is of gelatinous, resilient
consistency.

*** data from October Quarterly Report, Table 4.

**** Logan, Hoffman & Gebelein (1974)
AAPG Mem. 22: 140-194.

Tufted mat productivity ($85\text{mgC m}^{-2}\text{h}^{-1}$) was greater than that for smooth mat ($17\text{ mgC m}^{-2}\text{h}^{-1}$) and reflects its presence in environments where water is retained for longer periods than on smooth mat, which occurs on better drained sediment surfaces. It is probable that the area of smooth mat sampled was exposed to prolonged desiccation prior to our excursion, since smooth mat in Spencer Gulf shows much higher primary production rates (up to $184\text{ mgC m}^{-2}\text{h}^{-1}$).

TABLE 2. ANALYSIS OF WATER COLLECTED FROM 2m DEPTH ON SUBLITTORAL PLATFORM 2.8 km SOUTHWEST OF FLAGPOLE LANDING.

(Water filtered prior to analysis, through $0.45\ \mu\text{m}$ filter).

PARAMETER	mg l ⁻¹
Ca	700
Mg	2450
Na	19900
K	715
SO ₄	5200
Cl	35814
TDS (calc.)	64858
NH ₄ -N	0.20
NO ₂ -N	0.008
NO ₃ -N	0.09
Total N	0.85
Total P	0.30
PO ₄ -P	0.23

pH = 8.0 at T = 27C

Conductivity, $\mu\text{S.cm}^{-1}$ (25C) = 76178

Inorganic N : P + 0.298 : 0.230 = 1.30 : 1

NO₃-N : PO₄-P = 0.208 : 0.230 = 0.90 : 1

Pustular mat exhibited very high photosynthetic efficiency compared to the other mat types examined but did not support detectable sulfate-reduction (Table 1). On the other hand, the production of organic matter by smooth mat was sufficient to support the sulfate-reduction rate determined in the sediment immediately beneath the living mat (Table 1).

In contrast to the relatively high primary productivity rates of colloform mat, its measured accretion rates were "probably less than 1mm per year" (Logan, et al., 1974) which is considerably less than that for either smooth or tufted mat (Table 1). Logan et al. (1974) observed that colloform mats occupied environments that were mainly erosive. This was clearly demonstrated during our field trip when cyclonic weather conditions sloughed material from the subtidal stromatolite columns and the flat mats around them. This material was transported to the shoreline environment where it provided ample organic matter to support bacterial sulfate reduction (see October 1978 Quarterly Report, p. 7, Table 4).

The chemical data given in Table 2 show that the water on the sublittoral platform of Hamelin Pool is concentrated seawater with a salinity about twice that of oceanic seawater. N : P ratios were found to be about 1:1. Algae from coastal marine waters normally contain N : P in the ratio of 5-15 : 1 which indicates that N is limiting for primary production in this environment.

4. Iron in Shark Bay sediments.

Iron analyses have now been completed for the sediments collected at Shark Bay in 1978. The results are given in Table 4 together with those of sulphide content presented in the October 1978 Quarterly Report. They indicate that, for sedimentary samples taken from stations 1, 2, 3, and 7, the sulphide and iron contents were equimolar (within the limits of the analyses). This result suggests that all of the iron was combined with Fe in equimolar proportions. Thus pyrite was not a major component of any of the sediments. XRD analysis of a sample of sediment from station 1 showed that aragonite was the major component and that quartz and high magnesium calcite were minor components. No clays were detected. It is possible that the high iron in sediments from stations 1 to 4 originated from organic debris from the columnar stromatolites. The organic debris itself had a high iron content. It is also possible that considerable quantities of iron were concentrated from sea water and incorporated into some Proterozoic sediments by a process similar to that observed for stations 1 to 4 at Hamelin Pool.

TABLE 4. SULPHATE REDUCTION RATES, SULPHIDE
AND IRON CONTENTS FOR SHARK BAY
SEDIMENTS

STATION DESCRIPTION	$\mu\text{mol g}^{-1}$ SEDIMENT	
	SULPHIDE	IRON
1. Organic-rich thickly laminated black sediment	88	77
2. Same as for 1 but apparently more recent	56	57
3. Same as for 1 but further seawards	34	30
4. Same as for 1 but different location	51	-
5. Pustular mat sediment	0	9
6. Smooth mat sediment	6	37
7. Sandy sediment between columnar stromatolites	4	11

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
JUNE, 1979

SHARK BAY, WESTERN AUSTRALIA

J. Bauld, L.A. Plumb, G.W. Skyring.

Sulphur isotope data from sediments and porewaters in the intertidal zone at Shark Bay have been assessed. The range of isotope values is similar to that of the only available data from an (estuarine) intertidal environment in Southern California. Calculations from the primary data have also indicated that diffusion of seawater sulphate into intertidal sediments may be an important mechanism just as it is for subtidal sediments. This process results in the net burial of sulphide which is enriched in ^{32}S compared to the sulphate of seawater.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
JANUARY, 1981

STUDIES IN SHARK BAY, WESTERN AUSTRALIA
(locality map: Fig. 2).

PHYSICAL SEDIMENTARY PROCESSES

P.E. O'Brien (BMR).

Observations of physical sedimentation were made at sites studied by other members of the Shark Bay field party to evaluate the influence of sediment transport and deposition upon other processes under study. The most important results so far concern the role played by beach ridges in formation and development of intertidal and supratidal flats and the rate of beach ridge growth. Beach ridges up to 4 m high and composed of bivalve shells rim Hamelin Pool and Lharidon Bight. Their morphology and location suggest that they were constructed during storms.

The most important area of sedimentation controlled by beach ridges is around the shores of Lharidon Bight where ridges grow as arcuate spits across the sublittoral platform, forming large lagoons. These lagoons have somewhat restricted interchange of water with the rest of Lharidon Bight and develop large intertidal and supratidal flats. Tidal channels within these intertidal areas are prime sites for cyanobacterial mat burial and preservation.

Rates of beach ridge growth along the eastern side of Lharidon Bight have been determined by comparing air photos taken in 1957 and 1968 with observations made in the field. "Nanga Lagoon" is formed by a curved spit which has grown from the south and is curving back into shore. Between 1957 and 1968 the spit grew only 20 to 30 m but between 1968 and 1980, it extended by 300 m. Of the two more northerly lagoons, "Petit Lagoon" had reached its maximum possible development before 1957 while "Bauld Lagoon" ridge increased in length by 1200 m between 1957 and 1968, reaching its maximum possible length. These high sedimentation rates are probably the result of a few episodes of deposition during storms, so rates measured from year to year may be quite small. However, the net effect is very rapid development of large shallow lagoons and flats.

ORGANIC-RICH SEDIMENTS

M.R. Walter, P.E. O'Brien.

An understanding of the processes controlling the production, erosion, burial and preservation of organic matter in modern sedimentary environments aids in the search for and interpretation of petroleum source rocks, including oil shales.

Black muds apparently rich in organic matter were discovered on our previous field trip to Shark Bay (Bauld, J., Chambers, L.A., Skyring, G.W. 1979. Australian Journal of Marine and Freshwater Research 30:753-64). During November 1980 the presence of extensive areas of sediments with up to 4% (by weight) of organic matter was confirmed. Present indications are that organic carbon produced in benthonic mats on the sublittoral shelf and in the intertidal zone of Hamelin Pool (Shark Bay) is eroded during storms and transported both into the deeper central part of the pool and up into the upper intertidal and supratidal zones. Its fate in the central pool is unknown at present, but some of that in the intertidal and supratidal zones is buried and escapes oxidation. During November, diatom mats covered large areas of the sublittoral shelves, and microscopic observation of the organic-rich muds along the shoreline revealed abundant diatom frustules ("skeletons"), indicating that these organisms may be one of the major sources of buried detrital organic matter in the Hamelin Pool sediments. The black muds are being buried by prograding beach ridges.

Lagoons on the eastern shore of Lharidon Bight in Shark Bay, and the main tidal channel in Gladstone Embayment (Hamelin Pool) contain thick (up to at least 50 cm) buried cyanobacterial mats, indicating that these may be areas of preservation of autochthonous organic matter. The buried mats in Gladstone Embayment were discovered by G.R. Davies (Amer. Assoc. Petrol. Geol. Memoir 13:169-205).

CONTINENTAL AND MARINE GROUNDWATERS AT HAMELIN POOL AND LHARIDON BIGHT

James Ferguson, L.A. Plumb, P.E. O'Brien, D. Fitzsimmons, H.M. Thomas.

Hamelin Pool and Lharidon Bight form part of the semi-arid Holocene carbonate environment of Shark Bay, Western Australia. Coastal areas of these partly barred hypersaline basins contain both continental and marine groundwaters. Where intertidal and supratidal flats are broad and slope gently towards the hinterland,

marine brines are dominant and may evolve to extremely high salinities. At other locations, where beach dunes rise steeply from the landward edge of the intertidal zone, freshwater from the dune system may intrude into the intertidal zone.

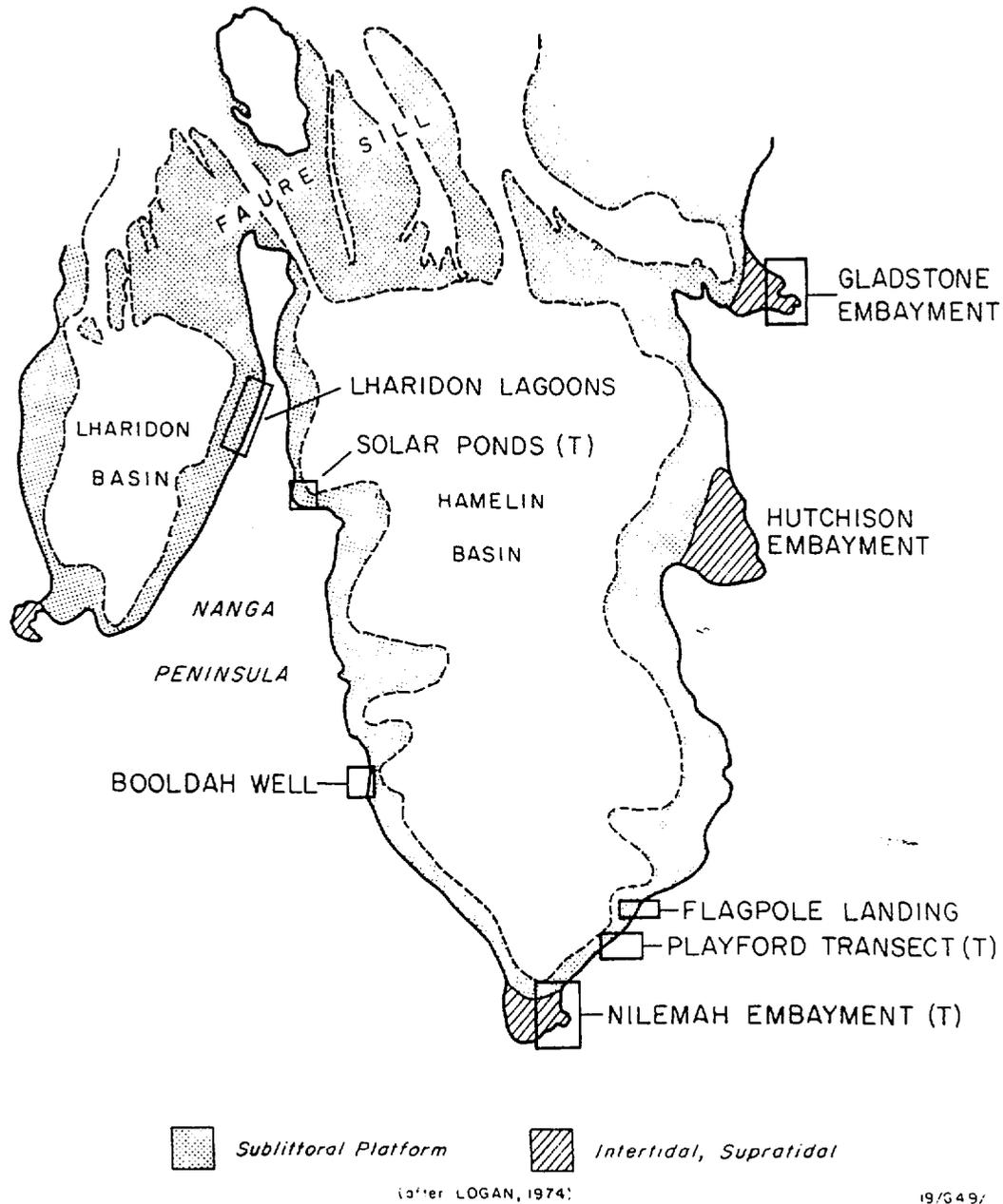


Fig 2: Groundwater sampling locations at Hamelin Pool and Lharidon Basin. Transects were established at those locations marked with a (T).

Groundwaters of Hamelin Pool and Lharidon basin have been implicated in a variety of processes occurring within the coastal environments, including the formation of the karstic collapse structures known as the Solar Ponds (P.E. Playford, pers. comm.), and the deposition of distinctive red "veneers" which coat the top surfaces of some fossil stromatolites. The most prominent result of the influence of the marine and continental groundwater systems is, however, the development of a wide variety of lithified carbonates. Carbonate precipitation and diagenesis appears to be occurring extensively at the present day in environments ranging from the freshwater dominated beach ridges to, possibly, submarine environments immediately seawards of the intertidal zone (P.N. Southgate, pers. comm.). The products of these diagenetic processes include lithified stromatolites, intertidal and supratidal beach rock and cemented coquina within beach ridges.

A hydrogeochemical investigation of groundwaters in coastal areas bordering Hamelin Pool and Lharidon Basin has been undertaken. The investigation had four main aims: (1) to establish chemical (including stable isotope) criteria which will distinguish continental from marine groundwaters within the coastal areas; (2) to identify the major chemically distinct types of groundwater entering the coastal areas; (3) to examine the chemical changes undergone by the continental groundwaters in the coastal areas as they evolve and mix with marine brines; (4) to characterize groundwaters which appear to have a major influence on the associated sediments of the coastal zone. For these purposes water samples were collected from seven hydrologically contrasting environments around Hamelin Pool and Lharidon Basin (Fig. 2) for chemical analysis and determination of their D/H, $^{18}\text{O}/^{16}\text{O}$ and $\delta^{34}\text{S}$ values. In addition, detailed sampling and piezometer measurements were carried out on transects across the peritidal zones at Nilemah Embayment and, to a lesser extent, across the area of the Solar Ponds (Fig. 2). The results of this investigation will be compared and contrasted with those of groundwater investigations of arid and semi-arid Holocene carbonate environments of the Persian Gulf and in Spencer Gulf.

PRODUCTION AND FATE OF ORGANIC CARBON IN BLUE-GREEN ALGAL (CYANOBACTERIAL) MATS

J. Bauld, L.A. Plumb, H.M. Thomas, G. Trengove.

Research activity during this quarter was limited to field work in Shark Bay and subsequent analyses of samples.

1. During November 1980, experimental studies were carried out near Flagpole Landing, Hamelin Pool, along a transect running from

the top of the intertidal zone out to the subtidal platform. All field experiments utilized $^{14}\text{CO}_2$ to measure photosynthetic activity of the various algal mats found along the transect. Preliminary investigations in this area took place in April 1978 (Bauld, J., Chambers, L.A., Skyring, G.W. 1979. Australian Journal of Marine and Freshwater Research 30:753-64).

Time-course experiments, using mats from various intertidal and subtidal locations, were carried out to determine total primary productivity and the proportion of this productivity subsequently excreted from the algal mat components as dissolved organic carbon (DOC) in comparison to that remaining in the algal biomass i.e. particulate organic carbon (POC).

The effect of salinity on POC and DOC production by intertidal tufted and subtidal gelatinous microbial mats was examined. Laboratory processing of these samples is not yet complete but indications from the raw data are that tufted mat has a broad salinity optimum similar to that observed for intertidal tufted mat at the Mambray Creek experimental site in Spencer Gulf.

Another experiment was carried out in an attempt to determine the rapidity of response of dried tufted mat which grows intertidally, to tidal inundation. Dry mat samples were soaked in Hamelin Pool sea water (littoral shelf salinity = 62-65‰) for periods varying between 0 and 14.5 h prior to a 0.5 h incubation period. Again, laboratory analyses of samples are incomplete but the data available suggest that photosynthetic activity is resumed within 30 min after wetting (- inundation) but at low levels which are maintained for several hours without a significant increase in rates.

2. A variety of microbial mat and stromatolite samples were collected from Flagpole Landing and other areas of Shark Bay, viz: Nilemah Embayment, Gladstone Embayment and Lharidon Bight, for microscopy, culture, and pigment analyses. Representative samples were sent to Professor Howard Gest, Indiana University, for cultivation of photosynthetic bacteria. These bacteria appear to be an important component of some mats.

3. Studies with M.R. Walter and Prof. W. Nicholas (ANU) on the role of meiofaunal grazing as an agent of decomposition and morphogenesis in stromatolitic mats were begun. Mat samples from the Flagpole landing experimental transect were collected and treated in various ways for later examination and

identification of the meiofauna, with particular emphasis on the nematode worm population.

4. A paper entitled "Saline lakes of the Eyre Peninsula South Australia" (by P. De Deckker, R.V. Burne, J. Bauld and J. Ferguson) was presented to the Australian Sedimentologists Group conference Dec 1-2, 1980.

SULPHUR STUDIES IN THE MODERN ENVIRONMENT

L.A. Plumb, G.W. Skyring, H.M. Thomas.

Samples for sulphate reduction rate measurements were taken at the following sites in Shark Bay, W.A., during November:

1. Playford's site (south of Flagpole Landing) - 18 samples.
2. Nilemah, Transect A - 9 samples.
3. Nilemah, Transect B - 6 samples.
4. Gladstone Embayment - 22 samples.

Laboratory processing of these samples has been completed. From the collected data sulphate reduction rates will be calculated.

1. Buried Algal Mat

The structure and textural features of algal-laminated sediments found in the tidal flat area of Gladstone Embayment, Shark Bay, W.A. have been described previously (Am. Ass. Petrol. Geol. Memoir 13), but neither this algal-rich, nor any other similar, sediment has been studied in terms of its sulphur isotopic distribution pattern. Such information is needed to assist in the interpretation of both sedimentary sulphide deposits and sulphur associated with preserved, fossil, organic matter.

In addition to those of Gladstone Embayment, sediments with a history of algal lamination to a depth of ≈ 50 cms have been found in tidal lagoons on the eastern coast of Lharidon Bight. Cores from both sites were frozen after collection and subsequently sectioned longitudinally. One portion was freeze-dried to preserve the material for detailed organic analyses and the other used for estimation of organic matter and pore water content, and for sulphide, sulphate and pyrite analyses. Preliminary results only are to hand.

2. Carbonate and Evaporitic Sediments.

Black pigmented carbonate sands and gypsum crystals from the supratidal flats at Nilemah, Hamelin Pool were examined qualitatively for sulphide content. Prolonged acid treatment released small quantities of sulphide, but the pigmentation appeared to be associated with a flocculent residue presumed to be



* R 9 0 0 8 9 0 2 *

of organic origin. Kevex analysis of this showed the presence of Fe. Examination of the black carbonate grains under the S.E.M. showed only an isolated organic structure which was possibly a mega-spore. Isolation of sulphide for isotopic analysis is planned.

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GROUNDWATERS OF HAMELIN POOL AND LCHARIDON BIGHT.

James Ferguson, L.A. Plumb, P.E. O'Brien, D. Fitzsimmons, H.M. Thomas.

Coastal areas around Hamelin Pool and Lharidon Bight contain three main types of groundwater. (1) Marine brines formed from the hypersaline seawater of Hamelin Pool and Lharidon Bight (2) Continental groundwater, which occurs partly as freshwater lenses within Pleistocene sands and coquina beach ridges. (3) Artesian groundwater which discharges from boreholes drilled to the artesian aquifer system which underlies the near-surface sands.

Much of the variation of the hydrological regime around Hamelin Pool and Lharidon Bight is related to the local topography of the coastal areas, which produces intertidal/supratidal zones varying in

breadth from about 100 metres at the Playford site south of Flagpole Landing, through about 300 metres at Flagpole Landing, to several kilometres in Nilemah, Gladstone and Hutchison Embayments (Fig. 3). In the broad tidal flats marine brines are the dominant groundwater type and they may evolve to salinities well beyond the gypsum salinity point before they encounter less saline continental groundwaters entering the supratidal zone. At the other extreme, where the supratidal zone is very narrow, continental groundwaters could intrude as far as the intertidal and sub-tidal areas.

Continental groundwater in the coastal areas occurs as freshwater lenses in the coquina beach ridges and also as considerably more saline waters in the underlying Pleistocene sands. These saline waters could be part of a regional groundwater system or they may have formed by downwards percolation of the freshwater from the overlying beach ridges. Possible exceptions to this type of groundwater regime occur at Flagpole Landing and Gladstone Embayment. At Flagpole Landing groundwater is discharging from the base of the coquina dunes at a sufficiently high rate to form extensive pools on the surface of the supratidal sediments. In contrast, at Nilemah Embayment surface groundwater is not present at the base of the dunes. This abnormally high discharge suggests that the Flagpole Landing groundwaters may contain artesian groundwater which discharges from an uncapped borehole

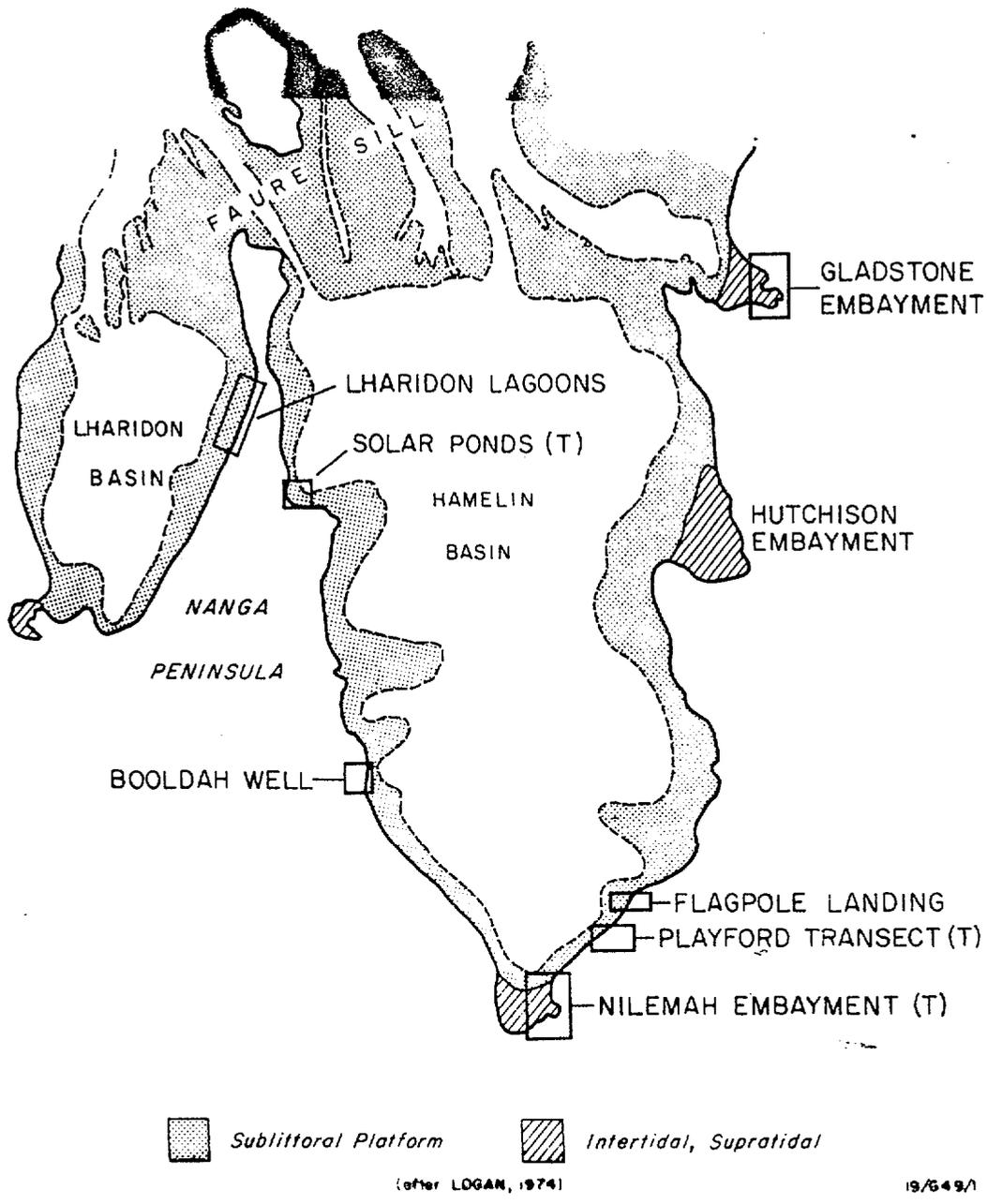


Fig. 3: Groundwater sampling locations at Hamelin Pool and Lharidon Basin. Transects were established at those locations marked with a (T).

at Hamelin Station, some 1 to 2 km inland. The groundwater regime at Gladstone Embayment may be considerably more complex than elsewhere. Preliminary observations and inspection of aerial photographs suggest that there may be extensive groundwater drainage into the high supratidal zone and saline flats immediately landward. Also, the supratidal sediments in this area are

Table 1 Chemical Parameters of Seawater and Low-salinity
 Meteoric and Artesian Continental Groundwaters,
 from Hamelin Pool.

<u>Location</u>	<u>Probable Origin</u>	<u>S^o/oo</u>	<u>pH</u>	<u>Alkalinity (meq.l⁻¹)</u>	<u>Weight ratios x 10²</u>					
					<u>Ca/Cl</u>	<u>Sr/Cl</u>	<u>Na/Cl</u>	<u>K/Cl</u>	<u>Mg/Cl</u>	<u>SO₄/Cl</u>
Well in coquina beach ridge (Booldah Well)	Meteoric	11	8.49	5.9	7.8	0.87	73	5.0	6.8	17
Borehole, Hamelin Station	Artesian	5	6.70	4.1	6.1	0.10	75	3.4	7.7	24
Hamelin Pool, Nearshore Surface water	Marine	78*	8.06	3.0	2.1	0.043	58	2.1	6.3	14

*Salinities 55-70 ‰ are typical (Hagan & Logan, 1974).

Table 2

Chemical Parameters and Probable Origins
of Groundwater Survey Samples from
Hamelin Pool and Lharidon Bay.

<u>Location</u>	<u>Probable Origin</u>	<u>S^o/oo</u>	<u>pH</u>	<u>Alkalinity (meq l⁻¹)</u>	<u>Weight Ratios x 10²</u>					
					<u>Ca/Cl</u>	<u>Sr/Cl</u>	<u>Na/Cl</u>	<u>K/Cl</u>	<u>Mg/Cl</u>	<u>SO₄/Cl</u>
Saline water beneath Coquina dunes, Nilemah Embayment (NB 20.14)	Meteoric component	33	7.58	2.9	2.8	0.18	56	2.2	5.7	12
Water from beneath lithified crust at base of dunes, Petit Lagoon (LBN)	Meteoric component	30	7.81	2.2	2.7	0.06	59	2.1	6.2	14
Water from base of dunes at Playford site (PAll)	Possible meteoric component	60	7.23	4.8	2.3	0.05	62	2.1	6.3	14
Water from base of dunes on Solar Ponds Transect (BH 31.16)	Possible meteoric component	73	7.35	2.8	2.0	0.05	59	2.1	5.9	12
Water from beneath lithified pavement at landward edge of supratidal zone, Nanga Lagoon (LBS1)	Marine	58	7.68	1.7	2.1	0.04	61	2.1	6.3	14
Water from area of high discharge at base of dunes, Flagpole Landing	Meteoric and artesian	30	7.62	3.2	3.2	0.18	64	2.6	6.0	23
Near-shore, surface seawater, Hamelin Pool	Marine	78	8.06	3.0	2.1	0.04	58	2.1	6.3	14

Evidence for a continental water component is strongest for water from beneath the dunes at Nilemah Embayment, which has high Ca/Cl, Sr/Cl ratios and is the least saline of groundwaters along a transect extending to Hamelin Pool (Figure 4). Continental water also appears to be present beneath the lithified crust at the base of the dunes at Petit Lagoon, but in a somewhat analogous environment at Nanga Lagoon the groundwater has essentially a marine composition. The origins of the groundwater at the base of the dunes at the Playford site and the Solar Ponds are not clear. The Sr/Cl ratios of the waters are about 20% higher than that of Hamelin Pool seawater, but a difference of this magnitude may not be significant.

The chemical composition of the Flagpole Landing groundwaters is particularly interesting because in some respects it is more like the saline continental waters beneath the coquina dunes at Nilemah than the artesian water of Hamelin Station borehole. This contrast is most noticeable in the Sr/Cl ratio, which is higher at the base of the dunes than it is at the inland borehole. Most likely the artesian water helps to flush saline, continental waters from the dunes, with the result that the discharged waters is of mixed predominantly saline continental water chemistry.

PRODUCTION AND FATE OF ORGANIC CARBON IN BLUE-GREEN ALGAL (CYANOBACTERIAL) MATS

J. Bauld, L.A. Plumb, H.M. Thomas, G. Trengrove

The dependence of bacterial sulphate reduction and other heterotrophic processes on cyanobacterial primary productivity is indicated by the observations that photosynthetically active mat supports higher sulphate reduction rates than does inactive mat and that the most rapid sulphate reduction rates occur immediately below the living cyanobacterial mat. Other major organic inputs appear to be lacking in the higher intertidal environment. It is in this context that the partitioning of photosynthetically fixed CO₂-carbon between cyanobacterial biomass (Particulate Organic Carbon = POC) and soluble, excreted compounds (Dissolved Organic Carbon = DOC) assumes considerable significance. While utilization of POC is delayed because of the requirement for decomposition and solubilization before becoming available as substrate, DOC provides a potential source of immediately available organic carbon for heterotrophic uptake.

The effect of salinity on cyanobacterial mat primary productivity (Σ [POC + DOC]) in intertidal environments has been examined by field experiments on a number of occasions. Artificial sea water,

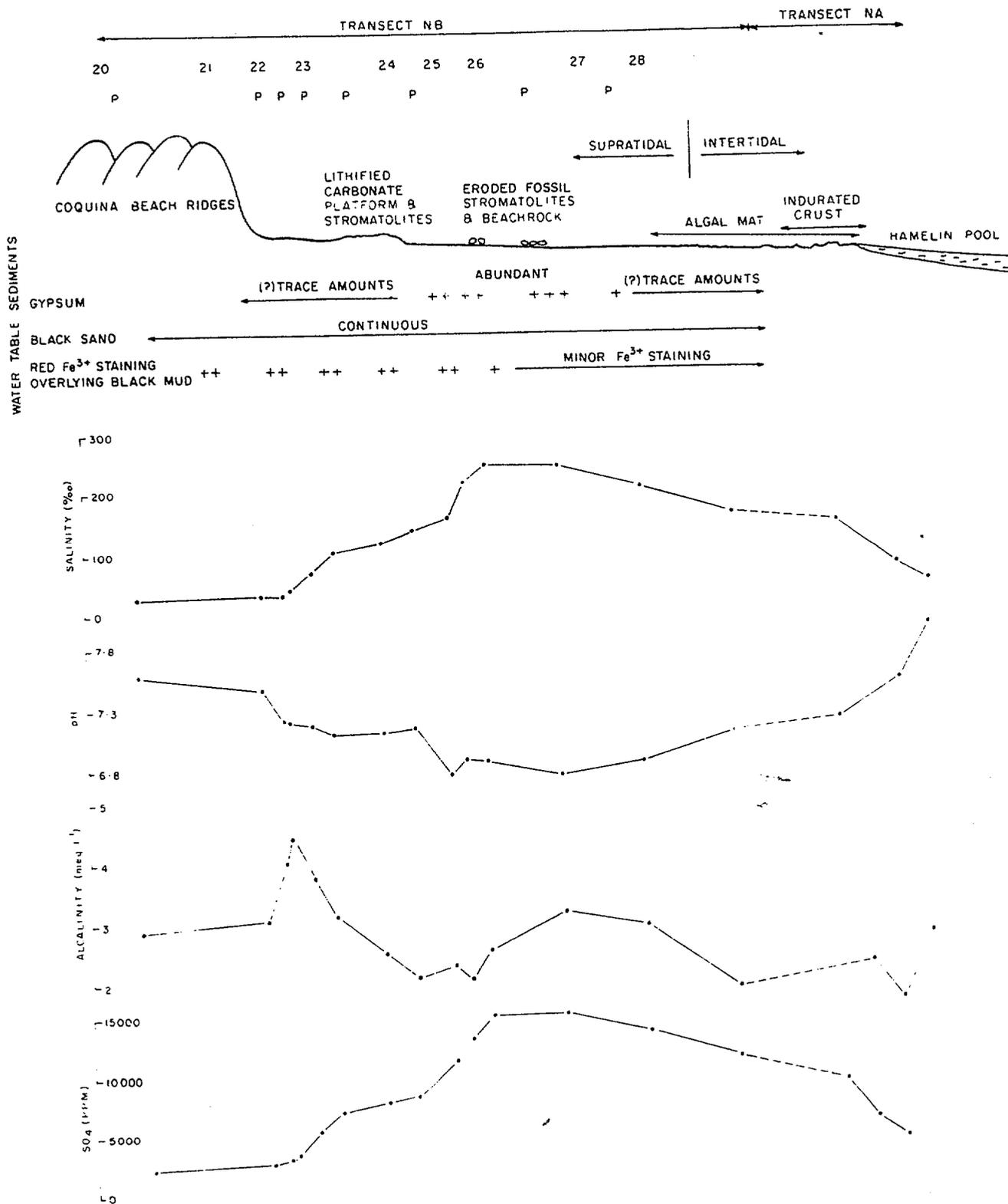


FIG. 4. CHEMICAL COMPOSITION OF GROUNDWATERS IN THE PERITIDAL ZONE OF NILEMAH EMBAYMENT

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made up to the appropriate salinities, was employed. The response of both smooth and tufted mats was generally like that shown for the POC data in Fig. 5, where a broad salinity optimum over the range 1-4 x sea water is apparent for tufted mat photosynthesis. Detectable DO^{14}C appears to be relatively constant over the salinity range tested but with a slight increase at $2^\circ/\text{‰}$.

As a proportion of the photosynthetically fixed carbon detectable DO^{14}C is greatest at the extremes of salinity examined. In the optimum range for photosynthesis ($12\text{--}89^\circ/\text{‰}$) DOC is 2-3%. When salinity falls to $2^\circ/\text{‰}$, DOC rises to 5%, and at $120^\circ/\text{‰}$ salinity DOC is 3%. These data indicate that over the range of salinities routinely encountered in the overlying water (ca. $40\text{--}100^\circ/\text{‰}$) the cyanobacteria which construct tufted mat (*Lyngbya* spp.) do not appear to be stressed and fixed carbon is well conserved. The increase in DOC at low salinities, as might be encountered during heavy but infrequent rainfall, suggests that organisms might be subject to osmotic stress which induces "leakiness".

We have so far observed one exception to the previously stated generalization of a broad salinity optimum for the intertidal cyanobacterial mats. During field work in Spencer Gulf in February, POC-DOC partitioning by smooth mat was examined at three salinities. Unlike previous experiments, $\Sigma(\text{POC}+\text{DOC})$ decreased substantially when the salinity was increased from $12\text{--}123^\circ/\text{‰}$ (Table 3). The data for $51^\circ/\text{‰}$ and $123^\circ/\text{‰}$ are consistent with previous experiments but $\Sigma(\text{POC}+\text{DOC})$ at $12^\circ/\text{‰}$ was very high. Under the stress of higher salinity ($123^\circ/\text{‰}$) detectable DO^{14}C rose to 6% but was very low at 12° salinity. So far this skewed salinity optimum remains unexplained.

Intertidal cyanobacterial mats are subjected to a fluctuating hydrological regime. Flooding on the high tide is followed by drainage and/or evaporation of any ponded sea water covering the mats which culminates in dessication. The dessicated state is terminated suddenly at the onset of tidal inundation or, possibly, rainfall. Mats may remain dry for only a few hours or for many days depending on the combined effect of tide height, and wind strength and direction.

Earlier experiments in which $\Sigma(\text{POC}+\text{DOC})$ was measured indicated that metabolic recovery of dessicated mat occurred within about 20 hours of wetting. An experiment to examine the excretion of DO^{14}C by dessicated-wetted Shark Bay tufted mat was carried out in November 1980. Unfortunately the results were inconclusive. The mat used was in poor condition and exhibited relatively low

Effect of salinity on Tufted Mat Shark Bay

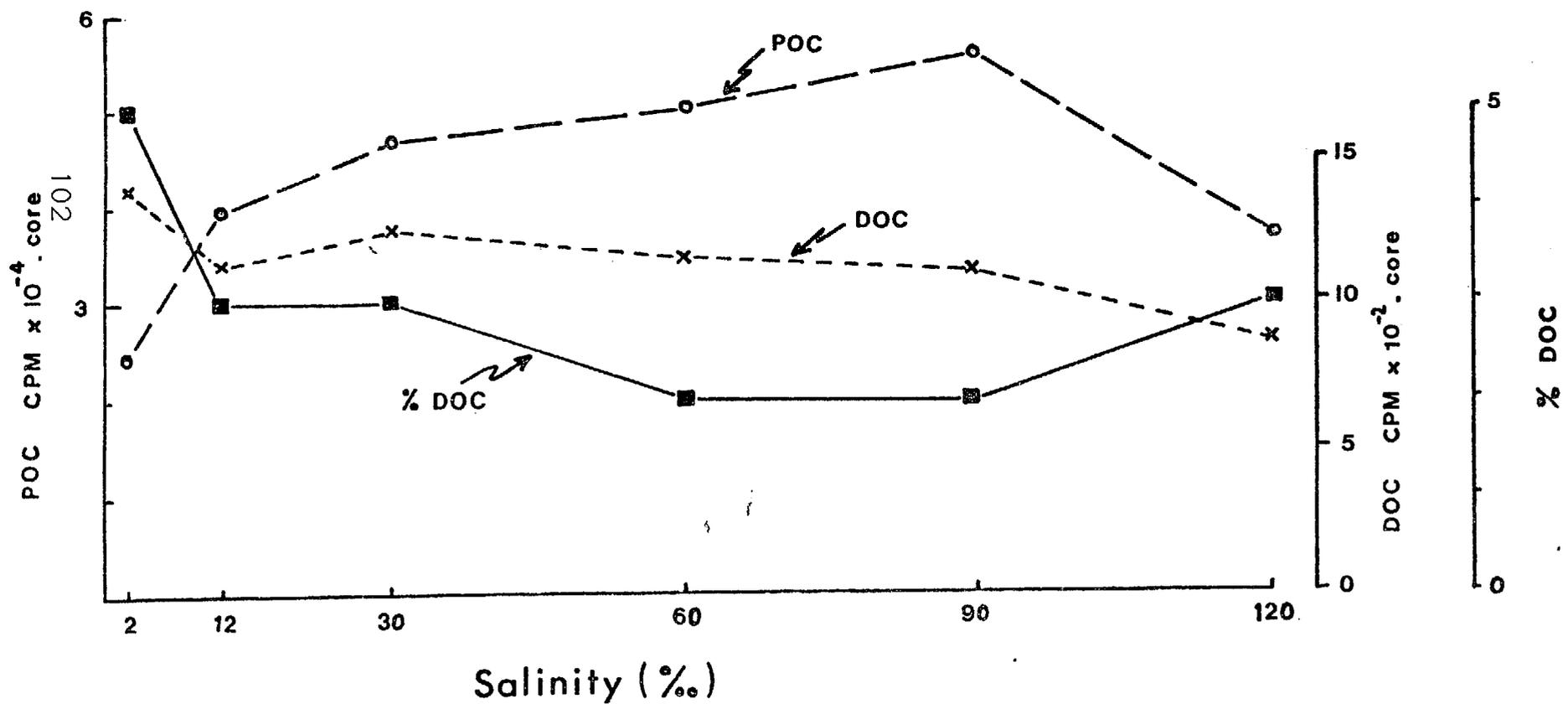


Fig. 5. The effect of salinity of tufted (*Lynghya*) mat, Hamelin pool, Shark Bay. Incubation temp., 27°C. Incubation period, 90 min. Salinity: Hamelin pool water, 68‰; ponded water, 95‰.

The mat used was in poor condition and exhibited relatively low photosynthetic activity. It did appear, however, that detectable but low photosynthetic activity resumed within about 30 minutes of wetting. $DO^{14}C$ was undetectable.

Table 3. Effect of salinity on photosynthetic $^{14}CO_2$ fixation by smooth mat and its partitioning into $PO^{14}C$ and $DO^{14}C$.

Salinity (‰)	POC*	DOC*	Σ (POC+DOC) *	$\frac{DOC}{\Sigma}$ (%)
12	216678	792	217470	0.003
51	142978	3199	146177	2.2
123	46123	2921	49044	6.0

*Counts per minute per core.

Incubation temp., 23-27°C. Incubation time, 120 mins.
Light intensity, 1200-2200 $\mu E m^{-2}s^{-1}$ (mostly 1800-2000 but fluctuating).

The process was re-examined by another field experiment in Spencer Gulf in February 1981. This time mat which had been recently dessicated, and appeared to have been in a healthy state when dessicated, was used. The results for $PO^{14}C$ are shown in Fig. 6. Recovery of photosynthetic activity was rapid commencing either instantaneously with, or within minutes of, wetting with Spencer Gulf sea water. Increase in activity was linear up to about 2 hours. After 5-10 hours there is some indication of a longer term increase in activity, possibly as a result of growth of the newly-active cyanobacteria. During this recovery period detectable $DO^{14}C$ (not shown in Fig. 6) was very low. $DO^{14}C$ reached a maximum of 0.01% of photosynthetically fixed carbon about 16 hours after wetting. At other times $DO^{14}C$ was either measurable at less than 0.01% or undetectable.

These data suggest that recovery from dessication to an active metabolic state can be characterised by efficient retention of all carbon fixed. This would be consistent with the opportunistic "lifestyle" required for effective survival and competition in the fluctuating high intertidal environment.

Recovery from desiccation
Smooth mat
Spencer Gulf

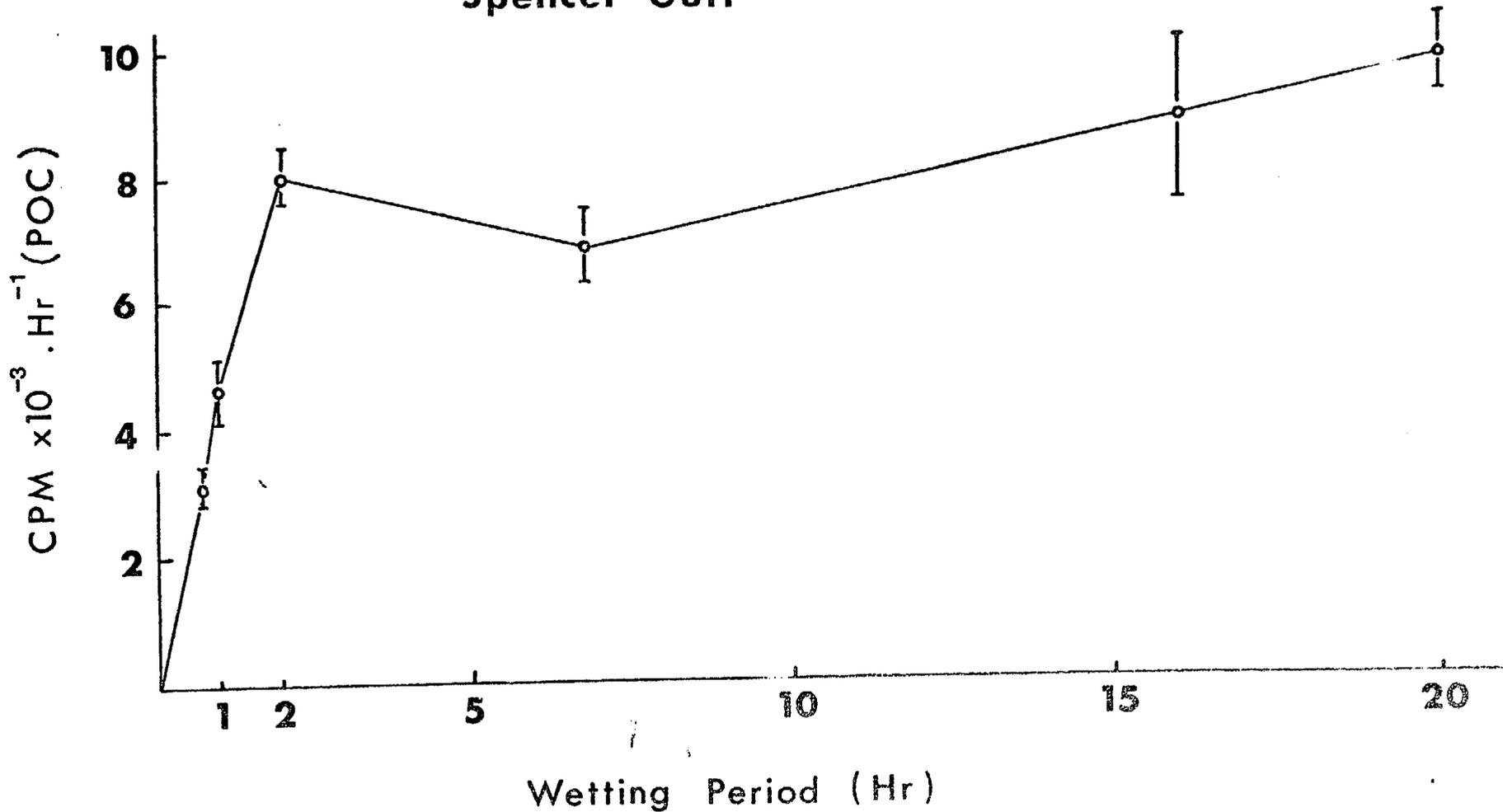


Fig. 6. Recovery of smooth mat (Spencer Gulf) from desiccation. Dry mat wetted and incubated in Spencer Gulf water of salinity 44‰. Incubation temperature, 30°C. Light intensity, 1800-2000 $\mu\text{E m}^{-2}\text{s}^{-1}$. The wetting times shown on the graph include the 30 min incubation period.

The cyanobacteria constructing smooth mat (mainly *Microcoleus* sp.) appears to be light-saturated for photosynthetic CO₂ fixation when light intensities reach 800-1000 μE m⁻²s⁻¹ (Fig. 7). Only PO¹⁴C data are shown in Fig. 7 since detectable DO¹⁴C was again very low. At about half of the light intensities examined the experimental values for DO¹⁴C were not significantly different from zero controls.

Where there was a significant difference DO¹⁴C was less than 0.005% of photosynthetically fixed carbon, except in the dark (5%). An experiment was also carried out in February with tufted mat but laboratory processing is not yet complete so we are unable to compare the two mat types with respect to light intensity. Interestingly, the proportion of DO¹⁴C excreted during dark CO₂ fixation was always much higher (5-20%) than the proportion of DO¹⁴C excreted during photosynthetic CO₂ fixation. This suggests that a different metabolic pathway operates and the possibility that the excreted compounds are qualitatively different from photosynthetically produced DOC.

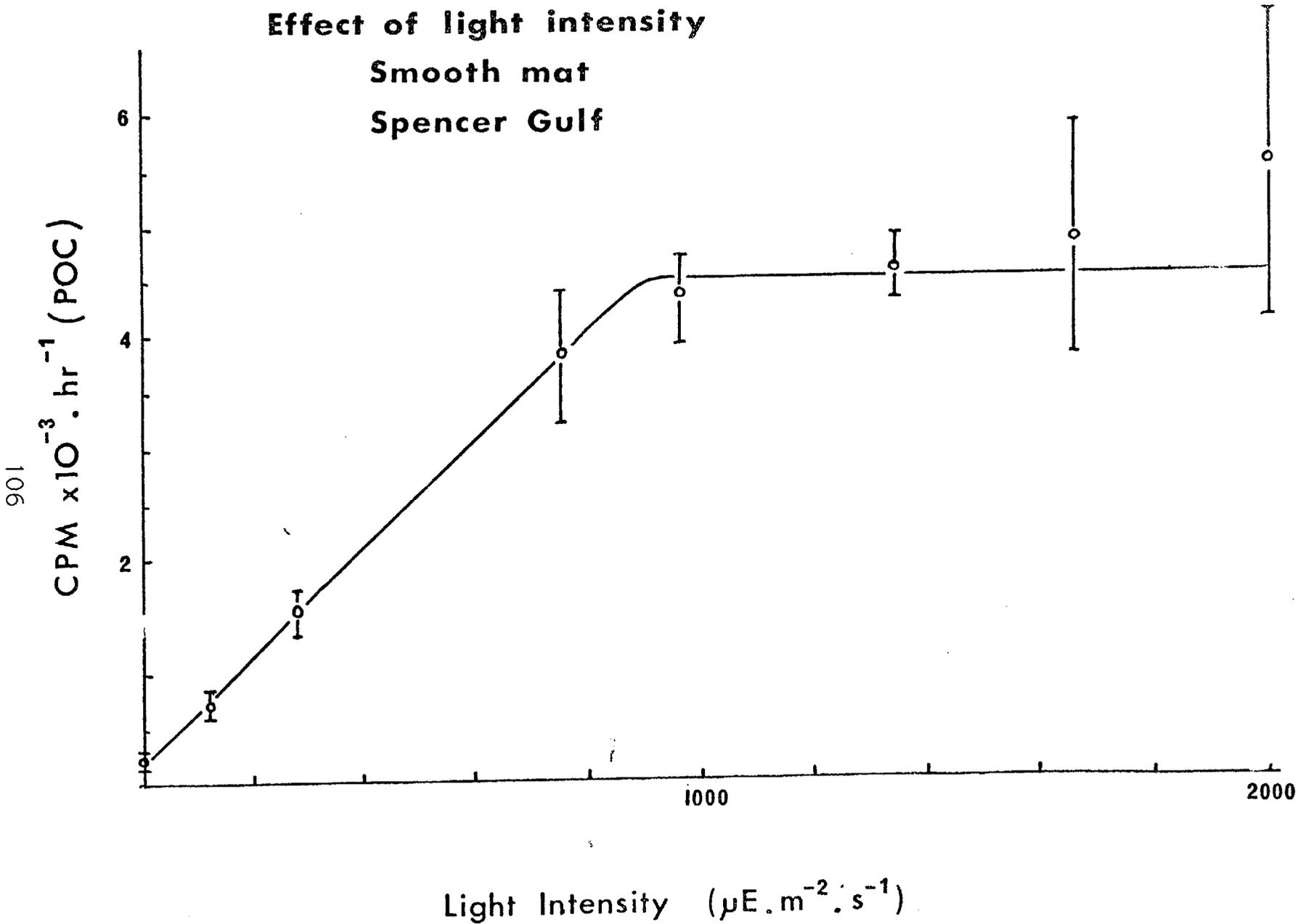


Figure 7. Effect of light intensity on photosynthesis by smooth mat, Spencer Gulf. Salinity, 43‰/oo. Incubation temperature, 28-31°C. Light intensity 2075-2200 $\mu\text{E} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. Incubation period, 80 mins.

BAAS BECKING GEOBIOLOGICAL LABORATORY
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INVESTIGATION OF MODERN SEDIMENTARY ENVIRONMENTS

The aim of studies within modern sedimentary environments is to determine the nature of those processes which, it is commonly proposed, have led to the formation and preservation of stratabound base metal sulphide mineralisation. In particular, this includes determination of the role of microorganisms in sulphate reduction and in base metal mobilisation, transportation and precipitation. In addition, the studies aim to characterise environments where these processes take place so as to aid in the identification of similar environments in the stratigraphic record.

In the current program the studies concentrate on shallow water environments in the upper parts of Spencer Gulf, but some attention is also being given to other areas. It is not expected that the environments studied are analogues of ore-forming situations. They are simply places where geobiological components of ore genesis models may be studied under natural conditions.

SULPHATE REDUCTION RATES IN SEDIMENTS FROM HAMELIN POOL, GLADSTONE EMBAYMENT AND NILEMAH EMBAYMENT (W.A.)

G.W. Skyring, L.A. Plumb, M.H. Reed.

Sulphate reduction rates in cyanobacterial mat-associated sediments of the hypersaline environments in Hamelin Pool (W.A.) were similar to those found in cyanobacterial sediments from Spencer Gulf (SA) (Bauld et al. 1979, 1980). In some intertidal locations on the shores of Hamelin Pool, there are deposits of sediment which, when forming, contain a large quantity of organic material which was dislodged from intertidal and subtidal columnar stromatolites by tidal waters. These sediments are characterized by high sulphate reduction rates and $\delta^{34}\text{S}$ ratios which suggest a partially closed system with respect to sulphate (Bauld et al. 1979).

In November 1980, sediments of the latter kind were found in the area now known as Playford's transect and in the same area as that studied by Bauld et al. (1979). These black, reducing sediments extended landwards of the high tide line and were covered by loosely packed shelly material of a prograding beach ridge. The sulphate reduction rates in the black sediments was 7.7 ± 3.9 mmol

$m^{-2}d^{-1}$ $285 \pm 169 \text{ nmol g}^{-1}d^{-1}$ ($n=12$). The sulphide concentration was $59 \pm 28 \text{ } \mu\text{mol g}^{-1}$. With respect to sulphate reduction rates in marine environments, these are quite high. The sulphate reduction rates were lower than those (1000 to $500 \text{ nmol m}^{-2}d^{-1}$) found in similar sediments by Bauld et al.1979. The sulphide concentrations were similar to those (34 to $88 \text{ } \mu\text{mol g}^{-1}$) found by Bauld et al.1979.

Table 1.
Sulphate reduction rates and other characteristics
of cyanobacterial mat associated sediments of
Gladstone Embayment (W.A.).

Sediment type	layer cm	Sulphate concentration in porewater mM	Sulphide concentration $\mu\text{mol g}^{-1}$	Sulphate reduction rates $\text{nmol g}^{-1}d^{-1}$
cyanobacterial mat, black	0-1	89	49	1880
black	1-1.5	87	45	292
grey	1.5-3.0	89	24	96
black	3-4	87	32	79
black	4-5	89	93	157
black	5-5.5	98	44	88
grey	5.5-7	81	49	20
black	7-8	78	26	3
black and grey	8-9.5	84	20	2
black and grey laminated	10-11	84	19	150
"	11-12	107	13	3
"	12-13	103	13	4
shell fragments, grey	13-15	95	9	2
laminated black and grey	15-17	95	4	0
grey	17-18	95	6	3
laminated black	18-20	101	25	3

Sulphate reduction rates were also determined for a laminated carbonate with organic matter from Gladstone Embayment. The sediments were colonized by cyanobacterial mat and were covered by tidal waters. The sulphate reduction rates, sulphide and sulphate concentrations and a brief description of 0-20cm layer is given in Table 1. The sulphate reduction rates were highest in the 0-1cm layer; below 5 cm the rates were very low. There was however a slightly higher sulphate reduction rate in the black laminated layer between 10 and 11 cm.

Although these cyanobacterial mat-associated sediments from Gladstone Embayment were not exactly analogous to those in Solar Lake (on the Sinai Peninsula) the pattern of sulphate reduction with respect to depth was very similar.

Sulphate reduction rates were also determined for sediments taken along surveyed transects at Nilemah Embayment. The groundwaters of this area were studied in detail by Ferguson et al. (see Quarterly Report, April 1980). The sulphate reduction rates for these sediments are given in Table 2 (cf. also Fig. 4, p. 25 Quarterly Report, April 1980). The rates were generally very low except for those found in the unconsolidated sediments at Station 2, Transect A. These rates (2 to 9 mmol m⁻²d⁻¹) were similar to those in sediments at Playfords' transect.

These, and previous studies in Hamelin Pool (Bauld et al. 1979, See also Quarterly Reports, July and October 1978) indicate that, in these stromatolite environments, there is translocation of large quantities of organic, stromatolite debris. In areas where this organic material collects and becomes part of the sediment, high sulphate reduction rates are observed.

GROUNDWATERS OF HAMELIN POOL AND LHARIDON BIGHT
James Ferguson, L.A. Plumb, P.E. O'Brien, D. Fitzsimmons, H.M. Thomas.

Marine and Continental Groundwaters in Peritidal Zones at Nilemah Embayment.

At Nilemah Embayment a combination of broad intertidal and supratidal flats and marine and continental groundwater input has allowed the two groundwater types to evolve through a number of chemical stages before they meet and mix near the middle of the supratidal zone. Thus, the salinity of the groundwaters increases from both the landward and seaward fringe of the area to a maximum of about 250‰. Concentrations of Mg, K and Cl in

Table 2. Sulphate reduction rates in sediments from Nilemah Embayment.

Transect	Layer cm	Sulphate reduction rate mmol m ⁻² d ⁻¹
A/2	0-5	58*
A/4	40-45	0.12*
A/7	0-5	1.5*
B/23	50-55	0.00*
B/28	40-45	0.03*

*the mean (x) of 3 determinations

the groundwaters are linearly related to salinity, which indicates that reactions involving these elements do not occur to a major extent within the tidal sediments. In contrast, concentrations of Ca, Sr, SO₄, alkalinity and the minor ions NO₂, NO₃ and silicate appear to be strongly influenced by inorganic and biological processes.

When seawater is concentrated by evaporation a small quantity of aragonite is precipitated and then at salinities about 4 x SW, gypsum starts to precipitate. This sequence occurs in surface seawater samples evaporating in tidal ponds in the Hamelin Pool and Lharidon Bight and, in these areas, gypsum precipitation starts at salinities close to the predicted value. The Ca and SO₄ concentrations in the incoming continental groundwaters at Nilemah are sufficiently close to those of normal seawater for their predicted gypsum precipitation point to be close to that of normal seawater. However, when the actual Ca and SO₄ concentrations in groundwaters along the Nilemah transect are compared to those predicted for evaporating seawater it becomes apparent that there are major discrepancies (Figure 4).

These discrepancies are of two types: (1) areas along the transect where Ca and SO₄ are lost from the waters in nearly equivalent proportions, but the $a_{Ca^{2+}} \times a_{SO_4^{2-}}$ product is below that necessary for saturation with respect to gypsum (A + A', Figure 4), and (2) areas where the waters have acquired excess SO₄ but not an equivalent excess of Ca (B and B', Figure 4). At present, the processes involved are not definitely known, but possible explanations can be given.

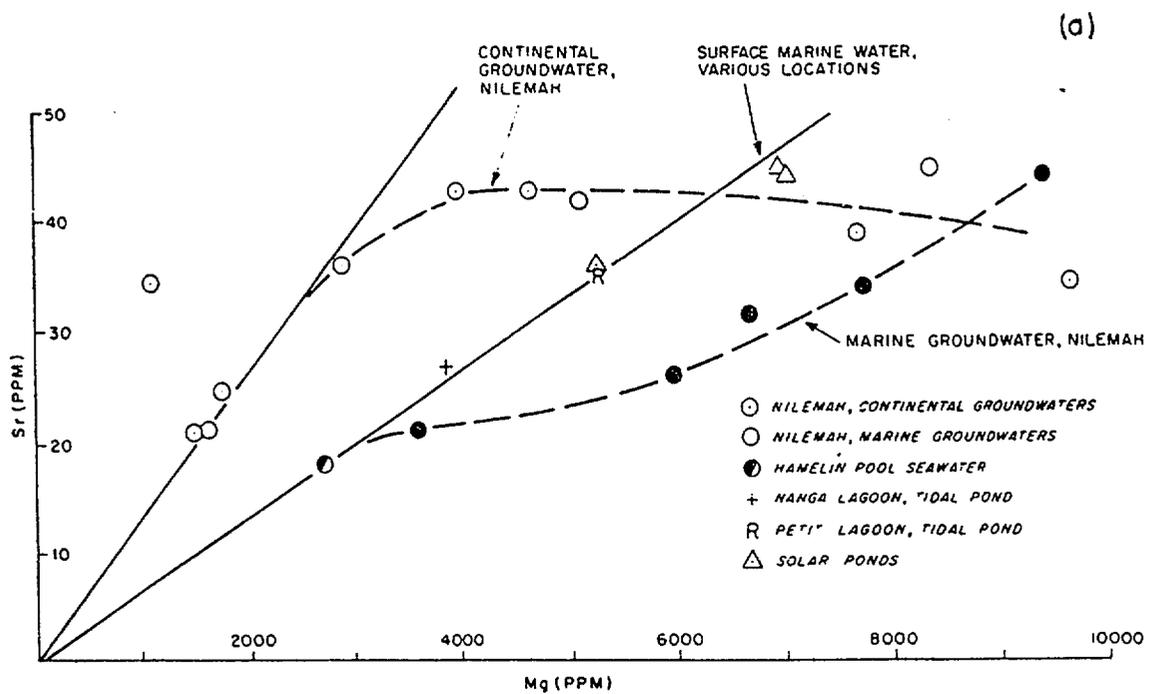
The broad area of high SO_4 concentrations at B¹ corresponds approximately to the area where the sediments contain large quantities of gypsum. Presumably, the high SO_4 concentrations result from dissolution of sedimentary gypsum when the waters become temporarily undersaturated with respect to

gypsum because of an influx of tidal or continental floodwater. The lack of an equivalent increase in Ca may result from the precipitation of aragonite. However, precipitation of the amount of aragonite involved seems to require that the carbonate alkalinity available in concentrated Hamelin Pool seawater be supplemented by alkalinity generated within the sediments by, for example, bacterial sulphate reduction. A petrological examination of the gypsiferous sediments to determine if aragonite cement is present has not yet been made.

The approximately equivalent decrease of Ca and SO_4 in zone A suggests that gypsum has precipitated from the groundwaters at this location. Most likely the groundwater chemistry reflects a period when the groundwaters were more saline. This period could have been followed by an influx of lower salinity, continental water, which at the time of sampling had not had time to re-equilibrate with gypsum in the sediments. In interstitial waters of sabkhas of the Persian Gulf gypsum precipitates at about 3.4 x SW salinity, which is lower than the value of 4 found for the surface marine brines of Hamelin Pool and Lharidon Bight, but is higher than the lowest value of about 2.5 x SW at which Ca and SO_4 concentrations decrease in the Nilemah groundwaters.

The apparent equilibration of the groundwaters in zone B with gypsum in the sediments and the disequilibrium at zone A may result from a combination of greater quantities of gypsum and smaller fluctuations in groundwater composition in zone B compared to those at the landward (and seaward) ends of the transect.

At the seaward end of the transect Ca and SO_4 are also being lost from the groundwaters at abnormally low-salinities (Figure 4), but the Sr concentrations in the groundwaters indicate that both gypsum and aragonite are precipitating in this area. The continental groundwaters at the landward end of the transect have high Sr contents, which increase linearly with increasing salinity to about salinity 3.1 x SW (Figure 5). The $\text{mSr}^{2+} \times \text{mSO}_4^{2-}$ product at this point is about $38 \times 10^{-2} \text{ moles}^2 \text{ l}^{-2}$, which is in agreement with a value of $35 \times 10^{-2} \text{ moles}^2 \text{ l}^{-2}$, which was determined for marine waters in sabkhas at Abu Dhabi. In both cases it appears



CHANGES IN Sr WITH INCREASING SALINITY FOR CONTINENTAL AND MARINE GROUNDWATERS FROM NILEMAH, AND FOR SURFACE MARINE WATERS FROM VARIOUS LOCATIONS

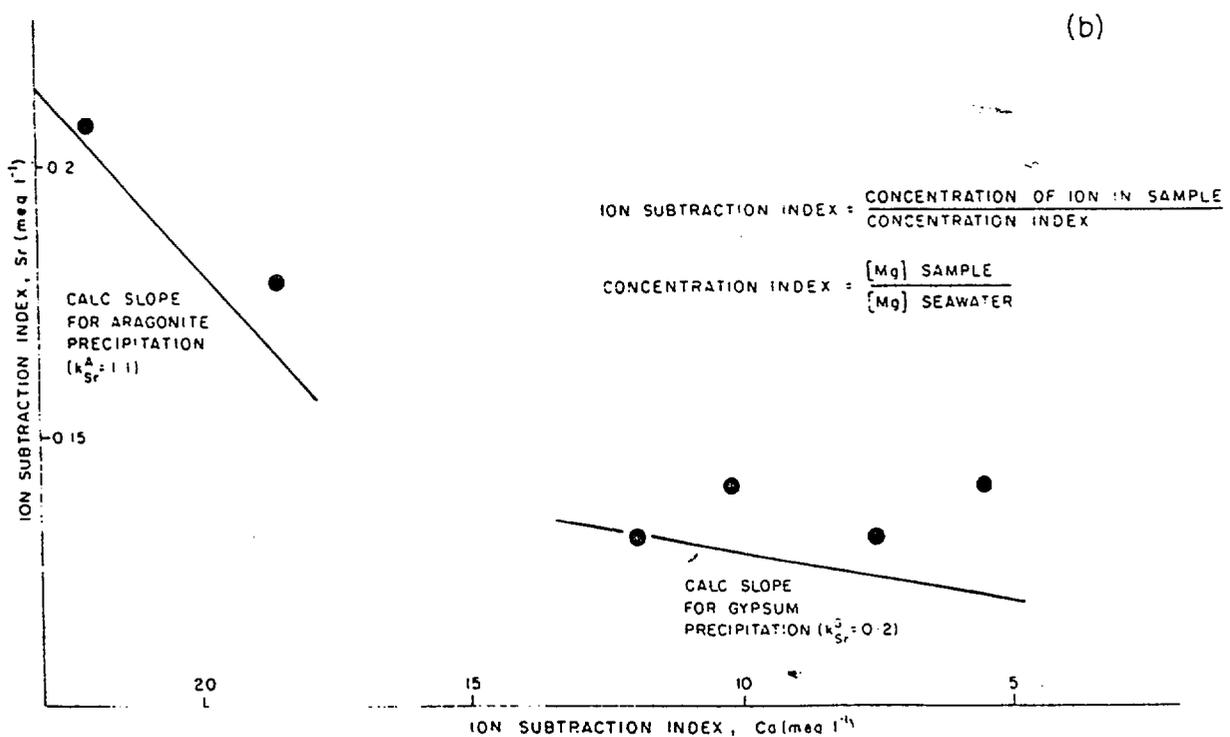


FIG. 5 Ca AND Sr ION SUBTRACTION INDICES FOR MARINE GROUNDWATERS FROM NILEMAH

that the Sr concentration is limited by the solubility of celestite. At the marine end of the Nilemah transect there is an abrupt drop in the Sr concentration at much lower $m\text{Sr}^{2+} \times m\text{SO}_4^{2-}$ values (Figure 5), which is unlikely to be a result of precipitation of celestite or co-precipitation of Sr with gypsum ($k_{\text{Sr}}^{\text{G}} \sim 0.2$; Butler, 1969). Ion subtraction data in Figure 5 indicate that the magnitude of the Sr loss is comparable to, although less than that expected if all of the Ca was being precipitated as aragonite ($K_{\text{Sr}}^{\text{A}} \sim 1.1$; Kinsman, 1969). As in zone B, this would require much greater quantities of carbonate than are available from Hamelin Pool seawater.

PRODUCTION AND FATE OF ORGANIC CARBON IN BLUE-GREEN ALGAL (CYANOBACTERIAL) MATS.

J. Bauld, L.A. Plumb, H.M. Thomas, G. Trengove.

A two-day visit was made to Roche Algal Biotechnology, Sydney to confer with Dr. L. Borowitzka and Mr. M. McKay on the most suitable techniques for laboratory culture of cyanobacteria from Spencer Gulf and Shark Bay mats. Since then we have been improving and refining media and conditions for growth of the cyanobacteria on hand.

In addition to laboratory culture of cyanobacteria time has been spent on sample processing, data compilation and analyses and manuscript preparation.

BAAS BECKING GEOBIOLOGICAL LABORATORY
 QUARTERLY REPORT
 NOVEMBER, 1981

ISOTOPE STUDIES IN THE MODERN ENVIRONMENT

R.V. Burne, James Ferguson, D. Fitzsimmons, P.E. O'Brien, L.A. Plumb, M. Thomas.

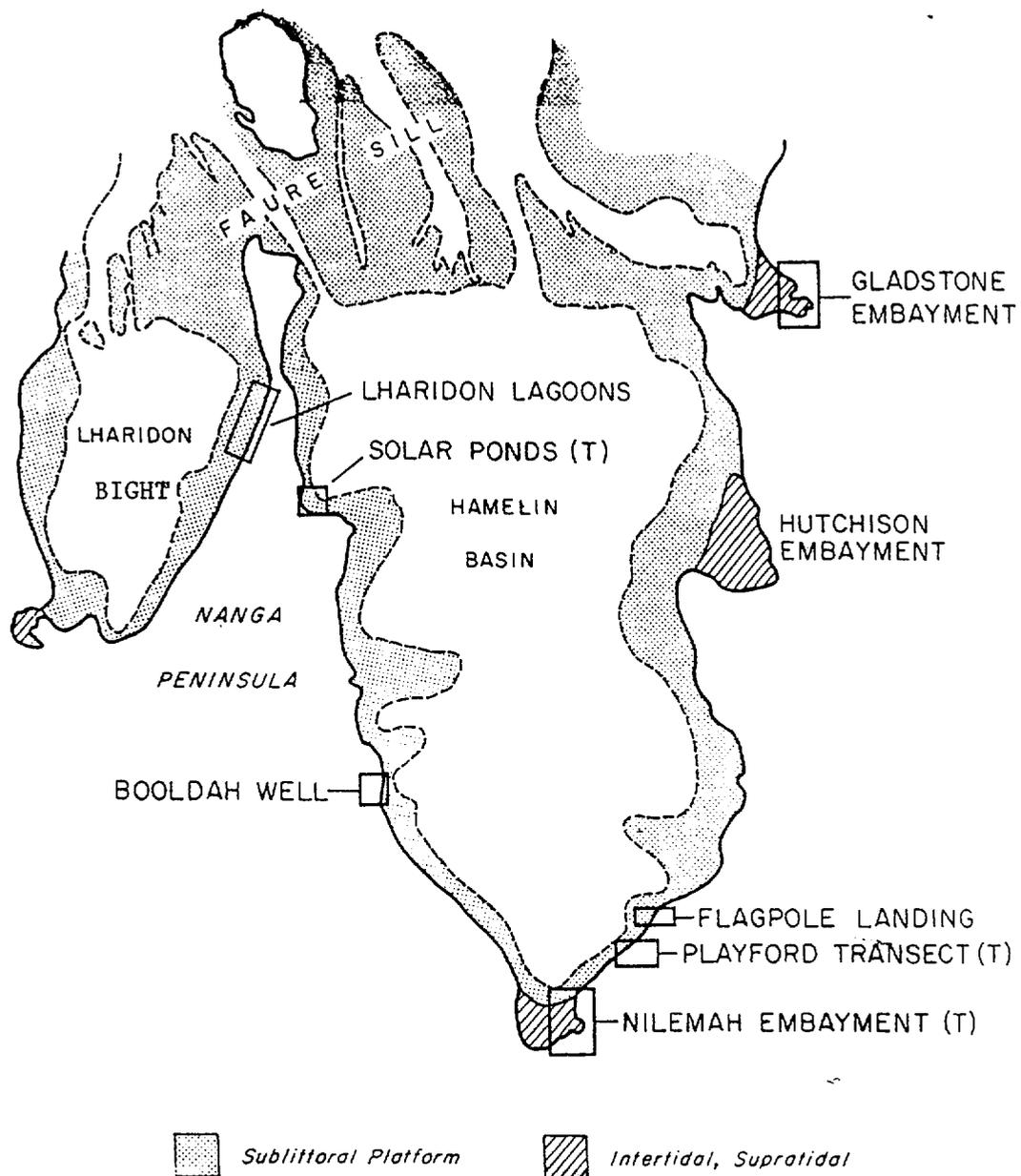
SULPHIDES IN TIDAL CHANNELS, SHARK BAY, W.A.

Sulphur isotope distribution in algal laminated sediments from tidal channels at Shark Bay, W.A. has been studied. The sampling sites are in tidal flats marginal to Lharidon Bight and Gladstone Embayment (see Fig. 1). The former site is subject to intermittent desiccation but at the other location this is unlikely since the channel has a direct connection with the South Gladstone Embayment. The sediments there were covered by 20 to 30 cm of water when samples were taken, while those in Lharidon Bight were topped by halite crystals.

Sulphide concentrations and isotope values for both sediments are given in Tables 1 and 2. The range of values (-17.2 to -31.8) is equivalent to fractionations of 1.038 to 1.052 relative to seawater sulphate. This is not distinguishable from fractionations in other

TABLE 1. Sulphide concentrations and isotope distributions in channel sediments of tidal flat environments at Shark Bay, W.A.

Depth Interval cm	Acid Labile Sulphide			
	Lharidon Bight		Gladstone Embayment	
	mg g ⁻¹ (dry wt)	δ ³⁴ S‰	mg g ⁻¹ (dry wt)	δ ³⁴ S‰
0 - 5	0.47	-17.2	2.4	-19.7
5 - 10	0.70	-19	0.93	-21.3
10 - 15	0.48	-24.1	0.15	-25.1
15 - 20	0.19	-23.4	0.14	-24.9
20 - 25	0.09	-25.3	0.20	-27.2
25 - 30	0.10	-25.1	0.06	-25.5
30 - 35	0.17	-27.6		
35 - 40	0.10	-32		
40 - 50	0.08	-29.4		



after LOGAN, 1974

9-349

Fig. 1: Groundwater sampling locations at Hamelin Pool and Lharidon Bight. Transects were established at those locations marked with a (T).

TABLE 2. Sulphur isotope distribution for zinc-reducible sulphide from sediments in tidal channels at Lharidon Bight and Gladstone Embayment, Shark Bay, Western Australia.

Site	Depth interval cm	$\delta^{34}\text{S}^{\circ}/\text{‰}$
Lharidon Bight	0 - 20	-25.4
	20 - 35	-27.7
	40 - 55	-28.8
Gladstone Embayment	0 - 10	-23.5
	10 - 15	
	20 - 25	-25.4
	25 - 31	-28.0

marine environments. Minute quantities of zinc-reducible sulphide (presumably pyrite) were found and the isotope distribution was generally ^{32}S enriched compared to the acid labile sulphide. This relationship is common in sediments but has most often been explained in terms of the acid labile sulphide being produced most recently in a system closed to sulphate. The trend of increasing ^{32}S content with depth in these sediments argues against a closed system. The same type of pattern has been observed in sediments of the Santa Catalina Basin and the Bali Trough over much greater depths.

ISOTOPE STUDIES IN SHARK BAY, W.A.

Gypsum, groundwater sulphate and sulphides have been analysed for sulphur isotope distribution and are detailed in Table 3. The sulphate values show a strong marine influence at both Nilemah and the Solar Ponds (Fig. 1). Even birridas (salt lakes) 1-2 km from the present shore-line have gypsum which is of marine origin. Along the Nilemah transect (see Fig. 2) there is an indication of lighter (e.g. +18.5 $^{\circ}/\text{‰}$) continental sulphate in samples near the beach ridges. These samples also have lower salinities consistent with a continental origin. Fluctuation of the values across the supratidal plain may indicate a zone in which either continental or

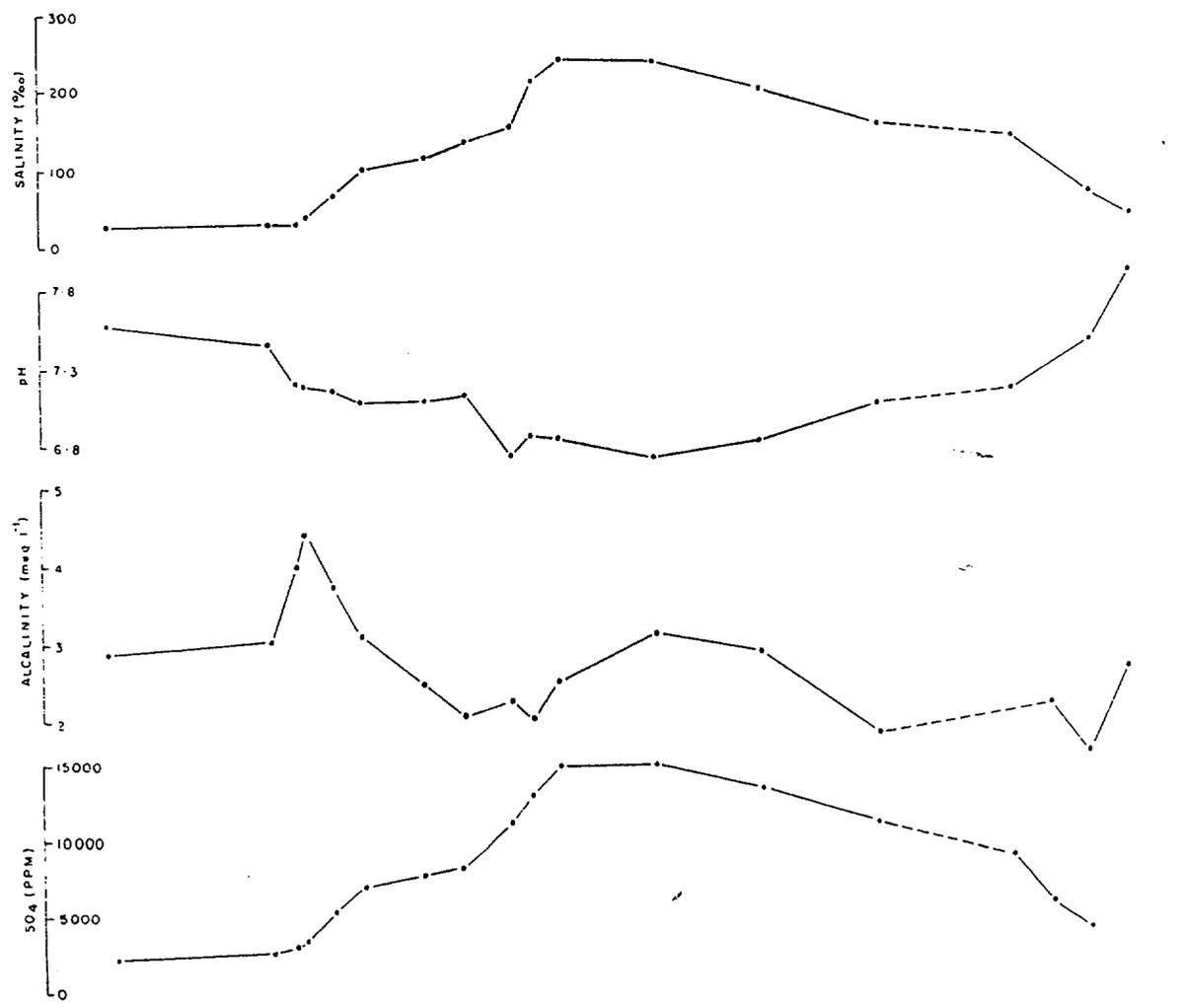
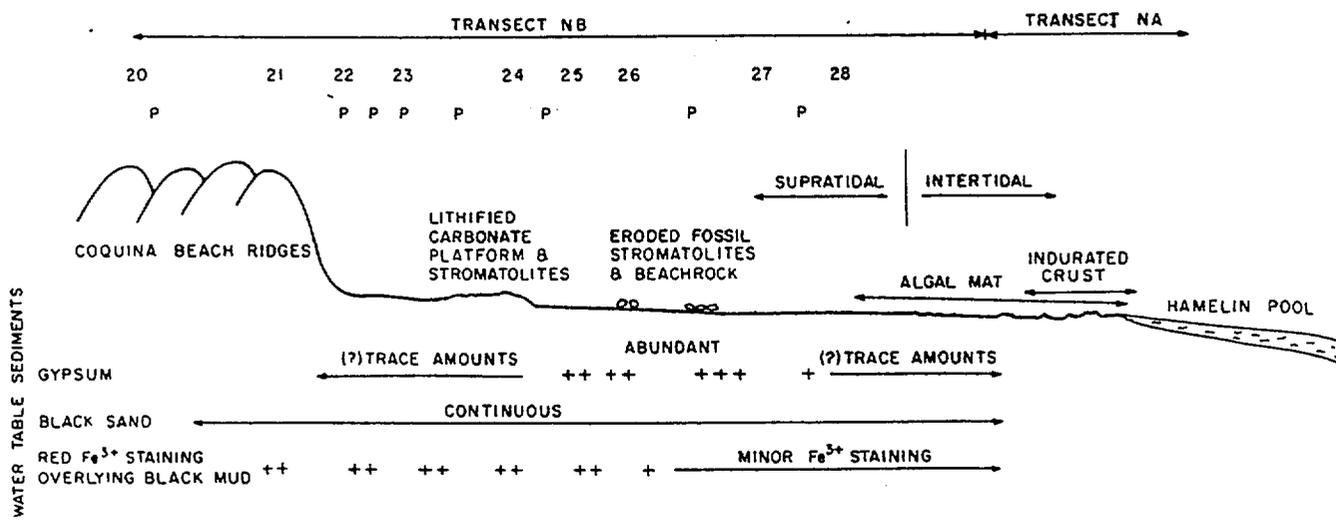


FIG. 2. CHEMICAL COMPOSITION OF GROUNDWATERS IN THE PERITIDAL ZONE OF NILEMAH EMBAYMENT

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TABLE 3. SULPHUR ISOTOPE DATA FOR GYPSUM, GROUNDWATER SULPHATE, AND SULPHIDE SAMPLES FROM SHARK BAY, W.A.

	GYPSUM	$\delta^{34}\text{S} \text{ ‰}$
Nilemah Transect	A 5	+22.3
	A 6	+22.2
Solar Pond		+22.4
Inland Birrida	1	+22.1
	2	+22.5
	3	+22.2

GROUNDWATER
SULPHATE

Nilemah Transect	B	20.14	+18.5
		21 (5)	+20.3
		22 - 6	+20.5
		22	+20.0
		22.15	+18.9
		27	+18.9
		23.33	+20.5
		24 - 12	+19.9
		25	+20.0
		25(5)	+20.9
Solar Pond	1		+21.8
	2		+22.0
	3		+21.6
Solar Pond Transect		31.6	+20.8
		33.16	+21.4
		24.47	+21.4
Playfords Transect			+23.4
Flagpole Landing			+17.9
Bore Water			+13.6

SULPHIDES

Nilemah Transect	A2	Acid	-14.2
		Labile	
		Zinc	-17.2
Nilemah Transect	A4	Reducible	
		Acid	-26.6
		Labile	
		Zinc	-32.2
	B23		
	B28		
		Reducible	

marine influence has dominated at different times. Deuterium and oxygen isotope analyses of the groundwaters are being undertaken and should help the interpretation. A different situation exists at Flagpole Landing where there is a noticeable groundwater seepage at the base of the dunes. The sulphate in this has a value of $+17.9\text{‰}$ and is thought to be influenced by the nearby flow of borewater in which sulphate is $+13.6\text{‰}$.

Dark coloured sediments below the water table in the Nilemah supratidal plain (Table 3 : A4, B23, B28) were initially thought to be principally sulphide, but acidification yielded only minor quantities ($6\text{--}7\ \mu\text{gS}^{\text{=}}/\text{g}$ wet sediment) and a black amorphous residue. In the low intertidal sediments (Nilemah Transect A2) however, sulphide concentrations were of the order $500\text{gS}^{\text{=}}/\text{g}$ wet sediment. The sulphides from the supratidal sediments are more ^{32}S enriched than the more abundant intertidal material (-26.6 and -32.2 versus -14.2 and -17.2). Relative to seawater sulphate these values represent the upper and lower ranges of fractionation in marine environments.

CYANOBACTERIAL ORGANIC MATTER - PRESERVATION OR DECOMPOSITION?

J. Bauld.

Cyanobacterial mats are one of the most productive photosynthetic systems in modern aquatic environments. The organic carbon resulting from their photosynthetic activities provides not only a carbon and energy source for biogenic H_2S formation and subsequent metal sulphide deposition, but also a potential source material for kerogen and hydrocarbon generation. Cyanobacteria were one of the major sources of organic matter before the evolution of land plants in the mid-Palaeozoic. Consideration of the microbiological and environmental constraints on the occurrence, primary productivity, decomposition, and preservation potential of modern cyanobacterial mats suggest the following: bacterial decomposition to CO_2 and CH_4 will proceed at salinities up to halite saturation; substantial preservation will not take place except at salinities beyond this; anoxic conditions alone will not prevent decomposition of cyanobacterial mat organic carbon; water activity is probably one of the most important factors limiting decomposition.

Mat constructing cyanobacteria appear well-adapted to environments of fluctuating salinity and periodic desiccation. A model which accommodates the environmental limits imposed by the physiology of cyanobacterial decomposers is consistent with

the shallow, fluctuating saline lake paleoenvironment invoked by others to explain some petroleum source rock and oil shale occurrences.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
JANUARY, 1982

BIOLOGY OF SULPHATE REDUCTION IN INTERTIDAL
SEDIMENTS

P.A. Trudinger, L.E. Hogle.

Background: Part of the current Baas Becking research program deals with the interrelationships between the carbon and sulphur cycles in marine sediments and the influence of sulphate reduction on sulphide mineralization and preservation of organic matter.

To date most of our knowledge of the ecology and physiology of microbial sulphate reduction has been derived from studies of a relatively few species of sulphate-reducing bacteria belonging to the genus *Desulfovibrio*. These organisms utilize only a few simple organic compounds which are generally incompletely oxidized. On the other hand studies in this laboratory and overseas indicate that sulphate reduction accounts for the decomposition of a large proportion of organic matter in marine sediments.

Recently several new genera of sulphate reducers have been discovered, members of which are capable of utilizing a wide range of organic carbon compounds including long chain fatty acids.

The purpose of this project is to reexamine the ecology of bacterial sulphate reduction in marine sediments in the light of this new information. The work will complement that of other laboratory personnel who are studying the fate of organic matter produced by cyanobacterial photosynthesis.

Progress

The initial approach is to look for enhanced sulphide production by sedimentary material in response to supplements of specific organic molecules. At a later stage the fate of the organic molecules will be examined.

Initial experiments have been set up with sedimentary material from Shark Bay, Spencer Gulf and Moretøn Bay.

To date, positive sulphide responses have been observed with supplements of the following acids:

Acetic (C₂), lactic (C₃), propionate (C₃), lauric (C₁₂), palmitic (C₁₆), stearic (C₁₈), and benzoic (aromatic).

Table 1. The isotopic compositions of Shark Bay Waters

LOCATION	δD	$\delta^{18}O$
NILEMAH TRANSECT		
LANDWARD	-24	-1.1
	-4	+0.4
	-5	+0.8
	-8	+0.9
	-11	+2.2
	-6	+4.0
	0	+3.8
	-7	+4.3
	-3	+2.9
SEAWARD	+6	+4.3
SOLAR PONDS TRANSECT		
LANDWARD	-17	+0.7
	+7	+3.3
	+11	+3.2
SEAWARD	+11	+3.8
SOLAR PONDS	+24, +27	+7.4, +8.1
PLAYFORD SITE	-1	+3.2
FLAGPOLE LANDING	-23	-1.5
BOOLAGOORDA BOREHEAD	-43	-4.8

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
JULY, 1982

INTRODUCTION

Considerable effort is being expended on exploring the usefulness of Shark Bay and various saline lakes as models for the development of both source and reservoir rocks on the Earth as it was before the evolution of land plants. Sedimentological, microbiological and geochemical aspects of that work are making steady progress.

STUDIES IN MODERN ENVIRONMENTS AND THE LABORATORY

SHARK BAY SEDIMENTOLOGY

R.V. Burne and M. Tratt.

Three weeks in June were spent undertaking field studies of stromatolites and peritidal sedimentation around Hamelin Pool, Shark Bay. The Australian Survey Office undertook detailed levelling along study transects, and these observations will be compared with tidal records in a similar fashion to the methods used in the study of Spencer Gulf. Special consideration was given to studies of Nilemah Embayment, and to areas of stromatolite colonisation at Carbla Point. In both cases the effects of Holocene sea level fall were seen to be of major importance. Preliminary indications are that the Holocene high sea level stand at Nilemah Embayment inundated a more extensive area than has formerly been suggested, and that some of the limestones previously considered to be Pleistocene calcretes may be beach rocks and coniatolites which formed at a higher Holocene sea level.

The stromatolite belts of the exposed shorelines are able to colonise the sandy high-energy substrate because of the extensive carbonate cementation that takes place in these high salinity sub-tidal settings. Under less saline conditions, high substrate mobility would prevent stromatolite accretion. The high organic productivity of the peritidal cyanobacteria leads to large amounts of organic detritus being produced, some of which is transported into the high intertidal zone where it may accumulate as a thick rubbery deposit which becomes buried beneath a prograding carbonate shell ridge.

This juxtaposition between an excellent potential petroleum source rock, and an overlying potential reservoir lithology may

represent a facies model of considerable importance and ready application to petroleum exploration.

GROUNDWATER INVESTIGATIONS AT NILEMAH EMBAYMENT, SHARK BAY.

James Ferguson, L.A. Plumb and R.V. Burne.

Water table levels along an accurately surveyed transect at Nilemah Embayment (transect NB) are now available for a 6-day period in mid-winter preceded by heavy rain, a 7-day period in late spring and one day in mid-summer, both of which followed almost dry conditions (Table 1).

Transect NB extends from a Holocene beach ridge across an area of the supratidal zone 100 metres wide which is bordered on its seaward side by a platform of Holocene beach rock. Seaward of this platform the transect continues from the high intertidal zone to the mid-intertidal zone, some 200 metres away (Fig. 1).

Water table levels along the transect slope towards the sea, indicating a net flow of relatively low salinity water from beneath the dunes across the supratidal zone and into the intertidal zone. On two occasions during the spring sampling period, this slope was reversed at the seaward end of the transect, presumably because of the residual influence of seawater from high tides. Similar reversals in slope at high tides have been observed in a number of United States Pacific coast beaches.

The limited data on water levels below the Holocene beach ridge indicate that the water table does not parallel the topography of the ridge, as has been observed for certain dunes in arid regions. It is, however, consistent with observations on the Pacific beach dunes where no rise in the water table under the crest of the dunes was observed, although in some areas there had been continuous rainfall for the preceding week.

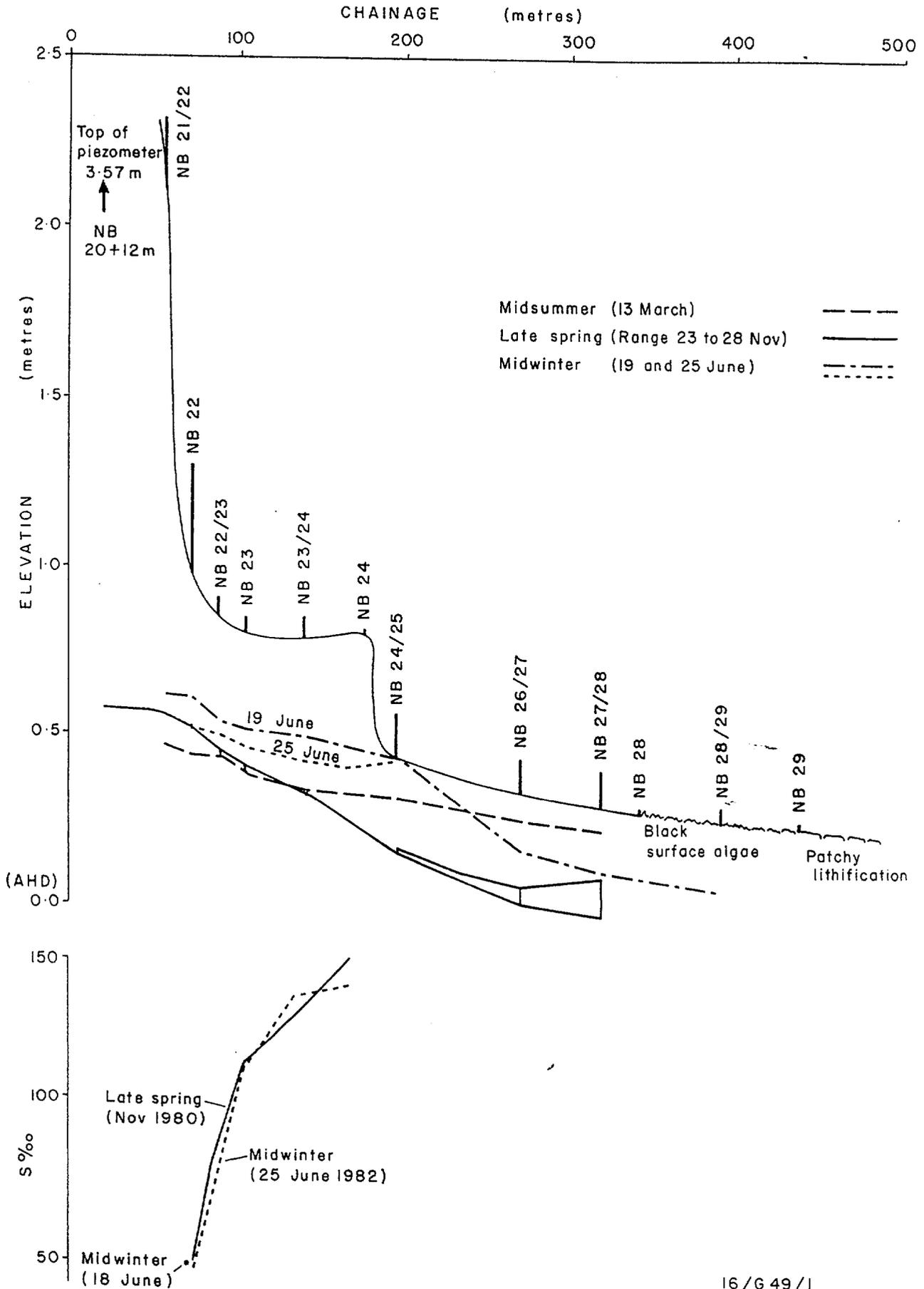
At the landward end of the Nilemah transect the groundwater levels show the expected seasonal differences being lowest in the summer, intermediate in spring and highest in the winter. The winter high was relatively short-lived and over a 6-day period the water table dropped to a level close to that observed in late spring. In the supratidal flat the decline in the winter high was slower, probably because of the lower permeability of the sediments in this area. In the supratidal/high intertidal zone the high level of the water table during the summer was unexpected, because tides are generally lower at this time of year.

Table 1 Summary of Temperature and Rainfall Data
 During the Months of Field Investigations
 at Hamelin Pool 1980 - 1982
 (measurements at Nanga)

	T ^o C	Rainfall
<u>Mid-Summer (March 1981)</u>		
Average Max.	31.7	
Range Max.	26 to 42	Nil
Average Min.	20.8	
Range Min.	16 to 27	
<u>Late Spring (November 1980)</u>		
Average Max.	25.5	0.4mm on 25th
Range Max.	23 to 30	
Average Min.	17.5	
Range Min.	15 to 20	
<u>Mid-Winter (June 1982)</u>		
Average Max.	21.9	20mm on 8th
Range Max.	19 to 27	4mm on 13th
		16mm on 14th
		2mm on 16th
		<hr/> 42mm total
		(+29mm on 29th)

Despite the seasonally different water table levels across the supratidal zone the salinity of the groundwater changed little from mid-winter to late spring. Data from elsewhere in Nilemah Embayment tidal flats indicate that at some locations there is a significant vertical salinity gradient in the sediments - the lowest salinity waters occurring in the topmost sediments. Even if vertical salinity differences were present at Nilemah NB transect, they may have been obscured by the groundwater sampling techniques, which tapped groundwaters over a depth of about 0.5 metres below the water table. If the less saline water was only a small proportion of the water in the top 0.5 metres then the "average" salinity of this water would not differ greatly from that in dryer seasons, which is, in fact, observed.

Fig. 1



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BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
OCTOBER, 1982

STUDIES IN MODERN ENVIRONMENTS AND THE LABORATORY.

ISOTOPE STUDIES IN THE MODERN ENVIRONMENT

L.A. Plumb, J. Ferguson.

NILEMAH TRANSECT, SHARK BAY

The ion chemistry of the groundwater in peritidal zones at Nilemah Embayment (August 1981, quarterly rept.) indicated a complex interaction between continental and marine derived brines, and sulphur isotope (November 1981, quarterly rept) and deuterium and oxygen isotope (January 1982, quarterly rept.) analyses were in general agreement. The ion chemistry alone does not permit a clear differentiation of continental or marine groundwaters, but does indicate different zones (I-IV) which are related to the topography (Fig. 1). Zone I lies beneath the Holocene beach ridge, and the groundwater has a relatively low salinity (150‰). Zone II spans the seaward edge of the beach ridge and Zone III lies beneath a lithified carbonate crust at the landward margin of the intertidal area. Salinity in II rises more steeply than in III. Zone IV contains intertidal sediments in which abundant gypsum has precipitated. Fig. 1 shows the deuterium and oxygen isotope distributions in these zones. The water of Zone I appears to have little marine influence and could represent an evaporated continental water (Fig. 2). The $\delta^{34}\text{S} = +18.5\text{‰}$ for sulphate in solution also indicates a continental component, although much of the dissolved salts could be of marine origin. In Zone II the waters appear to have considerable marine influence (Standard Mean Ocean Water, SMOW, is zero for both the deuterium and oxygen-18 scales). The four samples from this zone show increasing $\delta^{18}\text{O}$ and decreasing δD (Fig. 1) which is not characteristic of evaporative concentration but rather of seawater mixing with increasing quantities of an evaporated continental brine. $\delta^{34}\text{S}$ values for sulphate in these waters (shown on Fig. 2) also indicate a marine source (+20.5‰) altering to a sulphate containing a continental contribution ($\delta^{34}\text{S} = +18.9$). In Zone III both deuterium and oxygen-18 increase but again it appears to be the result of mixing rather than evaporation. The trend shown on Fig. 2 for this zone indicates mixing between an evaporated marine brine and a strongly evaporated continental water. The $\delta^{34}\text{S}$ values are very close to marine sulphate values. The fourth group show increasing marine influence and their

Fig. 1

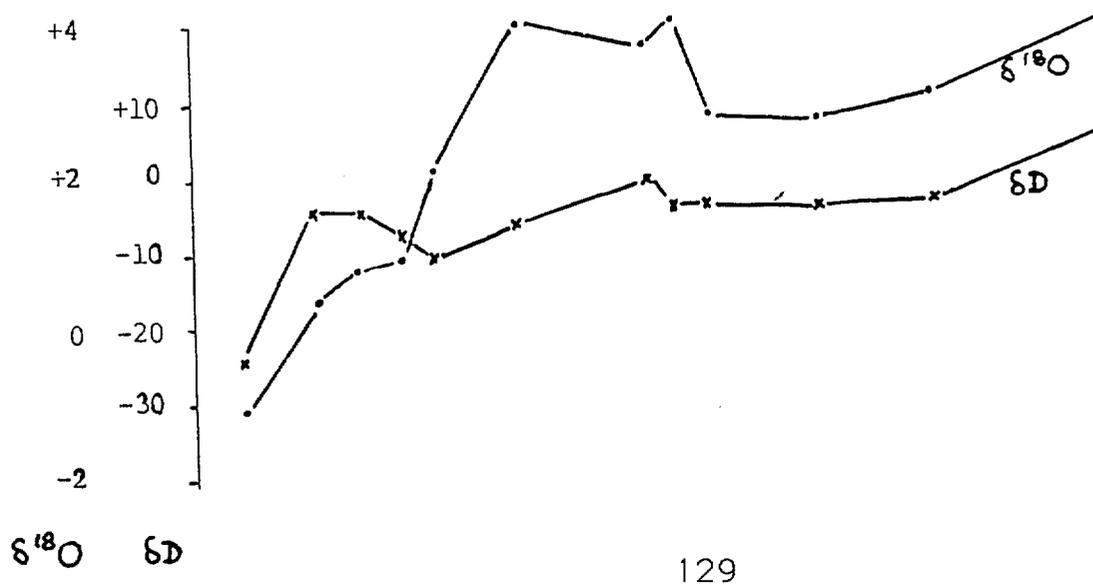
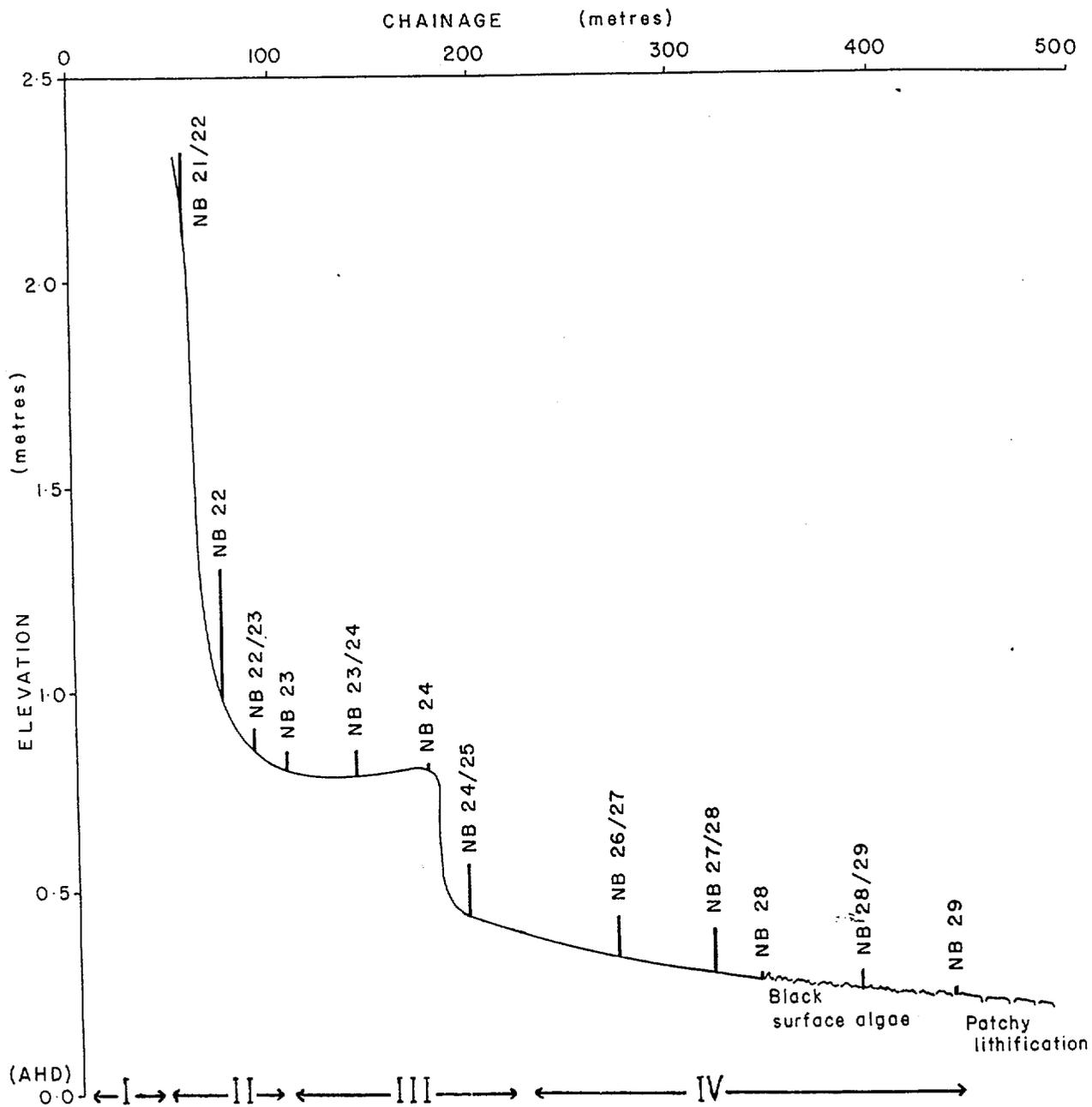
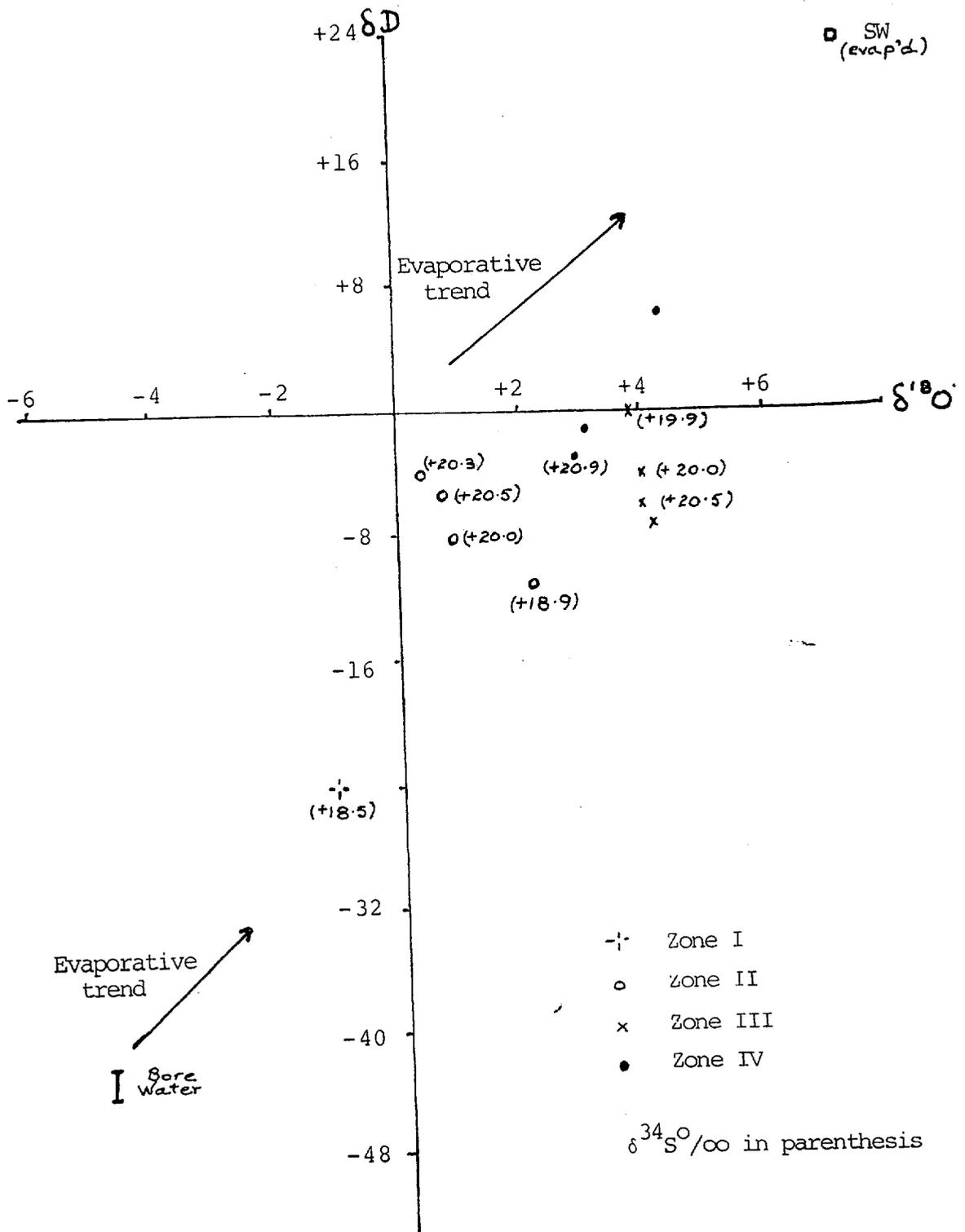


Fig. 2.



isotopic values all midway between those of evaporated seawater and the continental water beneath the beach ridge.

ROLE OF WATER ACTIVITY IN CYANOBACTERIAL MATS

J. Bauld, D.T. Ho.

Cyanobacterial mats which colonize marine intertidal areas, the margins of permanent salt lakes or the sediments of ephemeral salt lakes are exposed to irregular fluctuations in salinity which may progress to or beyond halite saturation, and to desiccation at all salinity levels.

Salinity and desiccation are two aspects of water activity (a_w) or water potential. These are energy terms used to describe the thermodynamic availability of water to organisms. Photosynthetic activity of marginal marine mats is substantially reduced at salinities beyond 2-3 times that of sea water, thus indicating the degree of control which may be exerted by the a_w of the environment.

Progress:

An earlier field experiment (Quarterly Report April 1981, pp. 28-31) indicated that, on wetting, recovery from desiccation was rapid for healthy smooth mat. In fact, the rate of photosynthesis increased linearly for about 2 hr after wetting. This suggested that water uptake into the mat was rapid.

We have measured the time-course of drying-wetting-drying for laboratory-maintained mats using conditions approximating those for an intertidal mat exposed to the air during midsummer i.e. temp. ca. 50°C.

The data are shown in Fig. 3. Water loss is fairly rapid and constant weight is reached between ca 3-18 hr. Most water loss has occurred within 2-3 h (Fig. 3). Water uptake by desiccated mat is even more rapid, being essentially complete within 1-2 h, a time interval similar to that for the recovery of maximum photosynthetic activity by smooth mat during a field experiment.

PRODUCTION AND FATE OF ORGANIC CARBON IN CYANOBACTERIAL MATS

J. Bauld, L.A. Chambers, D.T. Ho, I. Reichstein.

Photosynthetic CO₂-fixation by mat-constructing cyanobacteria provides the organic carbon required by the heterotrophic bacteria (including sulfate-reducing bacteria) present in these mats. The

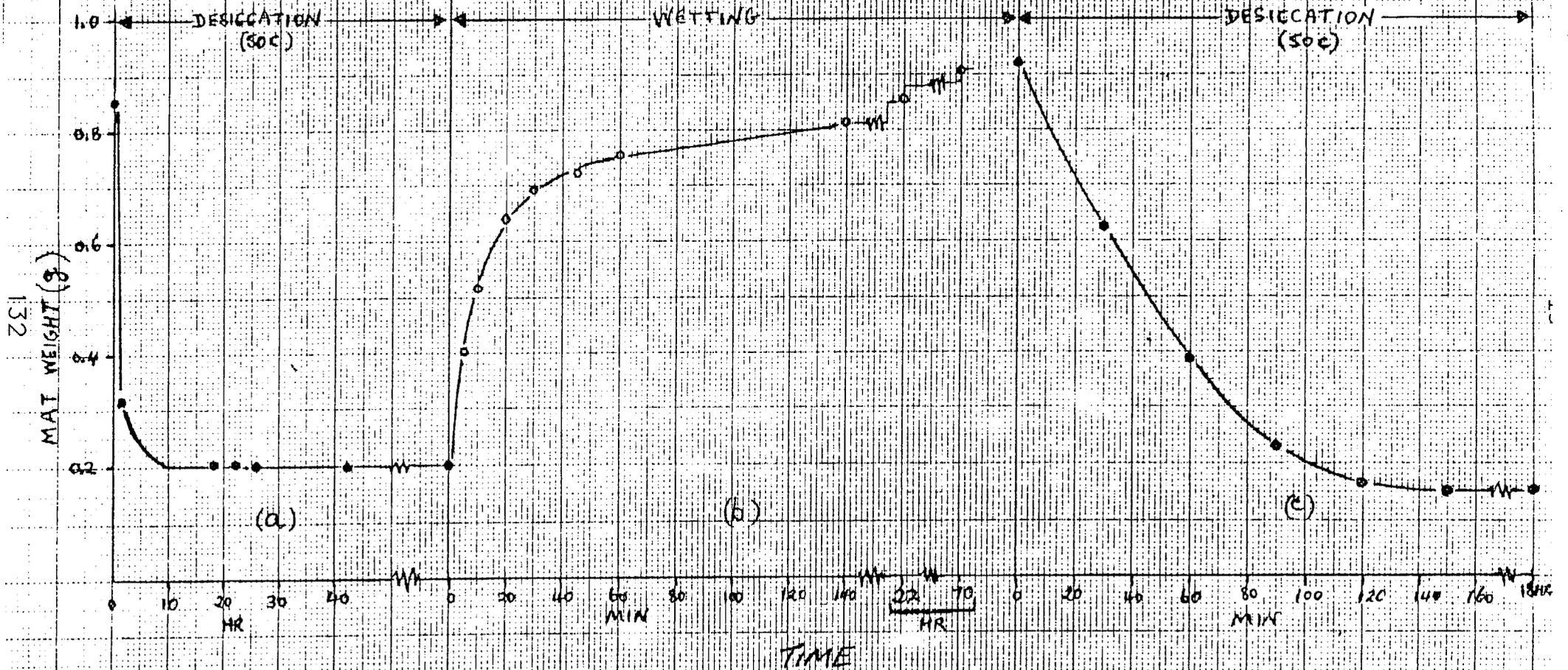


Figure 3. Effect of desiccation and wetting on samples of laboratory-maintained mat. Desiccation was accomplished by drying at 50°C, wetting by immersion in distilled water. (a) desiccation (40hr) (b) wetting (70min) (c) further desiccation (150min). Note changes on time scale.

organic carbon produced is available in two forms (i) Particulate Organic Carbon (POC) – essentially cyanobacterial biomass, (ii) Dissolved Organic Carbon (DOC) – small, soluble molecules excreted by healthy cyanobacterial cells into the surrounding environment. Total organic production is the sum of the two components i.e. $\Sigma(\text{POC} + \text{DOC})$. The DOC component of organic production potentially provides a source of immediately available organic carbon to drive bacterial sulfate reduction. We are investigating DOC production, environmental factors influencing its rate of production, and attempting to identify and quantify the small molecules which comprise the DOC and also these present in mat/sediment interstitial waters.

Progress:

Laboratory processing of field experiments carried out in Shark Bay (Playford's transect) is now essentially complete. Data processing is incomplete but the following information is available:

1. Environmental factors influencing DOC production.

(a) Total photosynthetic production of organic carbon [$\Sigma(\text{POC} + \text{DOC})$] by intertidal tufted mat was relatively constant at salinities between 3.5‰ and 70‰ but decreased at higher salinities (105‰ and 140‰).

(b) As salinity was increased from 3.5‰ to 105‰, excretion of DOC increased from ca 1% to ca. 6% of $\Sigma(\text{POC} + \text{DOC})$. Excreted DOC (%) rose substantially at higher salinities.

2. Physical proximity of phototrophic DOC sources and heterotrophic DOC sinks.

An earlier laboratory experiment (see Quarterly Report April 1982, pp 21-22), using a culture of filamentous cyanobacteria, indicated that dilution of cell biomass raised detectable DOC(%). The response of tufted mat to similar treatment under field conditions was examined. It was found that DOC(%) was similar for intact mat samples (normal experimental material) and for homogenized mat samples (ca 6-8%). However, 10-fold dilution of homogenized mat samples raised the DOC(%) detectable to as much as 30%. This concurs with the laboratory experiment in suggesting that use of intact cores may result in an underestimate of the actual quantities of DOC transferred from photosynthetic source to heterotrophic sink and is consistent with our earlier suggestions that, under natural conditions, producers and consumers are tightly coupled both physically and metabolically.

SULPHATE-REDUCING BACTERIA IN SHARK BAY SEDIMENTS

P.A. Trudinger, L.-E. Hogie.

Purpose:

To isolate organisms responsible for sulphate reduction in Shark Bay sediments; to determine their nutritional and environmental requirements.

Progress:

Isolation of bacteria continues. Fresh material from Shark Bay proved a rich source of organisms and cultures of sulfate-reducing bacteria capable of growing on lactate, acetate, benzoate or mixed fatty acids are now close to purity.

A filamentous organism (ca. 2μ X up to 200μ) has been enriched from a black, dense cyanobacterial mat surrounding the Point Petit bore hole. So far it has proved difficult to isolate but all indications suggest that it is a sulphate-reducer possibly of the genus, *Desulfonema*. It grows readily on mixed fatty acids and, in contrast to the other organisms studied, responds best to low salt concentrations. This would be consistent with the fact that the Petit Point bore hole water is low in salinity.

Much time in the last quarter has been spent in developing suitable gas chromatographic techniques for studying organic matter utilization production by the organisms.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
MAY, 1983

STUDIES IN MODERN ENVIRONMENTS AND THE LABORATORY

GROUNDWATER INVESTIGATIONS AT NILEMAH EMBAYMENT,
HAMELIN POOL.

James Ferguson, L.A. Plumb, I. Reichstein, B. Simeonovic.

Survey results on several transects across the peritidal zones and adjacent hinterland at Nilemah Embayment are now available and have been used to determine post-rainfall, winter water table levels across the widest part of the peritidal zone and to locate corresponding salinity data.

These data indicate that the hydrological regime is relatively complex and involves more than one type of meteoric water input. Zones of relatively low-salinity water with a meteoric water component occur at the landward margin of the peritidal zone and near the middle of the supratidal zone, where they are associated with slight topographic highs. The source of this water and the reasons for its preferential accumulation at these locations are not understood at present.

Despite the strong meteoric water influence there is a difference of less than 10 cm between water table levels close to the intertidal zone and those some 1200 metres inland, which is an indication that continental groundwater flow rates and discharge in the intertidal and subtidal zones are probably not large. The relatively gentle slope of the continental water table may also allow the effects of tidally influenced changes in the marine water table to extend inland for significant distances and certainly beyond areas of present-day carbonate lithification which occur in the high intertidal zone, landward of the areas of stromatolitic beach rock. The relationships between the intertidal hydrological regime and the various types of beachrock currently forming in that area will be investigated further during the May 1983 field season.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
AUGUST, 1983

ABSTRACT

Our projects on the hydrogeochemistry of the seawater-groundwater system and its diagenetic products, and the microbial ecology, of Shark Bay continued to make progress.

STUDIES IN MODERN ENVIRONMENTS AND THE LABORATORY

HYDROLOGY OF THE INTERTIDAL ZONE, NILEMAH EMBAYMENT.
James Ferguson, L.A. Plumb, M.A. Habermahl (Continental Geology).

Beachrock forming in the intertidal zone at Nilemah Embayment appears to be a favourable substrate for the establishment and subsequent growth of stromatolites. This beachrock is exposed in the low intertidal zone and preliminary sampling indicates that active cementation is occurring beneath the high intertidal sediments, forming a thin layer of lithified carbonate. The relationships between the lithification and its hydrologic and hydrogeochemical setting have been investigated using piezometric and salinity measurements along a transect extending from the high intertidal to the low supratidal zone (Figs. 3 and 1).

Piezometric measurements were made during winter when tides were relatively high and the groundwater table in the supratidal zone was low following a period of drought. Consequently, the tide height regularly exceeded the height of the groundwater table at distances up to about 1500 m inland from the intertidal zone, which would favour landwards movement of seawater. In fact, short-term differences in groundwater level were restricted to about 500 metres inland by limitations caused by the hydraulic conductivity and permeability of the sediments. During the two-week sampling period the height of the tides gradually increased, which caused a progressive change in the height and shape of the tidally controlled water surface in the study zone (Fig. 3). Initially, when tides were relatively low the shape of the groundwater surface was essentially convex and probably followed the basic groundwater table of the intertidal zone. As the tide heights increased the water table rose and its profile varied from convex after high tides, to an almost linear seawards to landwards slope when the high tide influence was at its maximum. In common with most intertidal zones, there is a significant "tidal lag" between changes in the tide height and the response of the

Fig. 3. Response of groundwater table in the intertidal zone to tidal fluctuations, Nilemah Embayment, Winter, 1983. 137

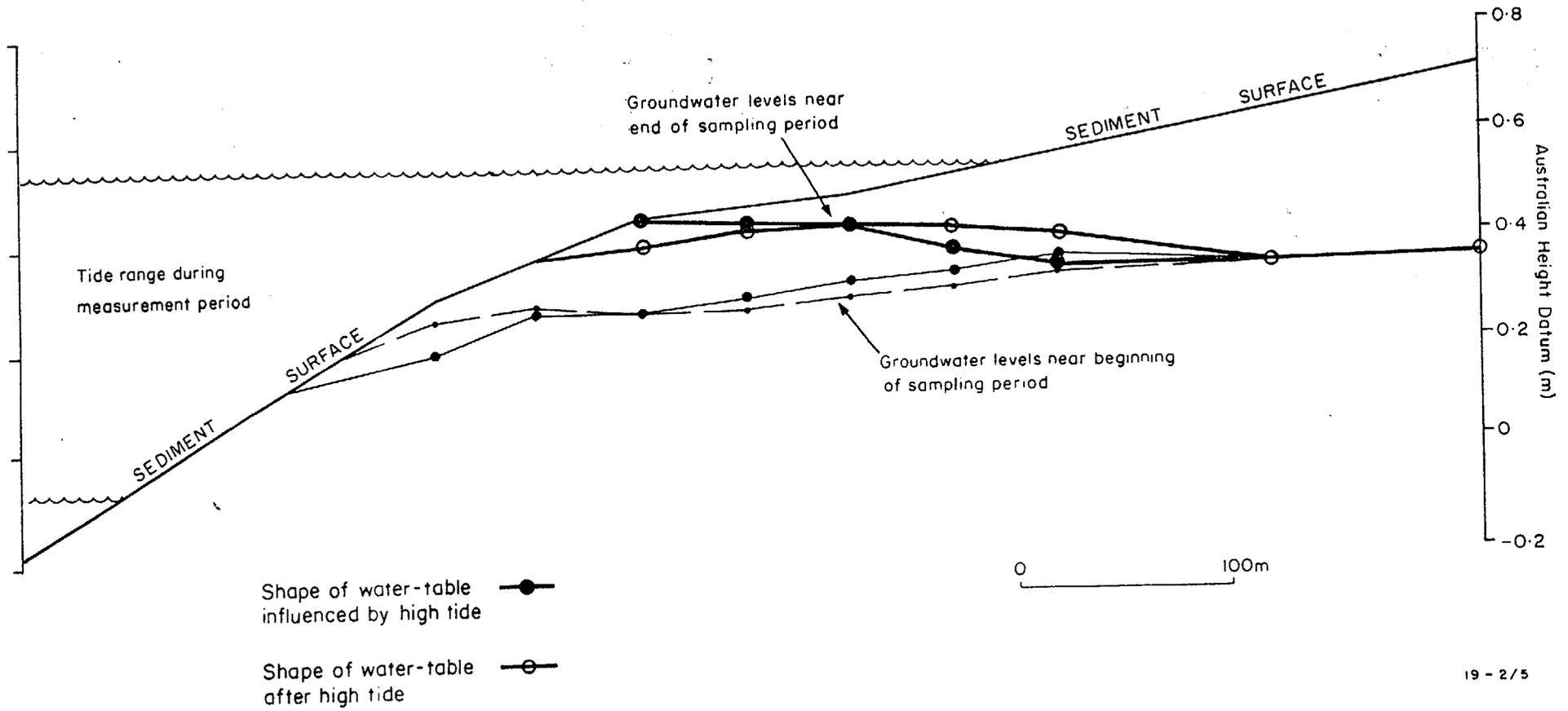
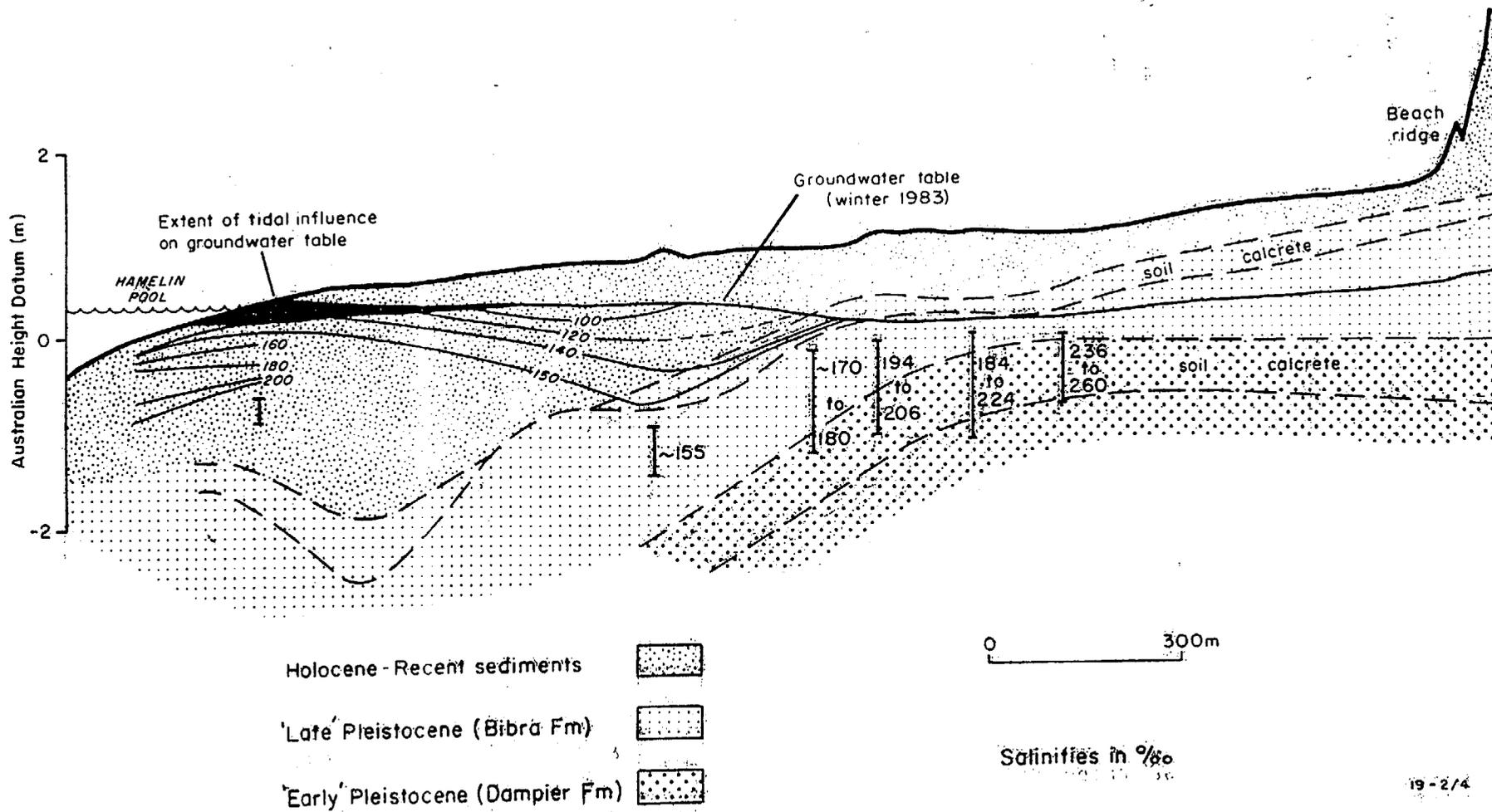


Fig. 4. Groundwater level and salinity profile across the intertidal and supratidal zones, Nilemah Embayment, Winter 1983.



19-2/4

groundwater table in the sediments. Future investigations will employ continuous monitoring of both tidal and groundwater levels to quantify this lag time and relate it to the hydrologic characteristics of the intertidal sediments.

The landward limit of the zone of tidally-induced water table fluctuations is co-incident with that of the sub-surface carbonate lithification which suggests a genetic relationship. A further indication of this relationship is the sharp increases in salinity with depth which occur in the intertidal zone (Fig. 4), which is consistent with a possible groundwater-fresh seawater mixing system. Further investigations of the mechanism of carbonate lithification will include determination of the saturation indices of the groundwaters with respect to various carbonate minerals and, possibly, comparison of the carbon and oxygen stable isotope characteristics of the groundwater dissolved carbonate and carbonate cements.

SULPHATE-REDUCTION RATES

G W. Skyring and S. Dobb

Sulfate reduction rates were determined in sediments from intertidal pools at Hamelin Pool, Shark Bay. The sediments were colonized by a thin layer of cyanobacterial mat. The study was part of one (in collaboration with James Ferguson and Lyn Plumb) in which chemical and physical changes in overlying tidal water from Hamelin Pool were monitored for several hours in order to calculate if carbonate was precipitating. Carbonate alkalinity, ammonia, sulfide and phosphate concentrations were also determined in the porewaters of these sediments. The data are being processed and will be reported subsequently. Because of the possibility of rapid pyrite formation in marine sediments experiments are continuing on the direct determination of non-acid volatile, pyritic reducible sulfur. Preliminary work suggests that authentic pyrite sulfur may be isolated as sulfide from sediments by reduction with tin in hot concentrated HCl.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
NOVEMBER, 1983

ABSTRACT

Carbon and oxygen stable isotope and other geochemical data have been used to investigate the mechanisms of formation of dolomite in two contrasting environments at Fishermans Bay, South Australia. Experiments in Hamelin Pool, Western Australia, were undertaken to investigate the mechanisms of carbonate and pyrite deposition in intertidal sediments.

STUDIES IN MODERN ENVIRONMENTS AND THE LABORATORY

SULPHATE-REDUCTION IN SEDIMENTS.

G.W. Skyring and S. Dobb.

Intertidal Pools and Sediments Hamelin Pool (Shark Bay)

This study, in collaboration with James Ferguson and Lyn Plumb, was part of one in which chemical and physical changes in tidal and porewaters were monitored for several hours to calculate if carbonate was precipitating (see Quarterly Report, Aug. 1983). Unfortunately, long term monitoring was prevented by several days of excessively high tides, but the data obtained are reported because they will be useful indicators when planning the extension of these studies.

The results so far obtained are given in Tables 1 and 2.

The pH of the surface waters in a selected intertidal pool appeared to be continually falling until flooding occurred with tidal waters. The pool had an average depth of 7.5 cm and evaporation did not appear to be a significant factor over the 2-3 hour experimental period. Active photosynthesis by the thin cyanobacterial mat covering them would be expected to raise the pH (see Quarterly Report, May 1983). Lowering of the pH could be affected by the following processes.

. oxidation of sulfide and ammonia to sulfuric and nitric acids, respectively.

Note: Neither sulfide nor ammonia was detected in the surface waters and even in the porewaters sulfide was undetectable. Ammonia diffusing from the sediment into the surface waters may be lost by biological oxidation to nitrate or degassing as NH_3 . Unfortunately there are no data for nitrate concentrations (see Note 7, Table 1).

- . Evaporation.
- . Respiration of CO₂ by the heterotrophic population of microorganisms.
- . Diffusion of the sediment porewaters which have a considerably lower pH (see Table 2).

Note: Gardner, L.R., 1973 (Geochim. Cosmochim. Acta. 37, 53-68) computed several models for sulphate reduction in marine carbonate sediments. Each of his models predicted a fall in pH, a

Table 1. Some chemical and physical properties of surface water and porewaters of a pool in the intertidal zone, Playford's transect (31/5/83 and 1/6/83)

Time	Sulfate mM	NH ₄ ⁺ μM	pH ⁽¹⁾	Salinity ‰	Temp. °C	Sulfate reduction rate ⁽²⁾ (n mol ml ⁻¹ h ⁻¹)
<u>Pool water</u>						
11.00	73	0	8.02		25.8	
12.45	59 ⁽³⁾	0	7.96		27.2	
13.45	66	0	8.11 ⁽⁴⁾		28.8	
<u>Sediment pore water</u>						
13.00	69	29	7.41 ⁽⁵⁾	70	24.0	27.6 (662)
15.15	59 ⁽⁶⁾	44 ⁽⁷⁾		68	24.0	17.3 (415)

Notes

1. The pH was measured with respect to an electrode standardized in an 2X.ASW -Tris HCl (0.005 molal) (Hansson, I.; 1973, Deep Sea Research, 20, 479-491). The pH data on these concentrated sea waters may be subject to some change pending a more thorough examination. However, it is clear that standardization of electrodes must be made in buffers of appropriate salinities. The temperature coefficient for Hamelin Pool water at 68‰ (salinity) was 0.0129 pH units per°C.

2. Sulfate reduction rates were measured on the sediments only. A ³⁵SO₄ method was used. Results are given with respect to the porewater. Entries are the average of 3 determinations. Entries in brackets are daily rates.

3. & 6. The sulfate concentrations in this experimental series appeared unusually variable. Similar values were noted in 1980 however. This will be investigated further.

4. Up to this time the pool was isolated, and as time progressed, the pH of the surface water (average 9cm in depth) decreased. Then tidal waters at pH 8.24 flooded in rapidly and pH of the pond water rose to 8.11.
5. The pH measured on the following day was pH 7.69 during a period of continuous flooding with tidal waters.
7. Gassing the porewater with O₂-free N₂ resulted in a loss of 90% of the ammonia.
8. Phosphate and sulfide were below detection levels in both surface and porewaters. The average of six sulfide determinations for the sediment was 6.5 μmol S⁻¹.

Table 2. Some chemical and physical properties of porewaters from the black muds of the high intertidal region of Hamelin Pool.⁽¹⁾

Date	Sulfate mM	Sulfide mM ⁽²⁾	NH ₄ ⁺ μM	pH	Alkalinity ⁽³⁾ meq l ⁻¹	Salinity ‰
30/5/83	70	-	31	7.29	4.650	68
2/6/83	70	1.00(4)	35	7.26	7.530	68

(1) The average sulfate reduction rate from six replicates was 197 μmol l⁻¹ day⁻¹ with respect to the porewater.

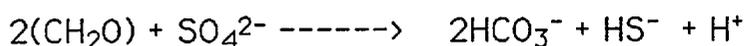
(2) The average sulfide concentration of the sediment was 23.4 μmol g⁻¹.

(3) Calculated according to the formula
 $TA = 1000/V_s \cdot VaN - 1000/V_s \cdot (V_s + Va) a_H/f$; where

TA = Total Alkalinity, vs sample volume, Va = volume of standard acid, N = acid normality, $a_H = 10^{-pH}$ and f = an empirical constant. A value of 0.77 was used for f. For Hamelin Pool, a value of 3.498 was obtained for total alkalinity.

(4) After filtering through a 0.45 μ millipore the sulfide concentration decreased to 0.86 mM.

rise in alkalinity, and of course a rise in HS^- (dependent on the presence of iron). With Fe_2O_3 present, sulfate reduction may cause precipitation of CaCO_3 at pH 7.55 or lower, but with a Fe-free CaCO_3 sediment sulfate reduction results in the dissolution of CaCO_3 . The molar ratio between alkalinity and sulfate reduced in a closed system is generally 2:1 according to the following equation:



Gardner's models predicted an asymptotic pH value of 6.93 but this would be raised to pH 7.7-7.9 to include the effects of ammonia (with reference to the Redfield equation). It is probable that the lower pH and higher alkalinities of the porewater in Hamelin Pool black sediments (with respect to that of surface water) is due to the activities of the sulfate-reducing bacteria.

On the basis of the present data the sulfide in the porewaters of the black sediments would have been produced in about 5 days by the sulfate reducers and the total alkalinity (corrected for sulfide, ammonia and borate) would be produced in 7 days. However, more data are required to confirm these trends.

The estimation of pyrite-S as sulfide and the possibility of rapid pyrite formation:

Dr. R.W. Howarth and his colleagues at Woods Hole, Massachusetts Marine Biological Laboratory have suggested in a series of recent papers that pyrite may be formed more rapidly than previously encountered in some organic-rich marine environments. Samples from the intertidal black sediments at Hamelin Pool were examined for rapid pyrite formation by determining the incorporation of $^{35}\text{S}^{2-}$ from $^{35}\text{SO}_4^{2-}$ into pyrite. This required the direct determination of pyrite-S in the presence of sulfate and organic-S (as cyanobacterial mat).

A number of trial experiments were done with authentic pyrite. Granulated tin as the reductant in boiling 20% SnCl_2 -10N HCl for 3 hours gave the highest recoveries of 83 to 90% of the S. Recoveries using SnCl_2 or Zn as reductants were unacceptably low.

In the presence of 1.0g $\text{Na}_2^{35}\text{SO}_4$ ($\approx 7\text{mmoles}$), a distillation period of 4 hours resulted in the reduction of 0.10% of the sulfate. The reduction of $^{35}\text{SO}_4^{2-}$ was not catalysed by the presence of authentic pyrite, zinc sulfide, cysteine or cyanobacterial sediment.

On the basis of these experiments, Hamelin Pool sediments from the intertidal zone appear to contain only very small quantities of

Sn-reducible (pyrite) S (7 to 26 $\mu\text{mol g}^{-1}$). From the data of the sulfate reduction experiments, there appeared no clear indication of the rapid incorporation of $^{35}\text{S}^{2-}$ into the "pyrite" component of the sediment. However, it was evident from these preliminary experiments that methodology will have to be refined to provide unequivocal evidence of whether or not rapid "pyrite" formation occurs in these and other marine environments being investigated.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
JANUARY, 1984

ABSTRACT

In an extensive drilling program numerous piezometers were successfully emplaced in a transect across the dunes and supratidal flats of Nilemah Embayment in Shark Bay. These will enable long term monitoring of groundwaters in a study of carbonate diagenesis, and the development of a hydrologic model for this area.

**HYDROLOGICAL INVESTIGATIONS AT NILEMAH EMBAYMENT,
HAMELIN POOL**

James Ferguson, L.A. Plumb, I. Reichstein, B. Simeonovic.

The hydrological regime of the intertidal zone at Nilemah Embayment (Q.R., August 1983) is strongly influenced by continental waters which may evolve in Pleistocene sediments overlying the Peron Sandstone. Furthermore, this groundwater appears to be involved in diagenetic processes in Holocene sediments at the interface with seawater brines.

A drilling program was therefore undertaken in the supratidal zone to extend the hydrological model. The aim was to establish piezometers for long-term monitoring of groundwater levels and to characterize groundwaters and identify them with sedimentary units. Four areas were drilled: (i) supratidal, (ii) carbonate beach ridge, (iii) a "backflat" area of old dunes and partly filled clay pans and (iv) aeolian sand dunes. Representative cores have been logged and sampled for thin sections and XRD, ion and isotopic (carbonates) analyses. Relevant porewaters were obtained for ion analyses and deuterium, oxygen and carbon (dissolved carbonate) isotope analyses. Preliminary groundwater data are shown in Table 1. In transect, salinity in the claypan area and alkalinity decreases. A slight reduction in salinity in the beach ridges and contiguous supratidal zone may reflect introduction of fresh water. In depth profile salinity generally increases as has been shown for the intertidal zone (QR, August 1983).

PRODUCTION AND FATE OF ORGANIC CARBON IN CYANOBACTERIAL MATS.

L.A. Plumb, I.C. Reichstein and D.T. Ho.

A large experiment using cyanobacterial-layered sediments from a tidal channel at Gladstone Embayment was initiated during the May 1983 field excursion. The aim was to extend the initial work with this material (Q.R. May 1983) in which, when sulphate reduction was inhibited there was accumulation of acetate under dark conditions but not in the light. Photoheterotrophic activity was inferred for the light conditions.

In the current experiment, fresh material was incubated in the field in both light and dark conditions with molybdate added to inhibit the bacterial sulphate reduction. Since the earlier experiment used material which had been stored aerobically in the dark, some material was stored either aerobically or anaerobically with \pm light for periods of 2, 4, 6 and 8 weeks: pore waters were then extracted and analysed for acetate, propionate and butyrate. Anaerobic + light storage conditions should represent the sediment conditions beneath a contiguous mat on the tidal channel floor. A series of incubations using molybdate, DCMU (to inhibit photosynthesis) and fluoroacetate (to inhibit acetate utilization) were conducted with fresh material and that stored for eight weeks anaerobically + light. Each core analysed was sectioned 0-0.5cm, 0.5cm-2.5cm and 2.5-6.0cm. Porewater was extracted and butylated for gas chromatography.

Table 1. Summary of preliminary data on groundwaters from drill holes landward of intertidal zone, Nilemah Embayment.

	Aeolian Dunes	Back Flat	Beach Ridges	Supratidal
Salinity ‰	50 to 75	100 to 150	≈100	80 to 150
Alkalinity meq/l	2.5	≤1.5	≈1.5	≈2.0
pH	7 to 7.5	≈7.1	≈7.5	≈7.4

The six- and eight-week storage samples have yet to be chromatographed but primary data of acetate, propionate and butyrate concentrations in pore waters are to hand for the bulk of the experiment.

POROSITY AND PERMEABILITY OF SUBTIDAL STROMATOLITES, HAMELIN POOL

M.R. Walter, B. Bubela, K.J. Armstrong, M. Kordas, J.M. Hayes (Indiana University).

The subtidal stromatolites of Hamelin Pool are highly fenestrate and can be considered as models for the study of the origin of porosity and permeability in ancient stromatolite reefs. In the small number of measurements made to date, the porosity of living subtidal stromatolites was found to be about 35%, and their permeability is 1.0 Darcy in a vertical direction and 4.4 Darcy horizontally. A subaerially exposed former subtidal stromatolite was found to have a porosity of between 19 and 26% and vertical and horizontal permeabilities of 0.6 and 2.3 Darcy's. The samples are all well lithified.

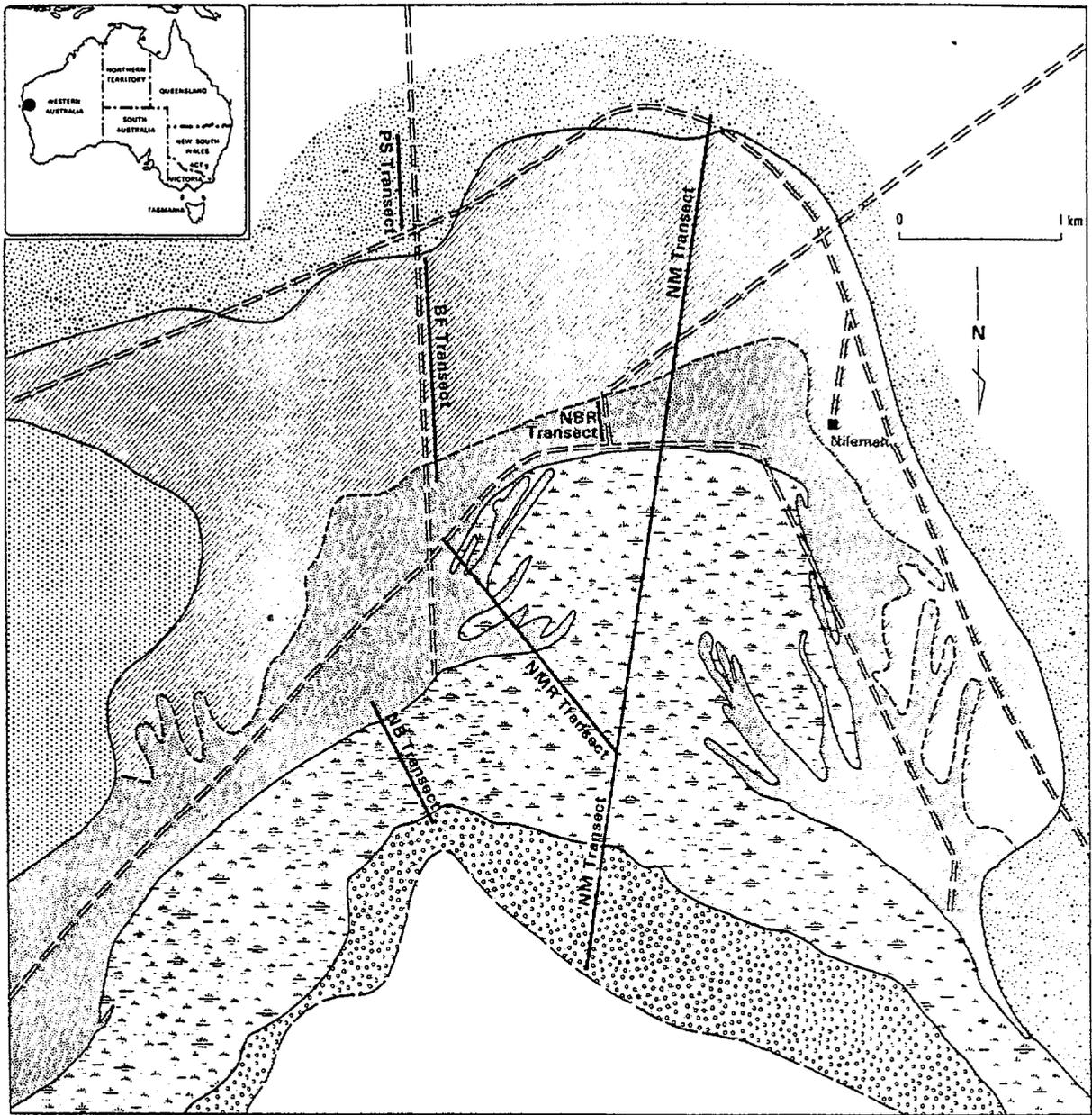
The pores of the subtidal stromatolites are at least partly filled with gas of probably biogenic origin. Samples have been collected on two occasions and one set of analyses is available: 20% H₂, 74% N₂, 4.5% O₂, 1.3% Ar, 0.37% CH₄. Isotopic analyses are underway. It is apparent from these analyses that despite the high permeability, anaerobic conditions exist at least locally within the columns. The fact that gas can be retained within the columns indicates that all the pores are not water-filled and therefore that the fenestrate porosity could be retained during diagenesis.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
MAY, 1984

HYDROLOGICAL INVESTIGATIONS AT NILEMAH EMBAYMENT,
HAMELIN POOL

James Ferguson, L.A. Plumb, B. Simeonovic, I.C. Reichstein.

The January 1984 quarterly report gave summary details of groundwater characteristics along drilling transects at Nilemah Embayment. Figure 3 locates these transects (PS, BF and NBR in relation to major geomorphic subdivisions, and previous transects across the intertidal zone (NB, NMR and NM). Figure 4 shows data in detail for Transects PS and BF through aeolian sand dunes and backflat areas. The plotted data are of the first accumulated water in drill holes and represent mixed waters. Where waters were sampled subsequently during drilling (P52 to BF11) the salinity (Δ Fig. 4) showed increased values with depth. Except for samples from BF15 this is a general trend (Table 1). The highly saline BF15 samples also show the greatest variability in Na/Cl and K/Br ion ratios. Water samples from these transects have been analysed by Dr. A.W. Mann, (CSIRO, Division of Mineralogy, Perth) for heavy metals. Anomalously high values were recorded for Pb and Cu with the greatest concentrations in the BF15 to BF18 region. Because of possible contamination (despite precautions) from the drilling operations further sampling is planned. It is interesting to note, however that ponded surface water remote from the drilling operations also showed enhanced concentrations.



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- | | | | |
|--|----------------------|--|----------------------|
| | Perron Sandstone | | Sublittoral platform |
| | Toolonga Calcilutite | | Tidal flats |
| | Beach ridges | | Back flat |

Figure 3. Locations of transects at Nilemah Embayment, Hamelin Pool

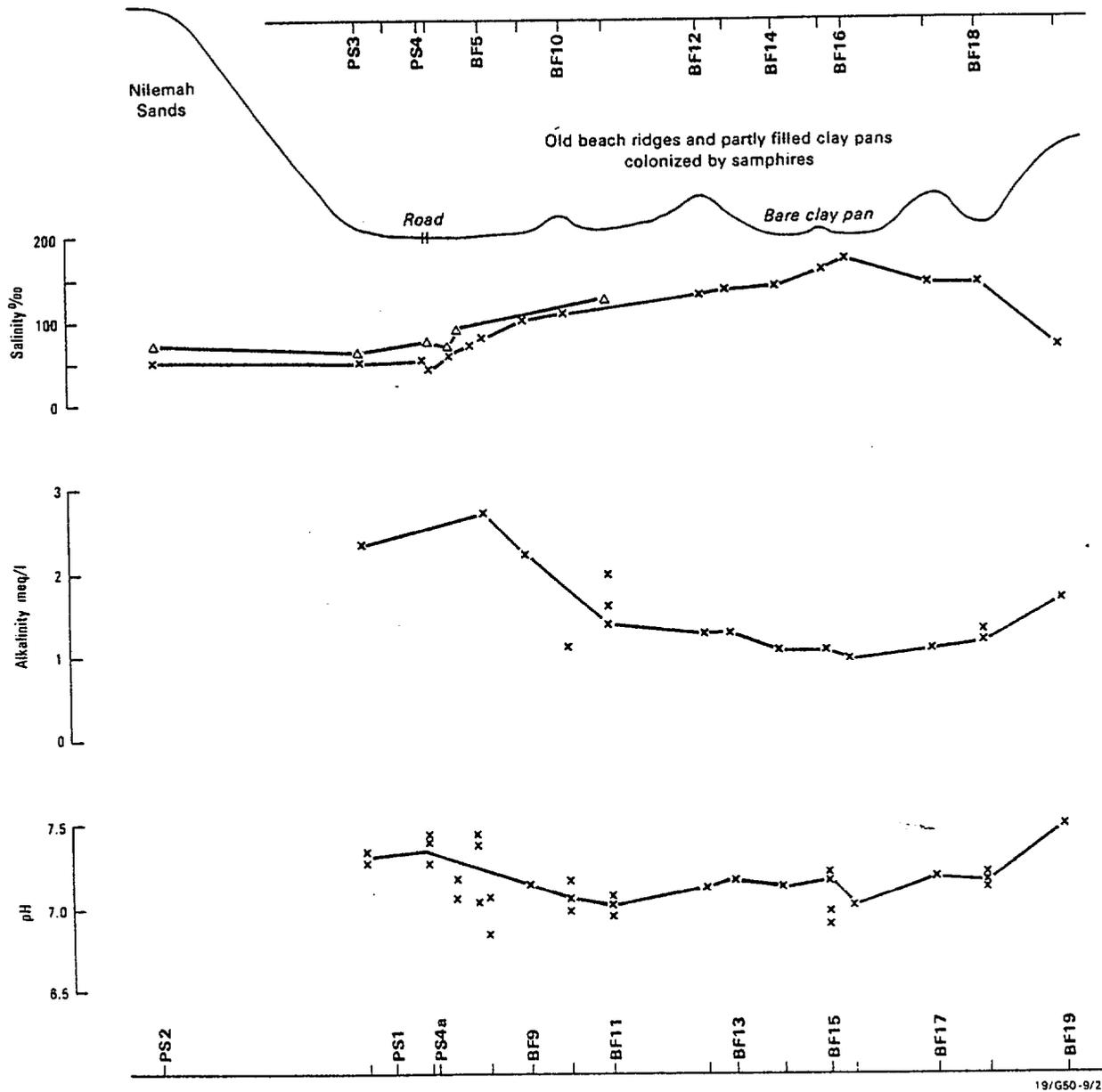


Figure 4. Geochemistry of groundwaters in "backflat" area at Nilemah Embayment.

Table 1 Salinity of porewaters of varying depths
in drill holes.

Core	Depth M	Salinity ‰
PS4a	2.6-4.1	39
	4.8	74
	5.6	74
BF2	2-3	62
	3.5	60
	4.9	92
	5.2	83
BF11	1.1	110
	1.25	106
	1.45	110
	1.70	110
	2.13	113
	2.45	112
	2.65	100
	2.80	112
	3.65	114
	4.36	115
4.86	121	
BF15	0.46-0.75	226
	0.76-1.06	208
	1.06-1.36	200
	>1.36	202
BF18	1-2.5	85
	2.5	118
	2.82	105

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
AUGUST, 1984

GEOBIOLOGICAL CONTROLS ON ORE FORMATION

ABSTRACT

Unusually high lead and copper values have been detected in sediments and waters in Nilemah Embayment, Shark Bay, where a detailed hydrogeochemical study is in progress.

GEOBIOLOGICAL CONTROLS ON PETROLEUM
FORMATION AND ACCUMULATION

ABSTRACT

Contrary to common expectations preservation of organic matter in marine sediments requires more than simply an anaerobic environment. High salinities in the Holocene environments being studied inhibit both bacterial sulphate reduction and methanogenesis and thus contribute significantly to the preservation of organic matter.

THE ROLE OF HYPERSALINITY IN THE PRESERVATION OF
ORGANIC MATTER IN LACUSTRINE AND EVAPORITE
ENVIRONMENTS

S. Lupton

The formation of petroleum source beds is dependent upon the preservation and subsequent diagenesis of organic material. Petroleum geologists have suggested that anoxic sedimentary environments are precursors for petroleum source beds due to a restraint on microbial biodegradation and carbon mineralisation (2). However, recent investigations, including studies undertaken by the Baas Becking Laboratory, have demonstrated that the almost complete biodegradation and mineralisation of organic material can occur anaerobically in both freshwater and marine environments (1, 5, 7).

The preservation of organic material in freshwater environments is usually associated with acidic conditions such as found in acid bogs and peats. It is generally known that low pH inhibits sulphate reduction and methanogenesis, which may lead to an accumulation of metabolic intermediates and a subsequent

inhibition of organic matter degradation (8). Such environments may undergo subsequent diagenesis to become sources of coal.

The factors leading to the preservation of organic matter in non-acidic lacustrine and marine sedimentary environments are harder to define. Hypersalinity has been suggested as a major factor determining organic matter preservation in some environments (3, 6). Organic matter preservation has been observed in the hypersaline sediments of Lake Eliza in South Australia (BBL Annual Report, 1983; Quarterly Reports, January 1984; May 1984) and salinity has been suggested as a major factor determining the activity of the sulphate reducing bacteria in both Spencer Gulf and Lake Eliza sediments (7, BBL Quarterly Report; May 1984).

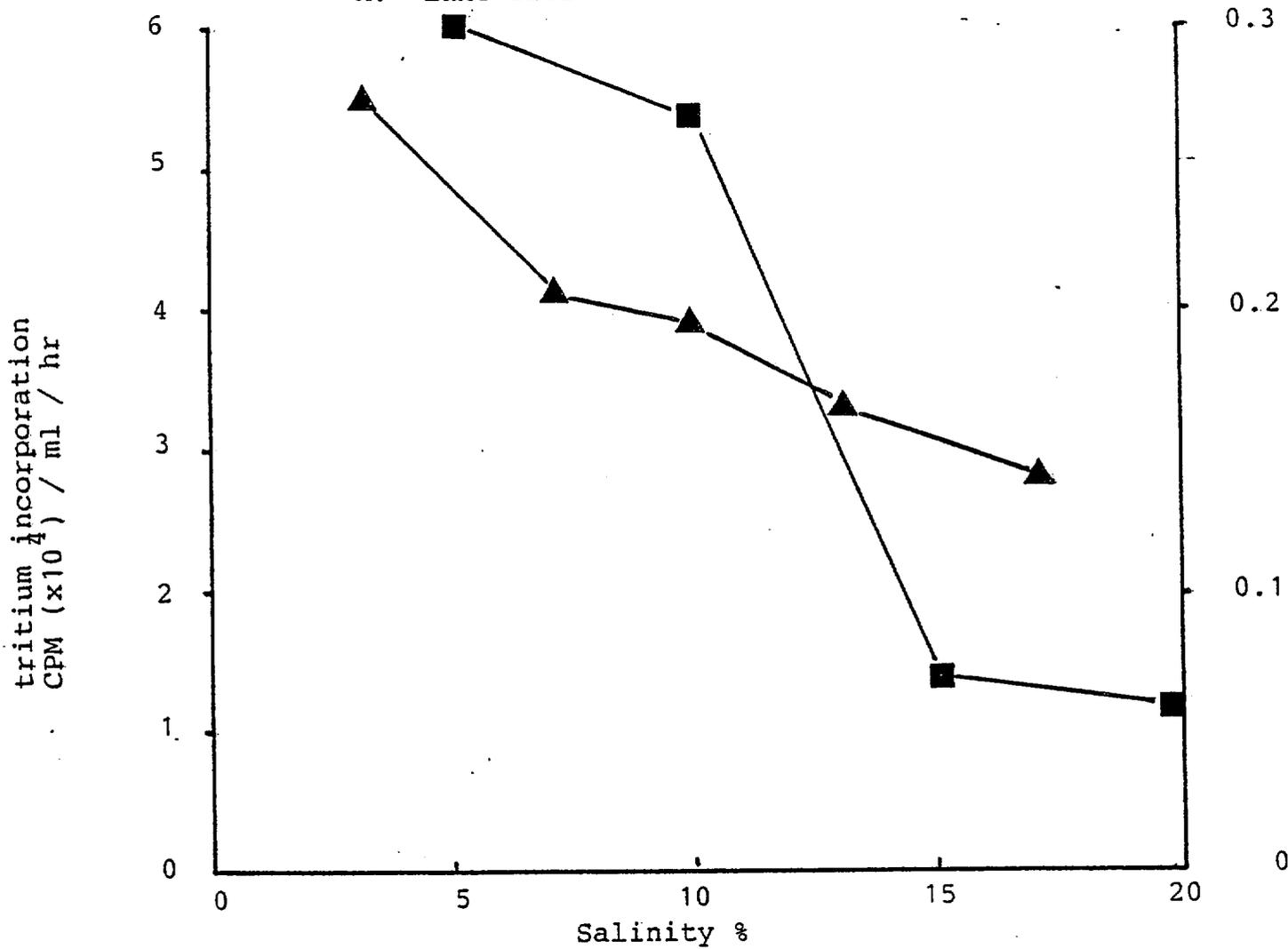
The aim of this project will be to determine the effect of salinity on anoxic microbial processes, both in laboratory cultures and natural sedimentary environments such as Lake Eliza and Shark Bay with respect to:

- 1) The inhibition of total microbial activity
- 2) Selective inhibition of sulphate reducing and methanogenic processes compared to fermentation processes
- 3) The accumulation of metabolic intermediates including H_2 and acidic end products.

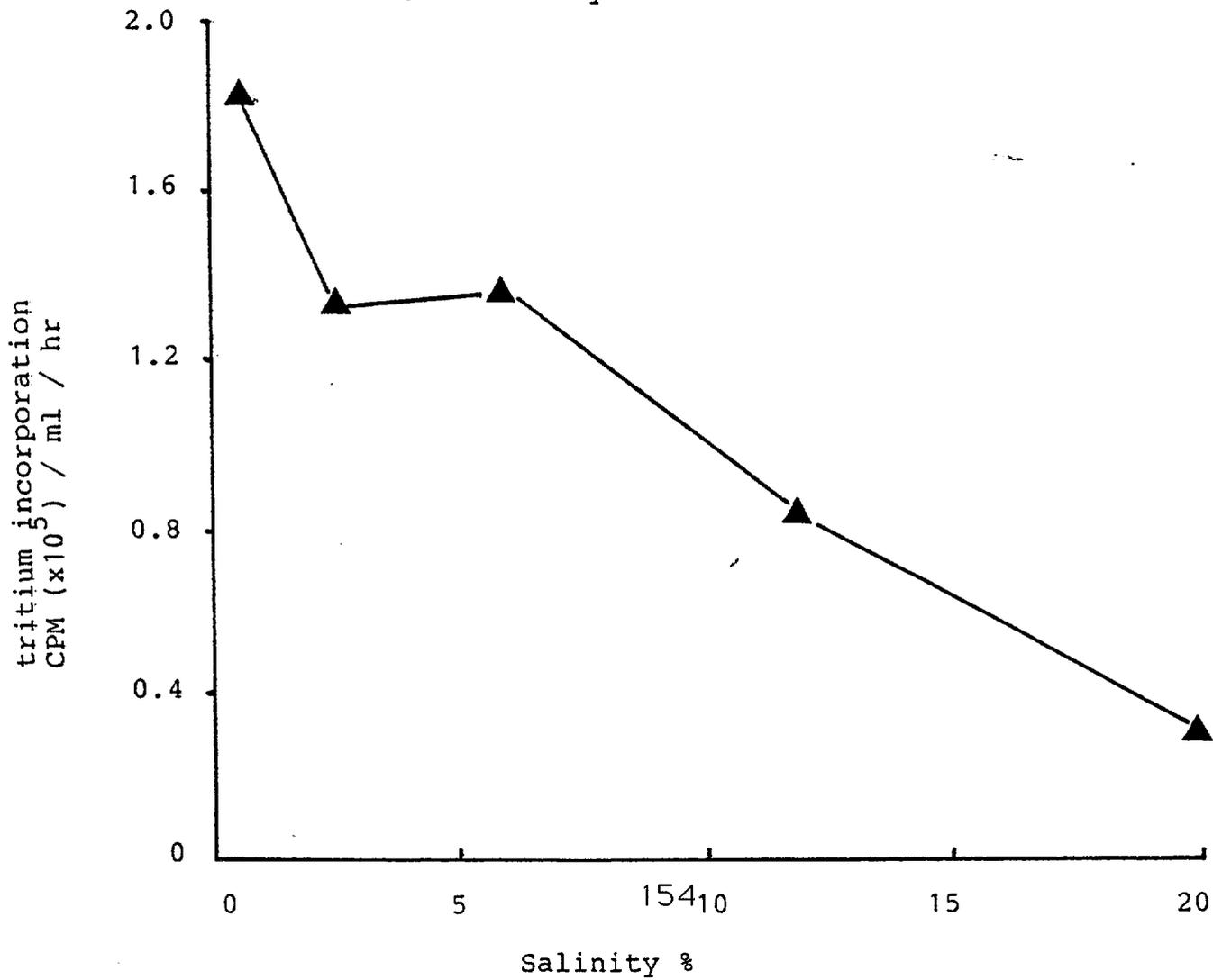
Preliminary results are presented in this report. Tritium incorporation is a measure of in situ microbial hydrogen metabolism (4). The influence of salinity on tritium incorporation by sediments from Lake Eliza and Shark Bay are shown in Fig. 1. Increased salinity decreased the in situ hydrogenase activity of both Lake Eliza sediment and anoxic sediment from Shark Bay, indicating that microbial hydrogen metabolism was inhibited. Growth of anaerobic micro-organisms in Lake Eliza sediment enriched with glucose was significantly greater at lower salinities compared to the enrichments at the in situ salinity (Fig. 1A).

The relationship between the rate of tritium incorporation and salinity suggests that hydrogenase activity in anaerobes is indeed significantly influenced by salinity but it is not possible to distinguish between the effect of salinity on hydrogen producing and hydrogen consuming bacteria. It would be of interest to determine the salinity tolerance of glucose enrichments of Lake Eliza sediment and to determine whether enrichments at high salinity respond differently than enrichments obtained at relatively low salinities and also to determine the effect of

A. Lake Eliza



B. Shark Bay



salinity on both hydrogen producing fermentative bacteria compared to hydrogen consuming sulphate reducers and methanogens.

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METAL CONCENTRATIONS IN CYANOBACTERIAL MATS AND SEDIMENTS AT HAMELIN POOL, SHARK BAY

J. Ferguson, L.A. Plumb, R.V. Burne, B. Simeonovic, I. Reichstein

The Fe, Mn, Cu, Pb and Zn contents of cyanobacterial mats; Holocene-Recent, Pleistocene and Cretaceous marine carbonate sediments; and Pleistocene sandstone and Pleistocene-Recent unconsolidated quartz sand from the Nilemah Embayment area and from Playford's Transect have been determined. The range and average of the metal concentrations in each group are summarized in Table 2. The samples range in composition from >95% carbonate (e.g. coquina) to almost carbonate-free quartz sands (e.g. some Nilemah sands) and no attempt has been made to show any partition of the metals between the carbonate and non-carbonate phases.

The Holocene-Recent carbonate sediments of the intertidal and supratidal zones contain small amounts of Fe and Mn and there is no evidence of abnormally high concentrations of Cu, Pb or Zn. Intertidal cyanobacterial mats have slightly higher Zn contents (13 ppm cf 5 ppm) than the carbonate sediments but otherwise the mats and the associated black muds are not enriched in metals. These algal mats and black sulphide muds were obtained from Playford's Transect where the adjacent country rock which could serve as an aquifer system transmitting terrestrial groundwaters to the coast, is a Cretaceous marine carbonate unit. Redbed and quartz aeolian dune systems which border the western side of Hamelin Pool may be more favourable sites for the formation of metal-enriched terrestrial waters and it is possible that algal mats and associated sulphide sediments bordering these areas may contain higher metal concentrations.

Compared to the intertidal/supratidal carbonates, stromatolites from the subtidal zone and the supratidal zone have lower Fe and Mn contents, slightly higher Zn and Pb contents and significantly higher Cu contents. No interpretation of this result has been attempted yet because it is subject to analytical confirmation.

Late Pleistocene marine carbonates (Bibra Fm) from one location at Nilemah have marginally higher Zn concentrations than the Holocene-Recent carbonates and are an order of magnitude higher in Pb. The high Pb concentrations persist into an underlying soil and lithified carbonate sediment which probably incorporates an early Pleistocene marine horizon (Dampier Fm). Below this, however, in earlier Dampier carbonates and interfingering quartzose sands (Nilemah Sands), Pb concentrations are not high.

Cu concentrations are low in both the late Pleistocene sediments and the underlying Dampier/Nilemah Sand units. These low concentrations are further reduced in areas where the iron oxides have been removed from the surface of the quartz grains. Zn concentrations in the Dampier/Nilemah Sand units are similar to those in the overlying late Pleistocene unit.

In carbonate-free Nilemah Sands underlying the areas of marine transgression the Fe content of the sediments is higher than in the overlying units but Mn, Cu, Pb and Zn are not. Nilemah Sands landward of the marine transgressions are similar in composition but have still higher Fe contents.

The Peron Sandstone, which is less than 1 metre thick in the areas sampled, has an Fe content marginally higher than that of the Nilemah Sands and its Zn content is twice as high.

The Cretaceous chalk samples encountered in this sampling program may not be typical of the deeper parts of the sequences because they have considerably higher Fe concentrations than occur in chalk from the Toolonga Plateau. The Mn, Cu, Pb and Zn contents of the Nilemah Cretaceous chalk are about three times those of the overlying sediments but it is not clear whether this indicates concentration of these metals or the presence of a more metal-enriched non-carbonate detrital component in the chalk.

Considered in terms of ore genesis models, the absence of metal enrichments in the cyanobacterial/sulphide mud zones is of significance because it adds to the growing volume of data which indicates that metals are not concentrated in modern sabhkas. If confirmed, the Cu enrichments in the stromatolites would be an exception to this generalization.

The high Pb concentrations (av. 77ppm) in the Pleistocene marine carbonates are the only sign that metal concentration processes have operated effectively at Nilemah Embayment. These high concentrations are not confined to the Bibra Fm and are not homogeneously distributed within this unit. Consequently, further work is needed to confirm that these enrichments are not strongly localized and to determine the component with which this Pb is associated in the sediments and the mechanism by which it is concentrated.

Evidence for the mobilization and concentration of Cu by processes proposed in genetic models for stratiform Cu deposits is tenuous, possibly because the Peron Sandstone sequence is thin

in the areas sampled and because the Cu contents of both the sandstone and the overlying Nilemah Sands are low. Nonetheless, mobilization of Fe (and possibly associated metals) in oxides coating quartz grains has occurred as evidenced by the presence of bleached zones in the quartz sands beneath the Pleistocene sediments. Also, reduction of Fe in the lowermost parts of the Nilemah Sands/Peron Sandstone is occurring at the present day, changing the colour of the sediments from fawn/red to mottled red/green. It is possible that this Fe is being concentrated at the interface of the sandstones and the Cretaceous Chalk and the marginally higher Fe and Cu, Pb, Zn contents of the uppermost Cretaceous Chalk sediments may be a result of re-precipitation of Fe as the Fe-containing waters encounter higher pH conditions associated with the carbonate sediments.

Table 2

Range and Average Heavy Metal Content of
Cyanobacterial Mats and Various Types of
Sediments from Hamelin Pool.

	<u>Fe</u>	<u>Mn</u>	<u>Cu</u>	<u>Pb</u>	<u>Zn</u>
Cyanobacterial Mats (3 samples) ¹	L. 2700	26	2	6	10
	H. 6000	46	4	6	16
	Av 4000	33	3	6	13
Black Muds assoc. with intertidal cyanobacterial mats (3 samples)	L. 3100	20	2	6	2
	H. 5500	26	4	10	8
	Av 4700	22	3	7	5
Holocene-Recent Intertidal Carbonates (17 samples)	L. 1400	16	<2	<5	2
	H. 6800	50	8	10	8
	Av 4200	34	3	6	5
Holocene-Recent Supratidal Carbonates ² (9 samples)	L. 11000	10	<2	6	2
	H. 5100	50	4	10	8
	Av 2100	20	<2	7	5
Coquina from beach Ridge (1 sample)	800	6	2	6	4

1. Excluding colloform mat

2. Tidal Pond Core is similar to intertidal sediments

Table 2 (continued)

	<u>Fe</u>	<u>Mn</u>	<u>Cu</u>	<u>Pb</u>	<u>Zn</u>
Holocene-Recent Stromatolites:					
(32 samples)	L. 225	<5	10	<5	6
(Pb: 7 samples)	H.1560	<5	42	24	16
	Av 640	<5	19	15	12
1 Beachrock sample from same analytical batch as stromatolites	960	38	14	10	16
Late Pleistocene Marine Carbonates (Bibra Fm) (9 samples)					
	L.2900	36	2	6	8
	H.6100	66	4	190	32
	Av4500	48	3	77	14
Soil (Depuch) grading into underlying lithified marine - uppermost sequence (6 samples)					
	L.3000	30	4	6	6
	H.5700	50	8	170	16
	Av4500	43	6	79	10
Soil (Depuch) grading into underlying lithified unit then into shell-rich layer - intermediate sequence (6 samples)					
	L.2600	30	<2	<5	6
	H.4500	50	2	10	14
	Av3300	37	<2	7	10

Table 2 (continued)

	<u>Fe</u>	<u>Mn</u>	<u>Cu</u>	<u>Pb</u>	<u>Zn</u>
Cemented, bleached Nilemah Sands. (5 samples)	L.1100	10	<2	<5	6
	H.2200	20	2	6	30
	Av1600	16	<2	<5	12
Soil (Depuch) with some shell fragments (4 samples)	L.1400	16	<2	6	8
	H.4200	46	4	6	16
	Av2400	33	2	6	11
Cemented, orange to brown Nilemah Sands (5 samples)	L.3400	50	2	6	6
	H.8300	190	4	10	14
	Av6600	130	2	6	10
Carbonate free quartz sand ?Nilemah Sands (3 samples)	L.9900	26	2	6	14
	H.12000	50	14	10	18
	Av10900	34	6	7	15
Nilemah Sands landward of marine transgressions (6 samples)	L.5900	16	2	<5	6
	H.89000	66	6	10	18
	Av21000	44	4	6	13
Person Sandstone (4 samples)	L.7200	20	<2	6	14
	H.41000	56	6	10	42
	Av24000	33	4	7	25
Cretaceous Chalk (2 samples)	L.30000	230	6	16	50
	H.35000	370	12	26	70
	Av32500	300	9	21	60

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
NOVEMBER, 1984

GEOBIOLOGICAL CONTROLS ON ORE FORMATION

ABSTRACT

Substantial new results are available on the microbial processes associated with the preservation of organic matter and the production of diagenetic sulphides in Lake Eliza and Shark Bay. Research on the use of strontium, carbon and oxygen isotopes to distinguish marine and non-marine carbonates shows that strontium can be an effective indicator where the other isotopes give equivocal results.

GEOBIOLOGICAL CONTROLS ON PETROLEUM
FORMATION AND ACCUMULATION

IN SITU HYDROGENASE ACTIVITY AND METHANOGENESIS
ASSOCIATED WITH ANOXIC SEDIMENTS AND
STROMATOLITES AT SHARK BAY, W.A.

S. Lupton

A. Hydrogenase Activity:

Gaseous hydrogen plays an important role as an intermediary metabolite during microbial transformation of organic matter. Hydrogen is produced as a catabolic end product by a variety of anaerobic fermentative bacteria and is consumed by both the methanogenic and sulphate reducing bacteria. A measurement of hydrogenase activity is thus a direct measurement of the activity of anaerobic microbial biodegradative processes. The aim of this study was to measure anaerobic hydrogenase activity in a variety of sedimentary sites at Shark Bay and to correlate this activity to specific bacterial degradative processes such as sulphate reduction (G.W. Skyring & L. Dibb, quarterly report).

Method:

hydrogenase activity was determined using the tritium incorporation radioassay. Sediment slurries were prepared in an anaerobic halophilic basal medium (60‰ salinity) prior to the addition of tritium gas.

Results:

1) Comparison of sedimentary sites:

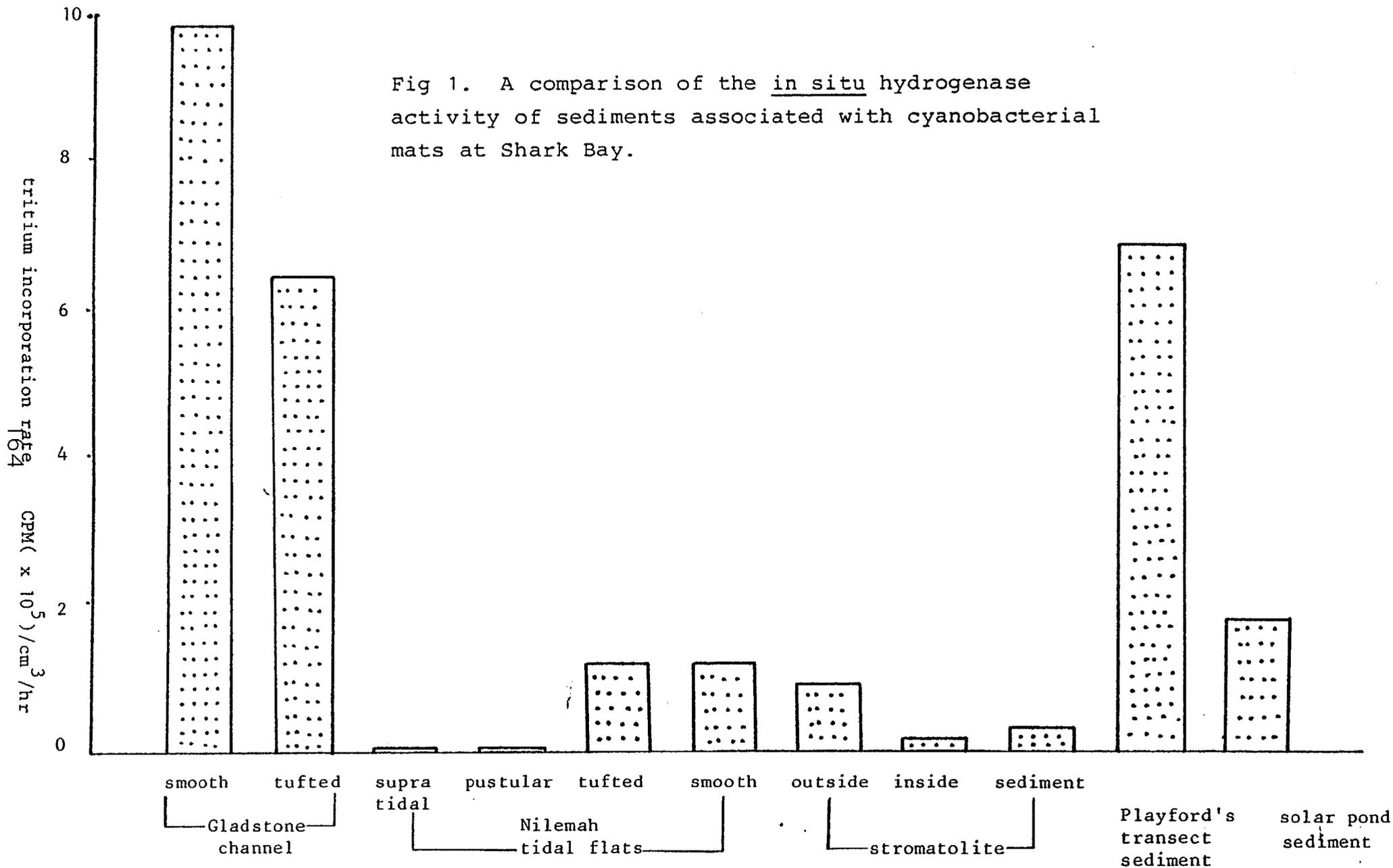
The greatest hydrogenase activity was associated with the reducing sediments underlying the smooth mat on the bottom of the Gladstone tidal channel (Fig. 1). High activity was also associated with the sediments underlying the tufted mat on the sides of the Gladstone channel and also the decaying cyanobacterial material deposited on the beach near Playfords transect. There was much less activity associated with the sediments underlying smooth and tufted mat at the Nilemah tidal flats, compared to the sediments underlying similar mat types at the Gladstone tidal channel. It should be noted that the sediments associated with smooth and tufted mats at the Gladstone site appeared to be darker and richer in hydrogen sulphide compared to the corresponding mat types and sediments at Nilemah. The permanent inundation of the Gladstone mats may be a factor in explaining the higher activity. Sediments underlying accumulated pustular mat debris in small solar ponds at the Nilemah site appeared to have less hydrogenase activity than sediments associated with accumulated cyanobacterial debris at Playfords transect, perhaps a reflection of the higher salinity of the solar pond (170‰) or a difference in composition of the decaying material. Some hydrogenase activity was associated with stromatolites, the greatest activity being associated with the loosely consolidated outer surface and only a little activity was found in the internal carbonate matrix. Slightly more activity was determined in sediments beneath and between the columnar stromatolites.

2) Aerobic and anaerobic hydrogenase activity associated with the smooth mat from Gladstone channel:

There was significantly more anaerobic hydrogenase activity than aerobic hydrogenase activity associated with the upper layers (0-5 mm) of the smooth mat from the Gladstone channel (Fig. 2), thus suggesting that significant anoxic microbial processes can occur within the mat itself. However, a small amount of black reducing sediment may have contaminated the mat during sampling and thus may explain some of the anaerobic activity detected.

B. Methanogenesis:

The pores of subtidal stromatolites have been reported to be partly filled with gas containing some methane (BBL Q.R., Jan. 1984). During the July field trip, gas from a subtidal stromatolite was collected for analysis and methane production from exogenous substrate was investigated.



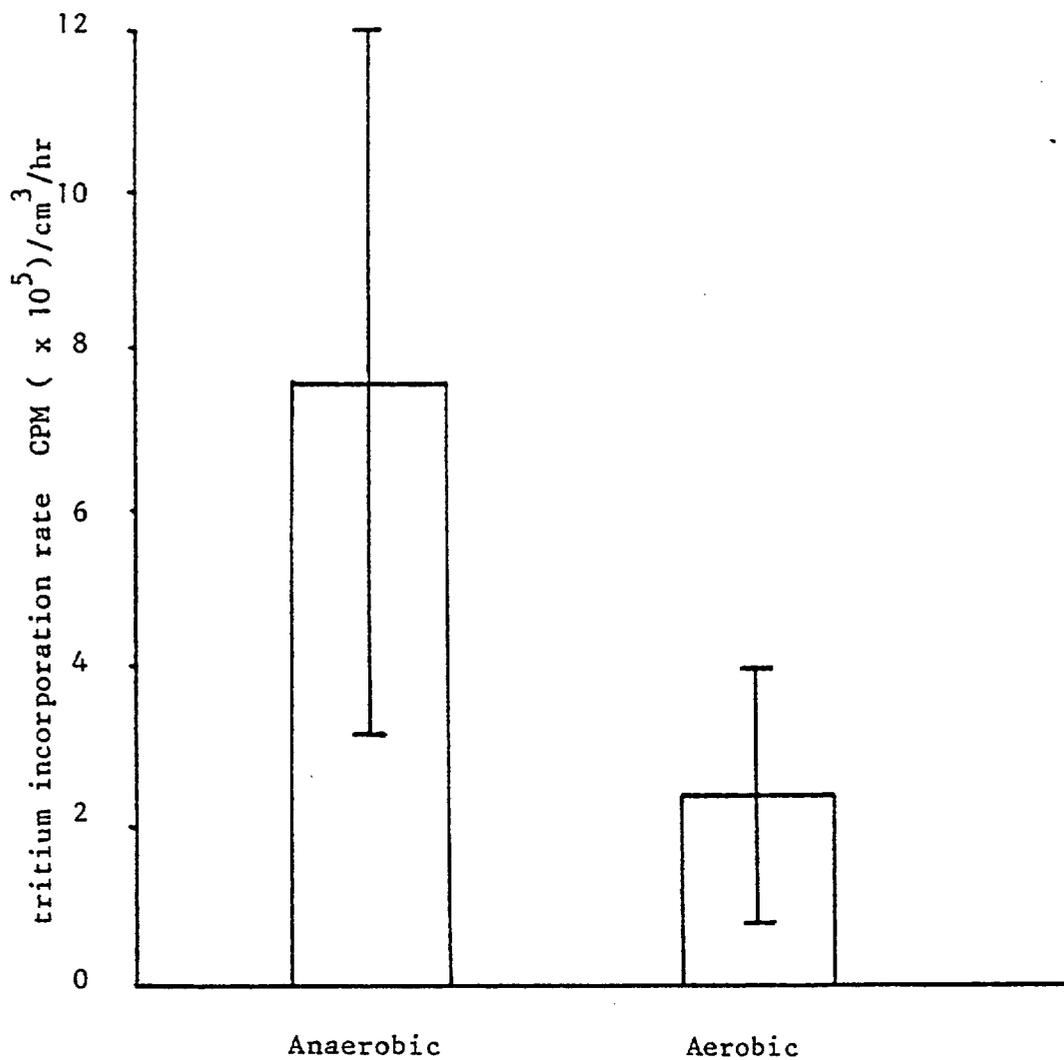


Fig 2. Aerobic and Anaerobic hydrogenase activity associated with the surface layer of smooth mat from the Gladstone tidal channel.

Method:

The stromatolites sampled were obtained approximately 1 km directly offshore from Flagpole Landing in 2 m of water. Gas samples were obtained by placing a plastic bag over the stromatolite and smashing the column with a hammer. The gas released accumulated at the top of the plastic bag and was brought to the surface where it was collected by syringe and injected into a 160 ml bottle completely filled with a solution of 100 μ m HgCl. The bottle was transported back to the lab for analysis by a Carle automatic gas analyser. To determine the effect of exogenous substrates on methanogenic activity, a stromatolite was sampled with a hard rock cover and 5cc of either crushed carbonate matrix or outerskin scrapings were added to 50 ml of anaerobic basal medium in 160 ml bottles. 0.5 ml of 1 M acetate, methylamine or methanol were added to the bottles. The bottles were incubated at ambient temperatures for 40 days prior to the analysis of the headspace gas.

Results:

The analysis of the stromatolite sampled during the July field trip detected no hydrogen or methane and a relatively high partial pressure of oxygen compared to that reported in the January 1984 quarterly report (Table 1). This would suggest that gas composition varies between localised areas within the stromatolites, e.g. anaerobic sites within some pores of the fenestrate carbonate column and aerobic sites associated with the outer cyanobacterial skin. Most of the gas in this sample was apparently obtained from within the aerobic photosynthetic zone. The majority of the internal pores may have been filled with seawater and thus been aerobic. The low anaerobic hydrogenase activity and rates of sulphate reduction detected in the internal carbonate matrix also suggests little anaerobic microbial activity within the body of the stromatolite. However, the technique used to sample the stromatolite gas during the July field trip may have led to air contamination and further samples of stromatolite gas will be obtained during the November field trip. The addition of methylated substrates and acetate did not stimulate methanogenesis in stromatolite material but as the stromatolite appeared to be an oxidised environment, methanogens could be expected to be absent (Table 1).

Table 1. Analysis of gas from subtidal stromatolite and the effect of exogenous substrates on methanogenesis

Sample	Gas Composition (%)			
	CO ₂	O ₂	N ₂	CH ₄
stromatolite gas	0.31	19.91	79.78	0
stromatolite skin/control	0.42	0	99.58	0
acetate	0.50	0	99.50	0
methanol	0.79	0	99.21	0
methylamine	0.80	0	99.17	0
stromatolite matrix/control	0.19	0	99.81	0
acetate	0.36	0	99.64	0
methanol	0.23	0	99.78	0
methylamine	0.25	0	99.75	0

THE EFFECT OF HYPERSALINITY ON AEROBIC MICROBIAL ACTIVITY IN SEDIMENTS OF SHARK BAY

S. Lupton

The anaerobic degradation of complex biopolymers can be divided broadly into two stages : 1) The fermentative breakdown of complex carbohydrates and protein polymers to lower molecular weight alcohols, fatty acids and hydroxyacids. 2) The oxidation of these organic compounds to CO_2 with the concomitant formation of reduced products i.e. methane or hydrogen sulphide. The fermentative oxidation of organic substrates is at the expense of the reduction of a metabolic end product or the production of molecular hydrogen and thus cannot lead to the complete decomposition of organic material. The complete oxidation of organic compounds to CO_2 can only proceed through the reduction of terminal electron acceptors such as CO_2 or SO_4^{2-} . In high sulphate environments, sulphate reduction is the major terminal process responsible for the oxidation of organic substrates to CO_2 (2, 7). Environmental factors which affect fermentative and sulphidogenic processes are therefore of great significance to the preservation and diagenesis of organic material in sediments.

Hypersalinity is one factor which may have a significant effect on microbial activity in anoxic sediments (BBL QR, August 1984). The effect of salinity on fermentative and sulphate reducing activity in enrichments of anoxic sediments from Shark Bay has been investigated. Preliminary results (BBL QR, Aug. 1984) indicated that increasing salinity negatively affected the in situ microbial hydrogenase activity. The aim of this investigation was to determine the effect of salinity on the activities of both the fermentative and sulphate reducing bacteria in enrichments of Shark Bay sediment, separately and in conjunction, with respect to a selective inhibition of either process.

Methods:

Black organic sediment was collected at Playfords transect during the July field trip. Enrichment cultures were prepared by adding 0.5 ml of sediment to 50 ml of anaerobic basal medium in 160 ml bottles sealed with rubber subá seals. The sodium chloride concentration of the medium varied between 0 and 200‰. Microbial growth was determined by optical density. Hydrogen sulphide production was measured with the DTNB technique and fatty acids were determined by G.C. Tritium incorporation was measured using the technique of Schink et al (5).

Results:

To determine the effect of salinity on fermentative processes in Shark Bay sediments, non buffered medium was used with glucose as a substrate. The decrease in pH was used as a measure of organic acid production. Salinity had a significant effect on microbial growth and organic acid production in fermentative glucose enrichments (Fig. 1). Although growth occurred at all salinities, the greatest acid production occurred at salinities below 150‰ and was very slow at 200‰.

To determine the effect of salinity on sulphate reduction, lactate was used as a substrate and growth and H₂S production were measured. As with the fermentative utilisation of glucose, lactate dependent sulphate reduction was also significantly inhibited by salinities greater than 100‰ and was greatly inhibited at 200‰ (Fig. 2). Therefore both fermentative and sulphate reducing activities in Shark Bay sediment show a similar response to increasing salinity with both processes being greatly inhibited at salinities of 200‰ and greater, although there appeared to be more relative growth in fermentative cultures at 100‰ than sulphate reducing cultures.

Interestingly, sulphate reduction was also inhibited in the complete absence of sodium chloride, as many marine sulphate reducers have an obligate requirement for sodium chloride (4).

Tritium incorporation is a measure of both the hydrogen producing activity of the fermentative bacteria and the hydrogen consuming activity of sulphate reducing bacteria (5). Increasing salinity decreased the rate of tritium incorporation in both fermentative and sulphidogenic enrichments (Fig. 3). However, tritium incorporation associated with sulphate reducing activity may be slightly more sensitive to salinity in the range 100‰ to 200‰ than that associated with fermentative processes.

In buffered medium, glucose fermentation could be coupled to the oxidation of organic acids and hydrogen by sulphate reducing bacteria. The effect of salinity on microbial growth and hydrogen sulphide production in buffered glucose enrichments were similar to that observed in the lactate enrichments (Fig. 4). Growth occurred at all salinities but sulphide production was not observed at 0‰ or 200‰ salinity. Analysis of the fatty acid composition of cultures at 7 and 14 days incubation, revealed that fatty acids ranging from C₂ to C₉ were produced fermentatively in all cultures but in those cultures with low sulphate reduction, there is a higher proportion of the high chain

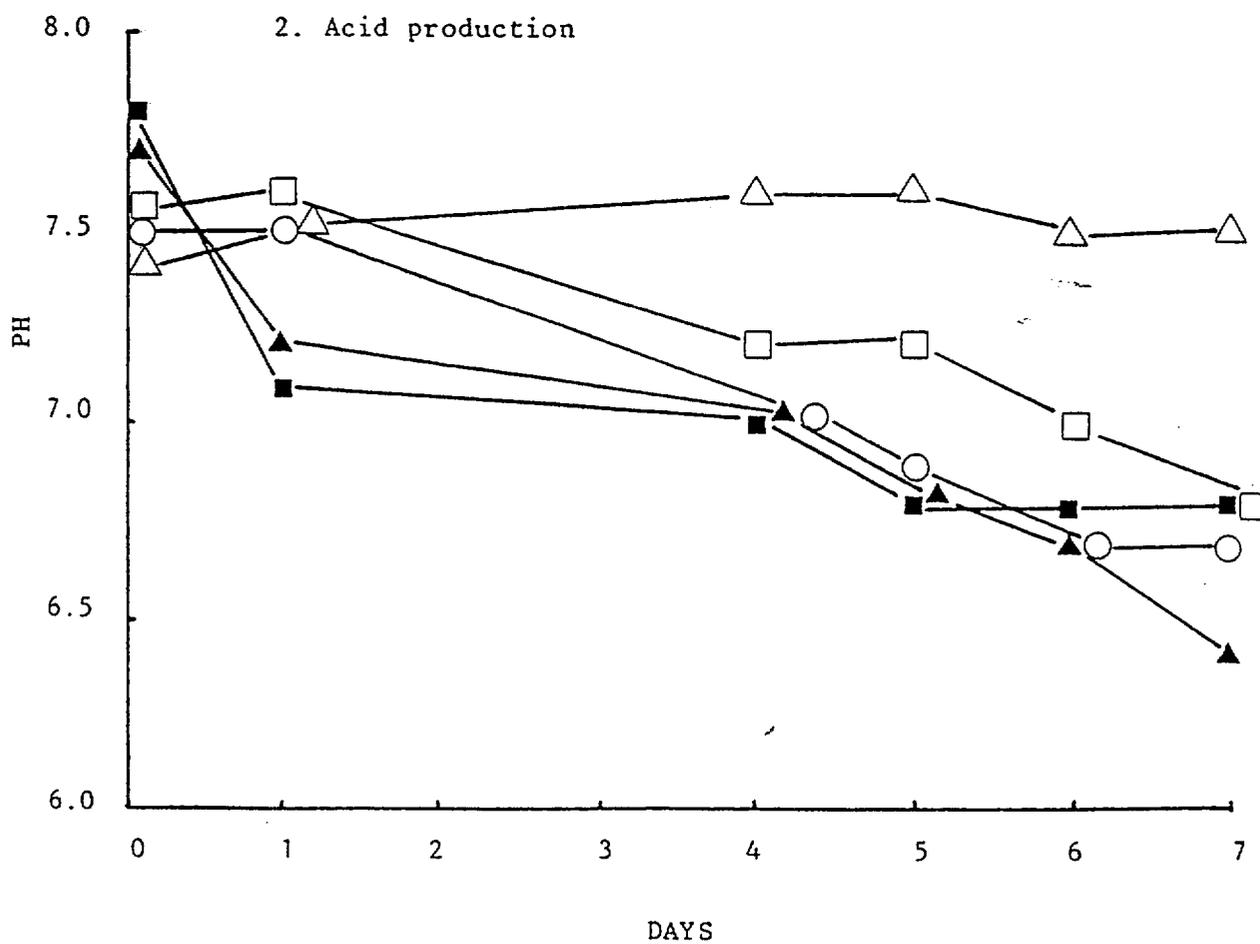
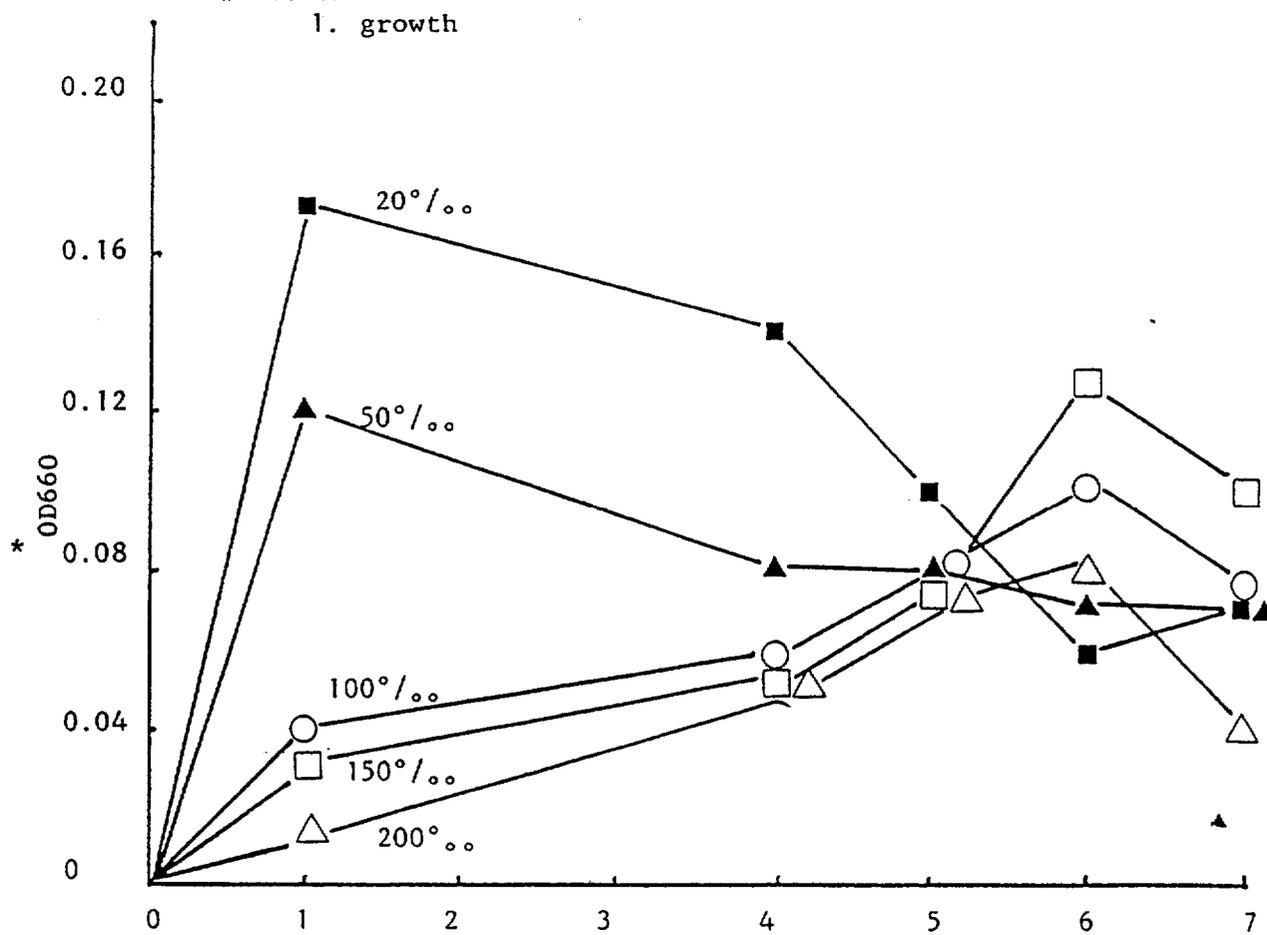


Fig. 1. The effect of salinity on bacterial growth and organic acid production in unbuffered glucose enrichments of Shark Bay sediment.

* Optical Density: Absorbance of culture measured at 660nm wavelength.

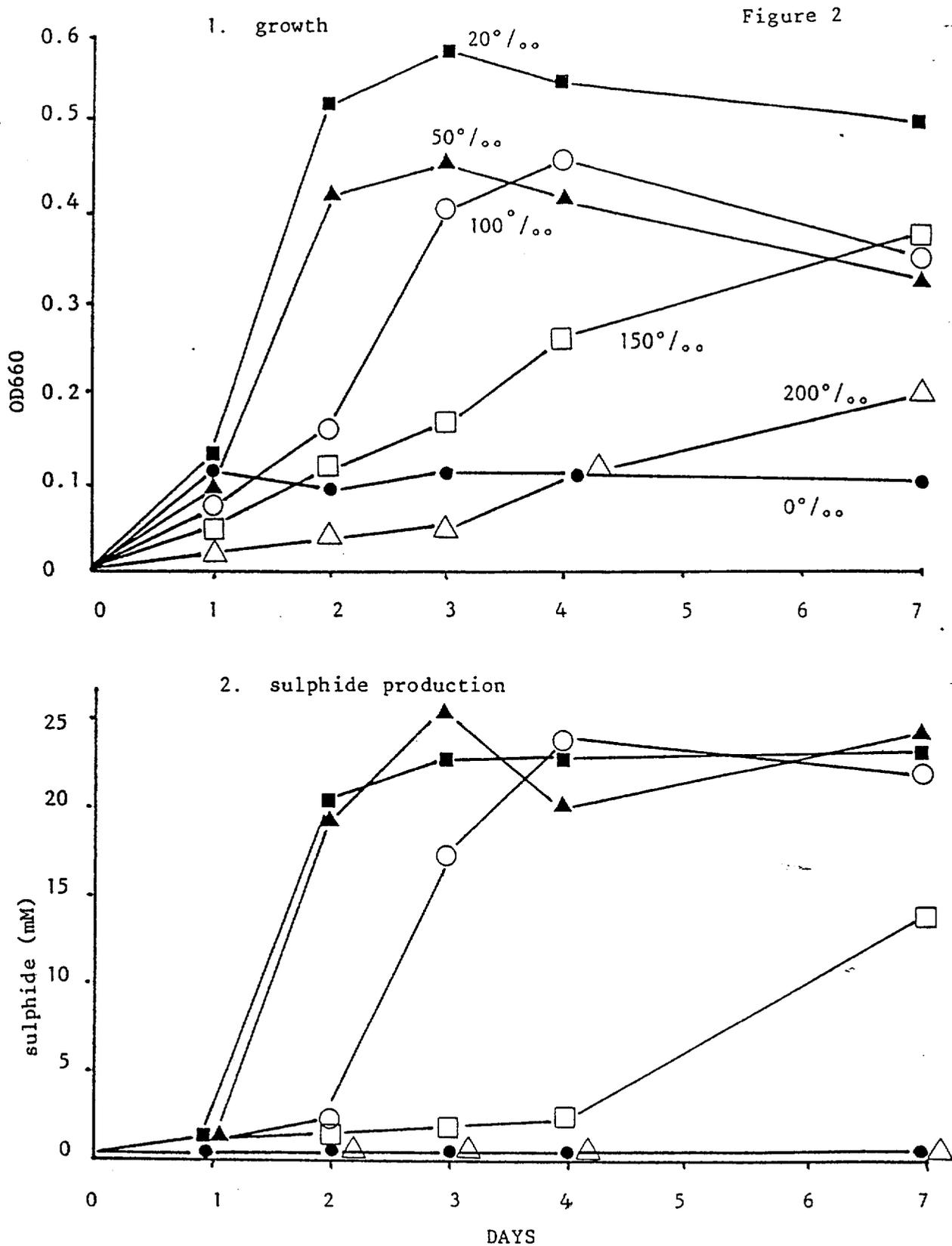


Fig. 2. The effect of salinity on bacterial growth and sulphide production in lactate enrichments of Shark Bay sediment.

Figure 3

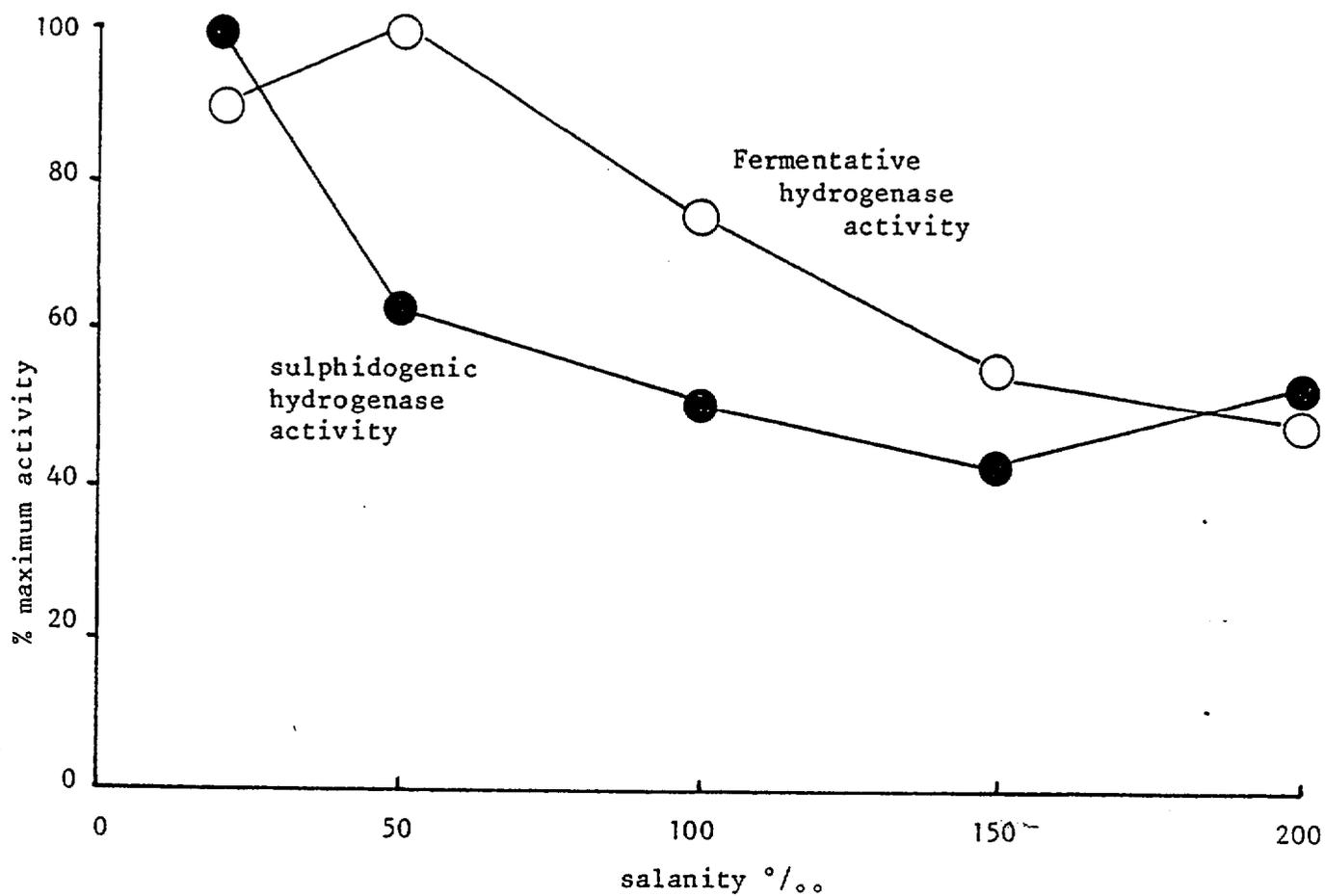


Fig 3. The effect of salinity on hydrogenase activity (tritium incorporation) in fermentative glucose enrichments and sulphate reducing lactate enrichments of Shark Bay sediment.

Figure 4

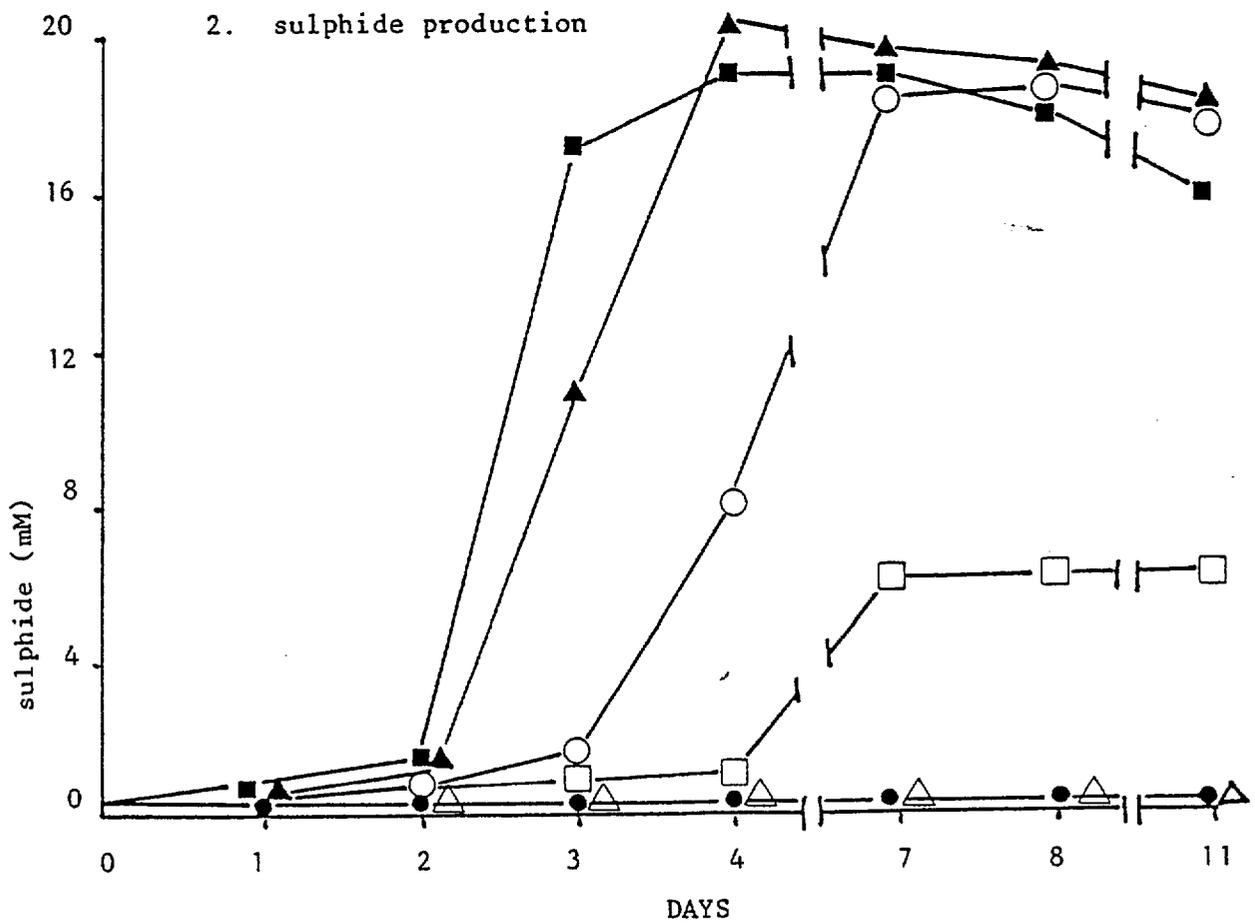
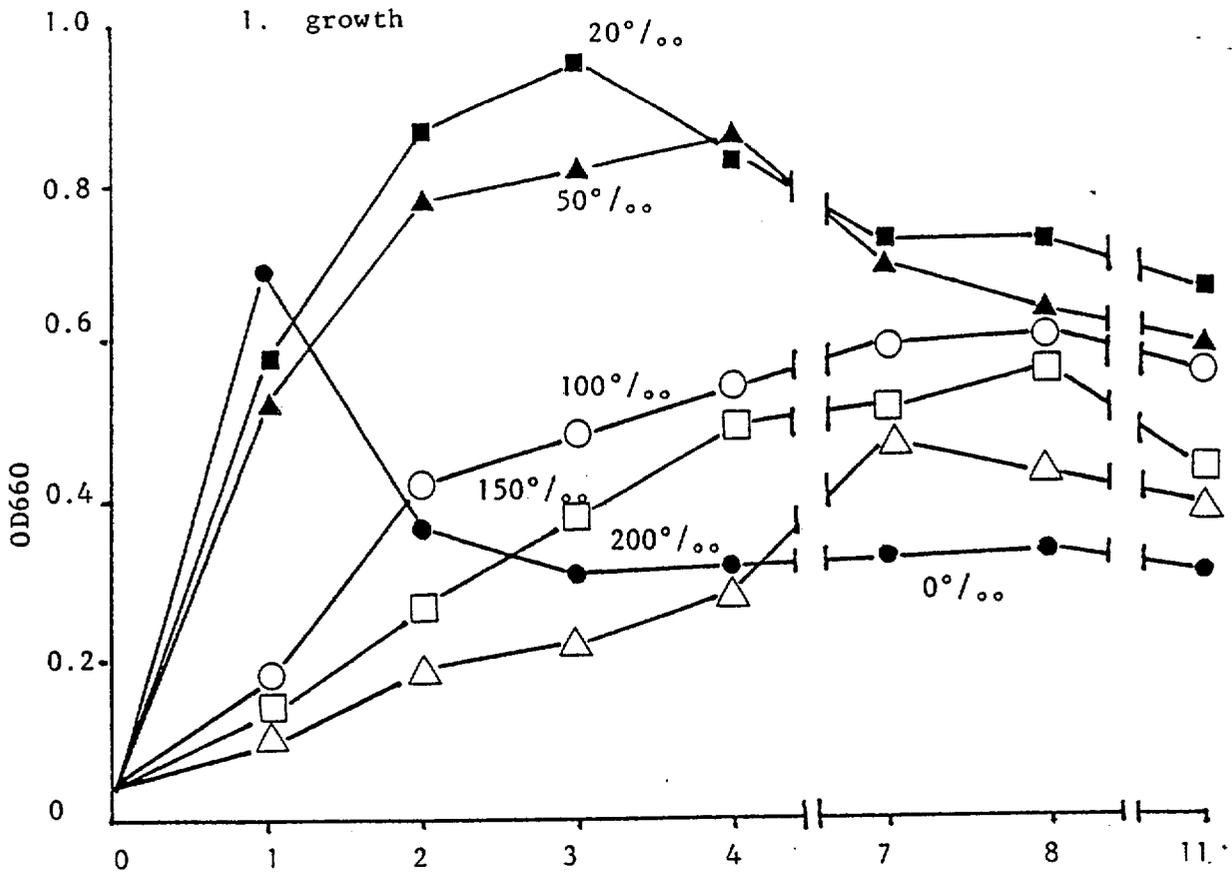


Fig 4. The effect of salinity on bacterial growth and sulphide production in buffered glucose sediments of Shark Bay sediment

length fatty acids (C5 to C9) than those with high rates of sulphate reduction (Tables 1 and 2).

Table 1. Fatty acid composition of glucose enrichments of Shark Bay sediment following 7 days incubation at 30°C.

Fatty acid	concentration (mM)				
	salinity ‰				
	0	20	50	100	200
C2	2.45	2.11	9.01	6.45	3.26
C3	2.76	2.27	2.92	1.41	2.17
C4	0.51	2.37	4.00	3.55	0.96
C5	0.09	0.10	0.29	0.40	1.34
C6	0.22	0.37	0.42	0.10	0.27
C7	0.08	1.03	1.15	0.35	1.04
C8	0.20	0.11	0.40	0.40	0.24
C9	0.10	0.18	0.13	0.13	0.50

Table 2. Fatty acid composition of glucose enrichments of Shark Bay sediment following 14 days incubation at 30°C.

Fatty acid	concentration (mM)					
	salinity ‰					
	0	20	50	100	150	200
C2	36.39	62.13	21.66	37.17	16.98	13.05
C3	1.95	10.25	3.20	4.45	1.28	0.73
C4	2.80	0.45	0	0.33	1.23	5.17
C5	0.08	0	0	0	0	0.08
C6	0.14	0	0	0	0	0.10
C7	0.08	0	0	0	0	0.09
C8	0.09	0	0	0	0	0.07
C9	0.30	0	0	0	0	0.07

Conclusions:

In summary, it has been shown—that:

- 1) anaerobic microbial processes are very active at the in situ salinities of Shark Bay sediments (50 - 70‰).
- 2) both fermentative and sulphidogenic processes are increasingly inhibited by increasing salinity.
- 3) sulphate reduction may be slightly more sensitive to very high salt concentrations compared to corresponding fermentation processes.
- 4) high salinity promotes the preservation of metabolic intermediates such as higher fatty acids.

In high sulphate environments the oxidation of fermentation products, such as higher fatty acids, is accomplished through the activities of the sulphate reducing bacteria. Fatty acids with up to 18 carbons are either oxidised completely to CO₂ or to CO₂, acetate and sometimes propionate (6). If high salinities were to prove more inhibitory to the oxidative process of sulphate reduction than fermentation processes, it would be expected that higher fatty acids would tend to be preserved under conditions of high salinity. At salinities of 200‰ when sulphate reducing activity was greatly inhibited, higher fatty acids were indeed preserved in glucose enrichment cultures of Shark Bay sediment. These results are similar to those observed in the hypersaline sediments of the Great Salt Lake, Utah. When exogenous substrates such as glucose, were added to sediment suspended in a medium of differing salinity, hydrogen was observed to accumulate at the high salinity (200‰) but not at lower salinities (BBL Annual Report, 1983), indicating an uncoupling of fermentative and sulphidogenic processes.

These results have a number of implications regarding the preservation of organic material in hypersaline environments. Sulphate reduction has been shown to be very efficient in the oxidation of organic material at salinities up to 200‰. However, at higher salinities, metabolic intermediates tend to be preserved. Thus, sediments with in situ salinities greater than 200‰ should show 1) a greater preservation of organic matter and 2) organic matter in a more reduced form than corresponding sediments of lower salinity. However, the preservation and accumulation of organic material in sediments is dependent upon the balance (or rather the imbalance) between the processes of primary productivity and microbial biodegradation. Hypersaline environments with good potential for preservation of organic material are those which are highly productive but which have

anoxic sediments with a salinity of 200‰ or greater. Environments of low productivity but with high saline sediments might not show a high content of preserved organic material. Similarly, environments with a high productivity, but with sediments of moderate salinity (<200‰), such as may be found in Shark Bay, would also prove to be poor candidates for organic matter preservation. Australian examples of hypersaline environments favouring the preservation of organic material may include Lake Eliza in South Australia and Hutt Lagoon in Western Australia, which is noted for its high salinity (>200‰) but also its large blooms of the halophilic algae, *Dunaliella* (1, 3).

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ROLE OF PHOTOTROPHIC SULFUR BACTERIA IN MICROBIAL MATS

J. Bauld, D.T. Ho.

Introduction:

The microbial mats investigated in Spencer Gulf and during the earlier field work in Shark Bay generally did not contain significant populations of phototrophic sulfur bacteria. However, several of the mat systems currently under investigation in Shark Bay contain well developed populations of such microbes, in particular members of the Chromatiaceae (Purple Sulfur Bacteria - PSB).

In contrast to other benthic communities where phototrophic bacteria play a dominant role in the construction and morphogenesis of the mat (e.g. the filamentous *Chloroflexus* in alkaline hot springs microbial mats), non-filamentous forms appear to predominate and it seems unlikely that the PSB in Shark Bay mats play a significant structural or morphogenetic role. In the latter mats macroscopically visible layers of PSB are "sandwiched" below an upper, surface layer of cyanobacteria and above a zone of bacterial sulphate reduction. The PSB thus operate at low light intensity, due to shading by the overlying cyanobacteria, and low redox potential as a consequence of underlying H_2S generation.

All known PSB are capable of photosynthetic CO_2 -fixation (primary production) utilizing H_2S (or other reduced S compounds) as a source of reducing power. This process is anoxygenic and obligately anaerobic. It is known that some PSB may also photoassimilate simple organic carbon compounds in the presence of H_2S , and this leads to several questions regarding the role(s) of PSB in carbon cycling within the mat community:

Major question

- * are naturally-occurring populations of PSB in the mats net producers or net consumers of organic carbon?

Subsidiary questions

- * can PSB grow on and/or assimilate organic carbon compounds in the absence of reduced S compounds?
- * are natural populations exposed to such conditions?
- * in the presence of reduced S compounds, CO_2 , and utilisable organic carbon sources, what is the balance between CO_2 -fixation (production) and organic assimilation (consumption)?

- * can this be determined for either, or both, field populations and laboratory cultures?
- * what are the dominant PSB in the mat systems under investigation and what is their potential for organic consumption (heterotrophy)?
- * do PSB compete with sulfate-reducing bacteria for organic compounds?

These and other questions are being approached by both field and laboratory based experiments. Data from the former is still being processed. The following describes some results from investigations carried out during a 5-month period at Indiana University in the laboratory of Professor H. Gest.

Organic carbon utilisation and salinity optimum of *Chromatium vinosum* strain HPC - a phototrophic sulfur bacterium from Hamelin Pool.

J Bauld, J.L. Favinger (Indiana Univ), H. Gest (Indiana Univ).

Organism:

Chromatium vinosum strain HPC was isolated by Gest and Favinger from intertidal sediments collected by Bauld at Playford's Transect, Hamelin Pool.

Objectives:

- * to determine whether strain HPC could grow on organic carbon sources in the absence of H₂S and the range of organic carbon sources utilised.
- * to determine the salinity optimum for growth.

Results and Discussion:

1. Carbon nutrition

C. vinosum HPC grew well on several organic carbon sources (Table 1) in the absence of reduced sulfur species. The redox potential of the medium was poised using ascorbate, a non-utilisable compound for HPC (Table 1). Six of the substrates tested, including acetate, supported growth irrespective of the presence or absence of added CO₂. Growth on propionate, butyrate and valerate occurred only in the presence of added CO₂. However, on initial transfer to the C₃-C₅ fatty acids, growth occurred in the absence of added CO₂ (presumably supported by carryover from the inoculum). Growth was never observed upon the second serial transfer. The reported utilisation of propionate, in the absence of added CO₂ or sulfide, by a strain of *C. vinosum* isolated from Lake Beloe sediments (Shaposhnikov et al, 1960) may be due to the apparent lack of serial transfers. These workers reported

the need for heavy inoculum and used long incubation periods. We have found that growth, with or without CO₂, is usually indistinguishable on the first transfer to propionate. Growth on butyrate and valerate was accompanied by the conspicuous accumulation of PHB granules.

In addition to fatty acids of chain length C₂-C₅, utilisable substrates included TCA cycle intermediates or those compounds which could be fed into the TCA cycle (Table 1). Doubling times were commonly 8-10 hours, occasionally as short as 6-7 hours and as long as 15-20 hours. Twenty-three other compounds were tested but all failed to support growth. Substrates not utilised included sugars, amino acids, alcohols and some TCA cycle intermediates. The inability of HPC to utilise several amino acids is consistent with the report of Wagner et al. (1973) which showed that *C. vinosum* strain D (the reference strain) was unable to use any amino acid as carbon source. Fructose appeared to support low levels of growth (ca 1 doubling/day to a maximum of 3 doublings) occasionally upon initial transfer of HPC but this was never sustained on subsequent serial transfer.

HPC exhibited strong photoheterotrophy, utilising 9 substrates, and is notable for its ability to utilise lactate, butyrate and valerate. Only one other strain of *C. vinosum* is also reported to use butyrate (Thiele, 1968), and two other strains to use lactate (Thiele, 1968; Trüper, 1968). Valerate - utilising strains of *C. vinosum* have not, to our knowledge, been previously reported, although *C. purpuratum* strain BN5500, isolated from the marine sponge *Ircinia*, can also utilise valerate (Imhoff and Trüper, 1980). In fact, except for its ability to utilise casamino acids and fructose (in the presence of CO₂ and sulfide), its carbon source spectrum is identical to that of HPC.

HPC was unable to utilise caproate (with CO₂) at concentrations of 1-20mM. It is of interest that glycolate, a compound excreted, often in large amounts, by microalgae including cyanobacteria (Fogg, 1971; Cheng et al., 1972), is not utilised by HPC or other *C. vinosum* strains. On the other hand, glycolate has been reported as an extracellular product of *C. vinosum* strain D under certain conditions (Asami and Azakawa, 1974).

2. Salinity

C. vinosum strain HPC was tested for photoheterotrophic growth (malate as carbon source) at various NaCl concentrations (Fig. 1) under static conditions as for organic carbon studies. After three sequential transfers at each of the salinities presented HPC did

not grow at 0, 0.1, and 10% NaCl. Growth at the salinity limits was slowest at 0.5% NaCl (d.t. = 22h), while at 8.75% NaCl the doubling time fell to 10h. The maximum growth rate occurred at 3.5% NaCl where the doubling time was 3.6h, and growth was also rapid (d.t. \leq 4.0h) at 2.5 and 4.5% NaCl. These rates compare favourably with those obtained during growth of agitated cultures (B. Fry, pers. comm). Although the initial enrichment for HPC was made using 5% NaCl, the salinity range for optimum growth of this strain (ca 2.5-4.5% NaCl) is considerably lower than the salinity of the Hamelin Pool water column (ca 65-70‰) and the pools of evaporating water ponded in the intertidal area (ca >95 ‰).

A perusal of published data suggests that the relationship between habitat, enrichment and growth salinities is quite variable. For example, *C. vinosum* strain 8214 (Trüper, 1970) which was isolated from a brackish pond using 3% NaCl, has a lower preferred salinity of 2% NaCl, the latter being more characteristic of its habitat. However, *C. purpuratum* BN5500 isolated from marine sponge fragments has a higher optimum, at 5% NaCl, despite enrichment using 3% NaCl (Imhoff and Trüper, 1980). Matheron & Baulaigue (1972) reported that their strain CA1812, later identified as a *C. vinosum* (Matheron and Baulaigue, 1983) grew best at 1-3% NaCl, with growth at 6% but not at 10% NaCl. Good growth was also reported in the absence of NaCl, consistent with its isolation from a brackish habitat (Matheron and Baulaigue, 1972). Several other *C. vinosum* isolates were reported to prefer salinities of 1-3% NaCl (Trüper, 1970).

Thus, while strain HPC is clearly an obligate halophile, it does not exhibit the elevated salinity optimum that one might intuitively expect from its highly saline habitat. There are two possible explanations for this result. It may be the consequence of continued maintenance of this organism at 2.5% NaCl since its isolation. On the other hand it is possible that ground waters of low salinity may feed into the sediments from which HPC was isolated.

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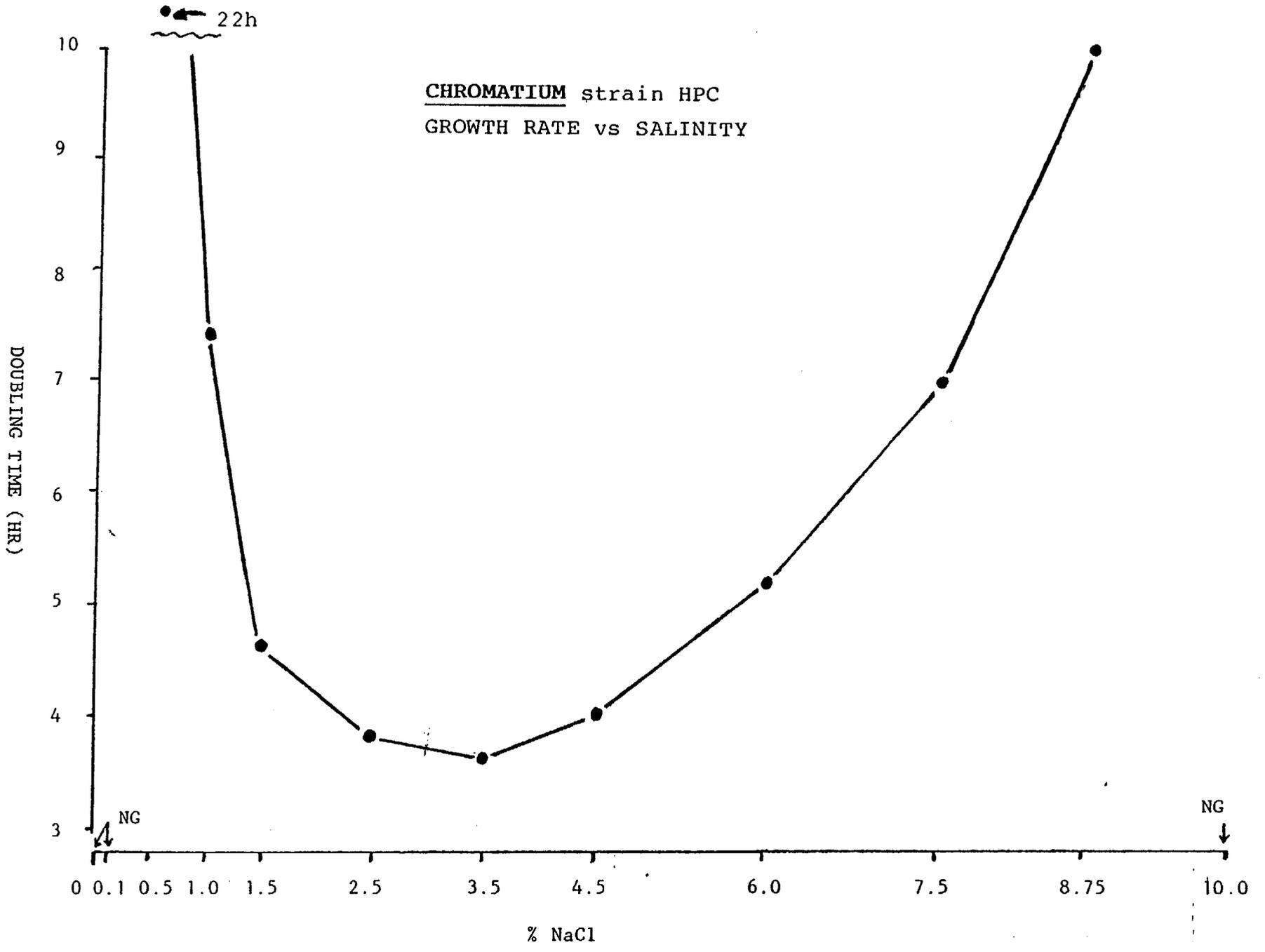


Figure 1. Response of Chromatium vinosum HPC to salinity as determined by rate of growth at various NaCl concentrations.

Table 1. Organic carbon substrates tested for utilization by *Chromatium vinosum* strain HPC.

A. Utilizable substrates:

acetate, propionate*, butyrate*, valerate*,
fumarate, malate, succinate
lactate, pyruvate

B. Non-utilizable substrates:

formate, caproate, tartrate, citrate, α -ketoglutarate,
gluconate, glycolate, ascorbate, glutamate,
aspartate, alanine, arginine, peptone, casamino acids,
fructose, glucose, mannose, ribose, sucrose,
methanol, ethanol, propanol, glycerol.

* utilized only in presence of bicarbonate (10mM).

Shark Bay, Western Australia

Nilemah Embayment

Core samples were taken along the Nilemah Transect NM (p13, Quarterly Report, May 1984) to coincide with the following:

- supratidal sediments where there was a subsurface reduced zone
- sediments colonized by crenulate and pustular cyanobacterial mat
- sediments colonized by tufted cyanobacterial mat
- sediments colonized by smooth cyanobacterial mat

Sulfate reduction rates were determined in the sediments of the reduced zone of the supratidal environment and in 5cm layers of the cores taken from the sediments colonized by cyanobacterial mats. Data are given in Tables 11 and 12. Sulfate reduction rates in the supratidal sediments taken from the 30-35cm and 45-50cm layers were below detectable limits. However the estimate for the 45-50cm layer was just above background and may be indicative of a very low sulfate reduction rate. Much longer incubation periods will be used in subsequent experiments since there must be some kind of microbial activity that results in the preservation of the reduced sulfur which is detected as tin-reducible sulfur (35 to 72 μ mol/g). Sulfate reduction rates in the sediments colonized by mats were highest in the smooth mat sediments, followed by tufted mat. Sulfate reduction was not

detectable in the pustular mat and this has been observed previously. Sulfate reduction rates in the sediments below 10cm were approaching unmeasurable limits, however there did appear to be low but detectable rates in the sediments beneath the tufted mat. There was also appreciable amounts of tin-reducible sulfide in these sediments below 10 to 20cm (Table 13). Marine waters must be moving through these sediments at a reasonable rate. What environmental conditions prevail to maintain conditions which result in the preservation of the "pyrite" in the subsurface layers is not yet known. Dr. F.S. Lupton has measured low but detectable hydrogenase activity in subsurface sediments and this is indicative of microbial activity.

Playford's Transect

Since our previous trip to Shark Bay in June 1983, a deposit of decaying organic sludge, around 50x10m in extent, has collected about 150m west of the line of Playford's transect. The area smelled strongly of H₂S and sulfate reducers was obviously very active. Several samples were taken from various parts of the sludge and sulfate reduction rates were determined. Some freshly formed and older buried sediments were also taken for age determination. The sulfide content of the suspended sediments was also determined. The porewaters from these samples were also analysed. The rates of sulfate reduction in this material were very high, up to 260umol/g/day. At this rate, sulfate at a concentration equivalent to that of Hamelin Pool water is turned over every 4 days. These very high rates are also reflected in the porewater chemistry. In this environment, incorporation of ³⁵S into the tin-reducible fraction was around 20%.

Microbial activity in subtidal stromatolites

Small cores were taken from a subtidal stromatolite off Flagpole Landing and sulfate reduction rates were determined for the soft sediment/microbial growth covering the stromatolite, for samples from the body, from the base of the stromatolite and from sediment slightly removed from the stromatolite. Sulfate reduction was occurring in the sediments covering the stromatolite and also in the sediments from the base and surrounding sediments. Sulfate reduction was not detected in the cemented carbonate matrix of the stromatolite. Dr. F.S. Lupton observed similar patterns for microbial hydrogenase activity. There was a grey mottled appearance to the stromatolite matrix; the pigmenting material was not soluble in acid but it was degraded by boiling HCl/Sn and sulfide was recovered during the digestion. It is presumed that the grey mottling was due to

pyrite. This will be checked subsequently. These studies will be continued to determine if sulfate reduction occurs at very low rates in the carbonate matrix of stromatolites and to determine the origin of the tin-reducible sulfur.

These studies at Shark Bay have increased current knowledge on anaerobic microbial processes occurring in the various cyanobacterial environments around Hamelin Pool.

Table 11. Nilemah, Shark Bay, June 1984, Transect NM
Sulfate reduction rates, $\mu\text{mol m}^{-2} \text{d}^{-1}$

DEPTH cm	PUSTULAR			TUFTED			SMOOTH		
	AVS	TRS	RATEM	AVS	TRS	RATEM	AVS	TRS	RATEM
0-5	0	105	105	218	867	1085	163	1132	1295
5-10	0	61	61	11	154	165	239	1951	2190
10-15	0	89	89	4	176	180	0	48	48
15-20	0	97	97	4	164	168	0	62	62
20-25	0	93	93	3	118	121	0	132	132
25-30	0	112	112	2	179	181	0	92	92
30-35	0	94	94	5	159	159			
35-40	0	72	72	1	164	165			
40-45	0	64	64	0	123	123			

Table 12. Nilemah, Shark Bay, June 1984, Transect NM
Sulfate reduction rates, $\text{nmol g}^{-1} \text{d}^{-1}$

DEPTH cm	PUSTULAR			TUFTED			SMOOTH		
	AVS	TRS	RATEG	AVS	TRS	RATEG	AVS	TRS	RATEG
0-5	0	145	145	110	200	310	520	1430	1950
5-10	0	60	60	10	200	210	90	2300	2390
10-15	0	70	70	10	190	200	0	60	60
15-20	0	110	110	1	10	190	190	60	60
20-25	0	110	110	0	130	130	0	150	150
25-30	0	130	130	0	180	180	0	100	100
30-35	0	90	90	0	150	150			
35-40	0	70	70	0	170	180			
40-45	0	70	70	130	130				

Table 13. Nilemah, Shark Bay, June 1984 Transect NM
Sulfide concentration of the sediment, $\mu\text{mol g}^{-1}$

DEPTH	PUSTULAR			TUFTED			SMOOTH		
	AVS	TRS	TOTS	AVS	TRS	TOTS	AVS	TRS	TOTS
0-5	0	3.82	3.82	2.40	7.25	9.80	2.50	9.3	11.8
5-10	0	1.14	1.14	0.10	3.10	3.20	1.02	10.9	11.9
10-15	0	3.93	3.93	0.08	3.20	3.28	0.64	9.9	10.5
15-20	0	1.17	1.17	1.77	28.4	30.2	0.03	79.4	79.3
20-25	0.62	31.5	32.1	2.16	56.6	58.9	0	40.6	40.6
25-30	0.23	41.7	41.9	0.06	70.9	71.0	0	21.5	21.5
30-35	0.40	53.2	53.6	0	69.7	69.7			
35-40	0.18	88.8	88.9	0	69.5	69.5			
40-45	0.30	26.0	26.3	0	69.1	69.1			

The symbols used in the preceding Tables are as follows:

AVS- Acid volatile sulfide

TRS- Tin-reducible sulfur

RATEM- Sulfate reduction rate as $\text{mmol m}^{-2} \text{day}^{-1}$, the sum of the rates calculated from ASV and TRS data.

RATEG- Sulfate reduction rate as $\mu\text{mol g}^{-1} \text{day}^{-1}$, the sum of the rates calculated from ASV and TRS data.

TOTS- Sulfide content of the sediment as $\mu\text{mol g}^{-1}$, the sum of the ASV and TRS fractions.

Sr⁸⁷/Sr⁸⁶ RATIOS OF CARBONATE SEDIMENTS

J. Ferguson, L.A. Plumb.

Eight samples of carbonate rocks and sediments from several modern environments have been analysed for Sr⁸⁷/Sr⁸⁶ to assess the potential of this technique to discriminate between the products of marine and meteoric water diagenesis. One sample, a subtidal/intertidal stromatolite of Holocene age, was considered to be an example of a minimally altered marine carbonate. The remaining samples are from Holocene and Cretaceous environments thought to have been influenced by meteoric groundwaters.

Although several of the samples had $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values within the normal marine ranges for the Holocene and Cretaceous, only the Holocene stromatolite has a Sr⁸⁷/Sr⁸⁶ value close to the marine range. All of the samples presumed to have been affected by meteoric waters have high Sr⁸⁷/Sr⁸⁶ values but the extent of the increase was not obviously related to the corresponding $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. It probably reflects both the groundwater province and the proportion of non-marine carbonate which is present. Thus aragonite cement precipitated from saline groundwater springs at Fisherman Bay shows a higher deviation from the marine value than a soil calcrete from Hamelin Pool, despite the fact that both are close to 100% non-marine carbonate and the calcrete has the more negative C and O stable isotope values.

Significantly, several meteoric water-influenced samples whose C and O stable isotope values are within the marine range, show small but analytically significant differences from the marine Sr isotope value (e.g. Lake Eliza: lithified "chip"; Sleaford Mere laminated carbonate). It appears, therefore, that the Sr⁸⁷/Sr⁸⁶ ratios could be the more sensitive indicator of non-marine influence in the diagenesis of marine sediments than stable isotope composition. The two techniques are essentially complementary, however, because the C and O stable isotope data may provide information on solution composition and precipitation temperatures. This additional information is most evident when the data for the dolomitised quartz sand from Hamelin Pool are considered. The C and O data are consistent with precipitation of dolomite from an evaporated marine water, although the $\delta^{13}\text{C}$ value is lower than those for adjacent marine horizons and the sediments are currently within the meteoric water zone. The Sr⁸⁷/Sr⁸⁶ value is higher than the marine value, but is not as high as the soil calcrete from the terrestrial

environments of the hinterland. Although this is evidence for some non-marine influence, it is not clear whether this was inherited from a soil calcrete precursor or whether it was inherent in the dolomitizing groundwaters.

Table 1. Strontium, Carbon and Oxygen Stable Isotope Ratios for Carbonate Sediments from Marginal Marine Environments.

Environment	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{SMOW}}$ (‰)
Modern marine samples			
Mean :	0.70907 ⁽¹⁾		
Range :	0.70901		
	to 0.70914		
Hamelin Pool; stromatolite (intertidal/subtidal marine)	0.70919		
Marine Sediments :	-	0 to +4	+29 to +31
Hamelin Pool; dolomitized quartz sand overlying a marine horizon	0.70947	0.3	+37
Hamelin Pool; calcrete in quartz sandstone in terrigenous environment	0.71045	-5.93	+27
Lake Eliza : Lithified "chip" probably cemented by carbonate precipitated from low-salinity meteoric groundwaters	(a) 0.70949		
	(b)	+2.0	+32
Fisherman Bay : Aragonite cement precipitated from saline meteoric groundwater	(a) 0.71476		
	(b)	-4.38	+22.60

Sleaford Mere : Laminated deposit, possibly from meteoric springs	(a) 0.70939		
	(b) -	+4.27	+34
Cretaceous Marine	0.70715 ⁽¹⁾ to 0.7077		
Hamelin Pool; altered Cretaceous Chalk	(a) 0.70881	-7.00	+26.5
Hamelin Pool; duricrust overlying Cretaceous Chalk	(a) 0.70974		
	(b) -	-8.34	+25

(1) W.H. Burke, R.E. Denison, E.A. Hetherington, R.B. Koepnich, H.F. Nelson, J.B. Otto. Variation of seawater Sr⁸⁷/Sr⁸⁶ throughout Phanerozoic time. *Geology*, 10, 516-519. (1982).

BAAS BECKING GEOBIOLOGICAL LABORATORY
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GEOBIOLOGICAL CONTROLS ON PETROLEUM
FORMATION AND ACCUMULATION

INTRODUCTION

In Shark Bay, research on bacterial sulfate reduction and methanogenesis has continued and a search for organic biomarkers has begun. This research is accompanied by sedimentological studies aimed at providing an environmental framework for interpreting biological and organic geochemical data.

SUBMARINE SEDIMENTOLOGICAL STUDIES IN SHARK BAY

R.V. Burne, R.E. Summons, R.W. Dunlop.

SCUBA was used to study variations in the sedimentary environments of the basin plain of Hamelin Pool, and to investigate the subtidal stromatolitic eco-systems offshore from Carbla Point and Flagpole Landing.

The stromatolites were photographed, and attempts were made to recover gas from the fenestrae of some examples, but no gas was encountered.

Observations were made at six stations along a transect running north-south down the axis of Hamelin Pool. Surface samples, cores, and photographs were obtained at all localities, which varied in depth from 6m to 8m. Cores and photographs were also taken at one station in the sea grass banks of the Fauré Sill.

A major contrast exists between the basin-plain environments of the northern and southern sections of Hamelin Pool. The northern environments show variation with increasing salinity as previously described by Hagan and Logan (1974) but all are characterised by firm bivalve and foraminiferal carbonate sand deposits. South of the latitude of Flagpole Landing a previously undescribed environment is encountered, with very fine-grained diatomaceous silts forming a fluid floc at the sediment surface. These areas support an active community of fish, shrimp, small gasteropods, and live *Fragum*. Detailed investigations of the sedimentology and organic geochemistry of samples from this environment are in progress.

ORGANIC GEOCHEMICAL STUDIES IN SHARK BAY

R.E. Summons, R.W. Dunlop, R.V. Burne.

Sediment cores from the north-south transect of the basin plain of Hamelin Pool, and from the adjacent sublittoral platform have been sampled and are undergoing organic geochemical analyses concurrently with their sedimentological description.

In the short term, the general distribution of organic matter, both laterally and vertically is being determined as will its gross characteristics such as H/C and O/C ratios. Several cores have been subsampled for simultaneous determination of microbial activity.

As a longer term aim, we will determine the distribution of specific groups of biomarkers, particularly free hydrocarbons, fatty acids and sterols which should be markers for both primary producers and degradative bacteria. It has already been determined that a highly unusual branched C-20 hydrocarbon (2,6,10-trimethyl-7-(3-methylbutyl)-dodecane) and related C-25 alkene and alkane can be used to distinguish the sediments of the hypersaline Shark Bay waters from the oceanic sediments to the north (R.W. Dunlop and P.R. Jeffries, *J. Org. Geochem.*, 1985, in press). The former of these compounds has been reported from several environments including the Great Salt Lake (Utah, U.S.A.) but its exact source organism has never been determined. By simultaneously quantifying the distribution of this and other biomarkers and various parameters for microbial activity in Shark Bay it is hoped that the identity of the major groups of organisms contributing organic matter to Shark Bay will be established.

SULFATE REDUCTION IN HOLOCENE ENVIRONMENTS

G.W. Skyring, S. Dibb

Hamelin Pool, Shark Bay - November 1984 Field Trip

A vibrocorer was used to collect subtidal sediment cores from six stations in Hamelin Pool. After the cores were split and examined, replicates were sampled for sulfate reduction rate determinations and also for porewater extraction and chemical analyses (sulfide, ammonia, alkalinity, pH, salinity, phosphate). A novel centrifuge tube assembly was used to collect the porewater under low oxygen tension. Most of the analyses associated with these studies have now been completed and the data are being processed. Drs Summons and Burne discovered an extensive area of subtidal sediment in the southern part of the basin which was black, smelling of hydrogen sulfide and, at least for the upper 10cm, appeared to be highly organic. A 140cm core was obtained at this location and preliminary data suggest that the sulfate reducers are very active in the upper 10cm but their activity can be detected to a depth of 40cm. Sulfate reduction below that depth was not detectable. Sulfate reduction rates were also determined for several intertidal locations and these were supplemented with porewater analyses. The extensive survey of sulfate reduction in Hamelin Pool environments is now almost complete.

METHANOGENESIS IN SULPHATE RICH SEDIMENTS OF SHARK BAY

S. Lupton

Methanogenesis in sulphate containing marine surface sediments is barely detectable and must play an insignificant role in the mineralisation of organic matter and the total carbon flow (2, 3). However, methanogenesis in such environments may be significant in the mineralisation of nitrogen containing compounds (2) and may be quantitatively more important in environments of high salinity (BBL Annual Report, 1983). Quaternary ammonium compounds such as choline and betaine are produced as osmoregulatory compounds by a wide variety of bacteria, algae and invertebrates in high salinity environments (5, 6) and these compounds can be degraded anaerobically to trimethylamine, a suitable substrate for methanogenesis (2).

The aim of this study was to determine whether quaternary ammonium compounds in sediments of Shark Bay supported either methanogenesis or sulphate reduction and to isolate cultures of micro-organisms capable of utilising these substrates.

Method:

Black, organic-rich sediment was collected from pools between adjacent intertidal stromatolites at Flagpole Landing, Shark Bay. Ten ml of sediment was added to 150ml serum vials containing 40ml of anaerobic Shark Bay seawater. The vials were flushed with N₂ gas and 0.1ml of 2% Na₂S solution was added as a reductant. Substrates were added to give a final concentration of 2mM. The vials were incubated at room temperature for 20 days, after which time 1ml of the headspace gas was analysed on the Carle automatic gas analyser. For enrichment cultures, 0.1ml of culture was removed from the vials and inoculated into a basal medium containing 10mM substrate. The cultures were incubated for 7 days at 30°C before transfer (1ml) to new medium. Following the second transfer, 1ml of the headspace gas was analysed as previously. The sulphide concentration of the cultures was determined using the DTNB technique.

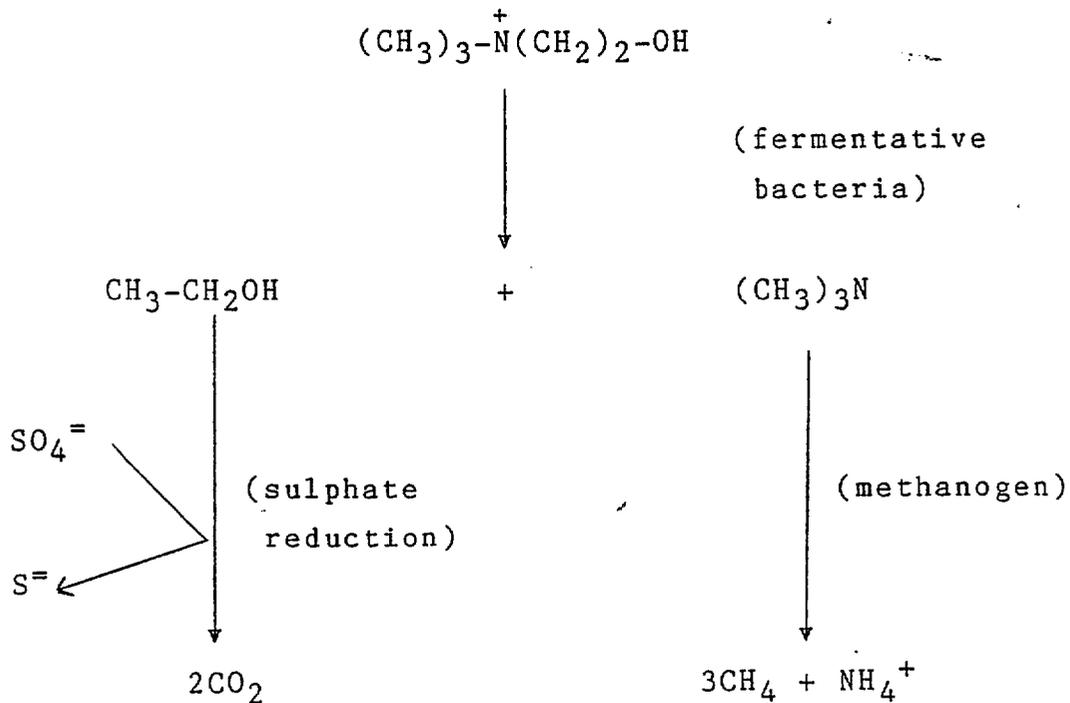
Results:

The addition of trimethylamine stimulated the greatest production of methane from Shark Bay sediment (Fig. 1). Choline and methionine also stimulated methanogenesis but neither butyrate nor lactate stimulated methane production. No methane was produced in vials containing sediment without added substrates. A similar result was found in enrichment cultures

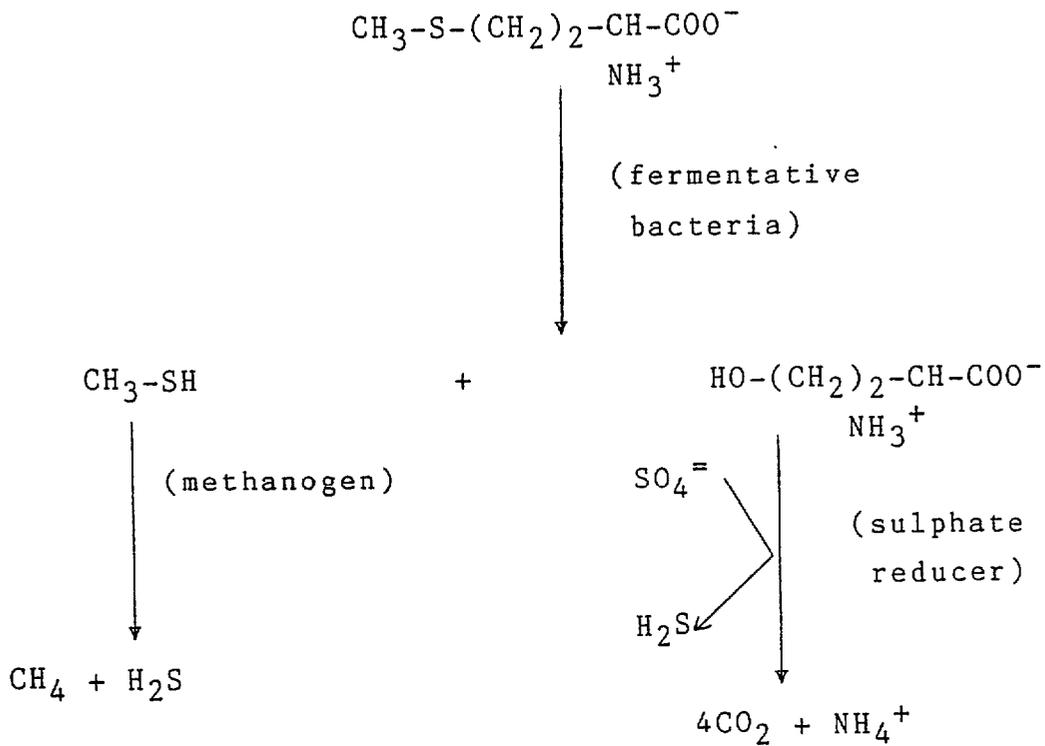
(Fig. 2). Again, the greatest concentration of methane was observed in the headspace of trimethylamine enrichments but methane was also present in choline and methionine enrichments. Low levels of hydrogen sulphide were present in trimethylamine cultures but significant hydrogen sulphide was present in choline and methionine cultures. The greatest hydrogen sulphide concentrations were present in the butyrate and lactate enrichment cultures. The concentration of CO₂ in the headspace of the enrichment cultures appeared to correlate with the concentration of dissolved H₂S. Again, the highest levels of CO₂ were found in the butyrate and lactate cultures.

Discussion:

Trimethylamine was shown to be a methanogenic precursor in the high sulphate-containing sediment from Shark Bay. Trimethylamine did not stimulate sulfidogenesis and CO₂ evolution, suggesting that this substrate was metabolised exclusively to methane. Quaternary ammonium compounds such as choline were also shown to promote methanogenesis, presumably via trimethylamine as a metabolic intermediate. As well as stimulating methanogenesis, choline did promote simultaneous sulphate reduction, presumably through the utilisation of ethanol by sulphate reducers.



Like choline, methionine also promoted methanogenesis. Analysis of the headspace gas during methionine degradation revealed the presence of an unidentified peak, possibly methylmercaptan, a suitable precursor for methanogenesis (4).



As with choline, methionine simultaneously stimulated sulphide production as well as methanogenesis. However, as well as sulphide produced by utilization of the amino acid intermediate by a microbial consortia including sulphate reducing bacteria, it is possible that sulphide could be generated directly from the utilization of methylmercaptan by the methanogen.

Osmoregulatory compounds such as choline and more commonly, glycine betaine, can be produced in significant quantities by cyanobacteria living in hypersaline habitats (5). The extensive cyanobacterial mats in Shark Bay are subject to a wide range of salinities, including hypersaline conditions (1). The biodegradation of this material under anoxic hypersaline conditions may involve methanogenesis as a significant process for the mineralisation of nitrogen containing osmoregulatory compounds. If this is the case, then the methanogens have a significant role in both carbon and nitrogen recycling within the mat-sediment ecosystem. However, significant methanogenesis

was not detected during the decomposition of algal material collected from the surface of subtidal stromatolites (BBL Q.R., Nov. 1984). Further investigations are required to quantitate methanogenesis during the decomposition of cyanobacterial material in environments of varying salinity within the Shark Bay field site and also in cyanobacterial mat systems in hypersaline environments such as Hutt Lagoon, W.A.

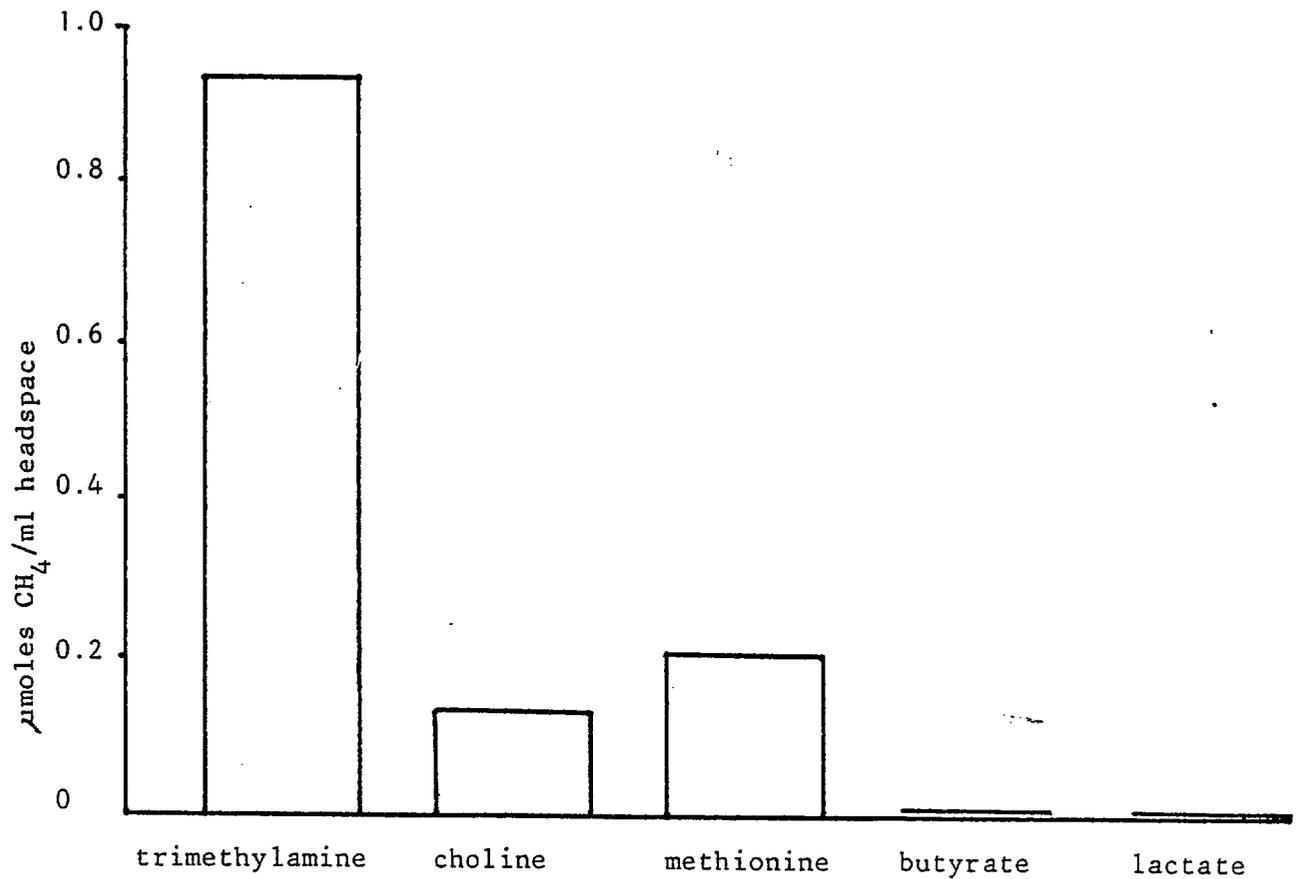
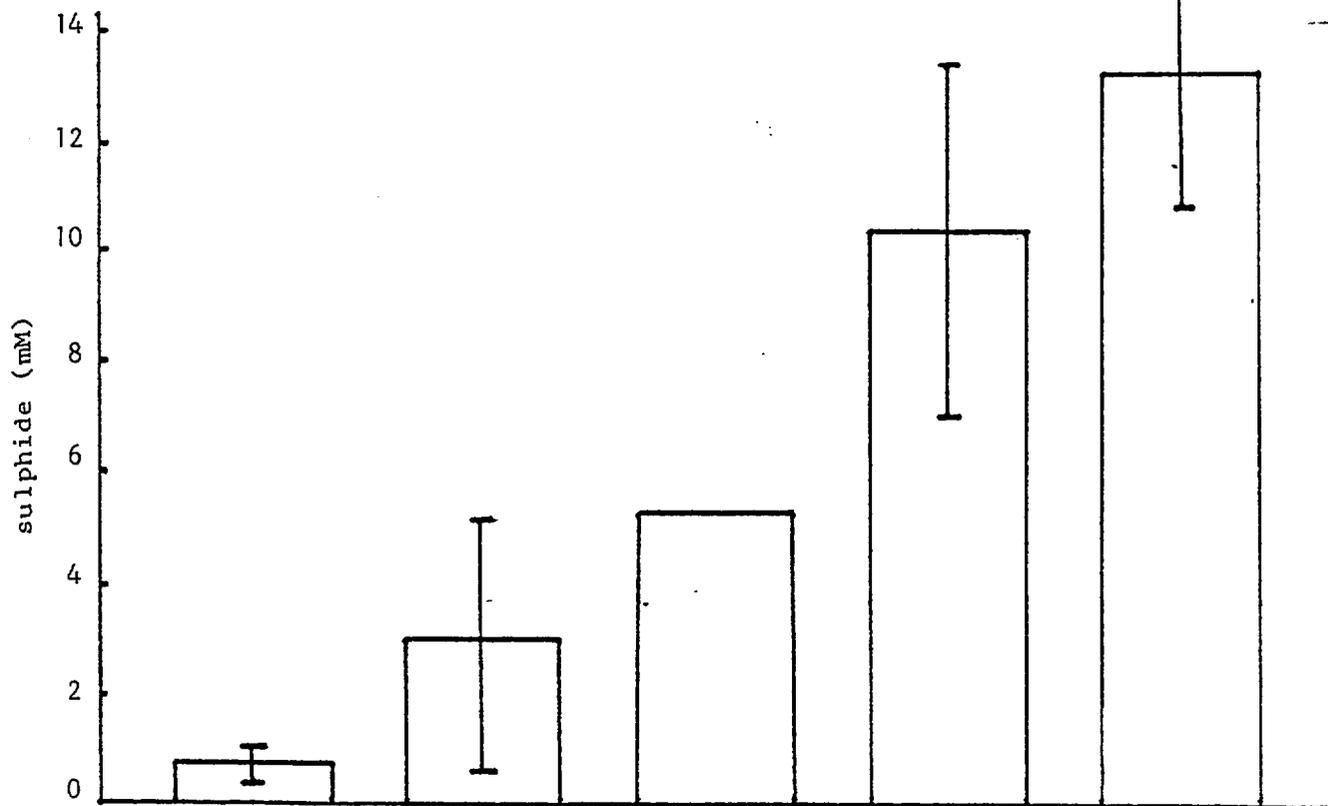


Fig. 1. The effect of exogenous substrates on methane production in Shark Bay sediment.

A Sulfide



B Methane and carbon dioxide

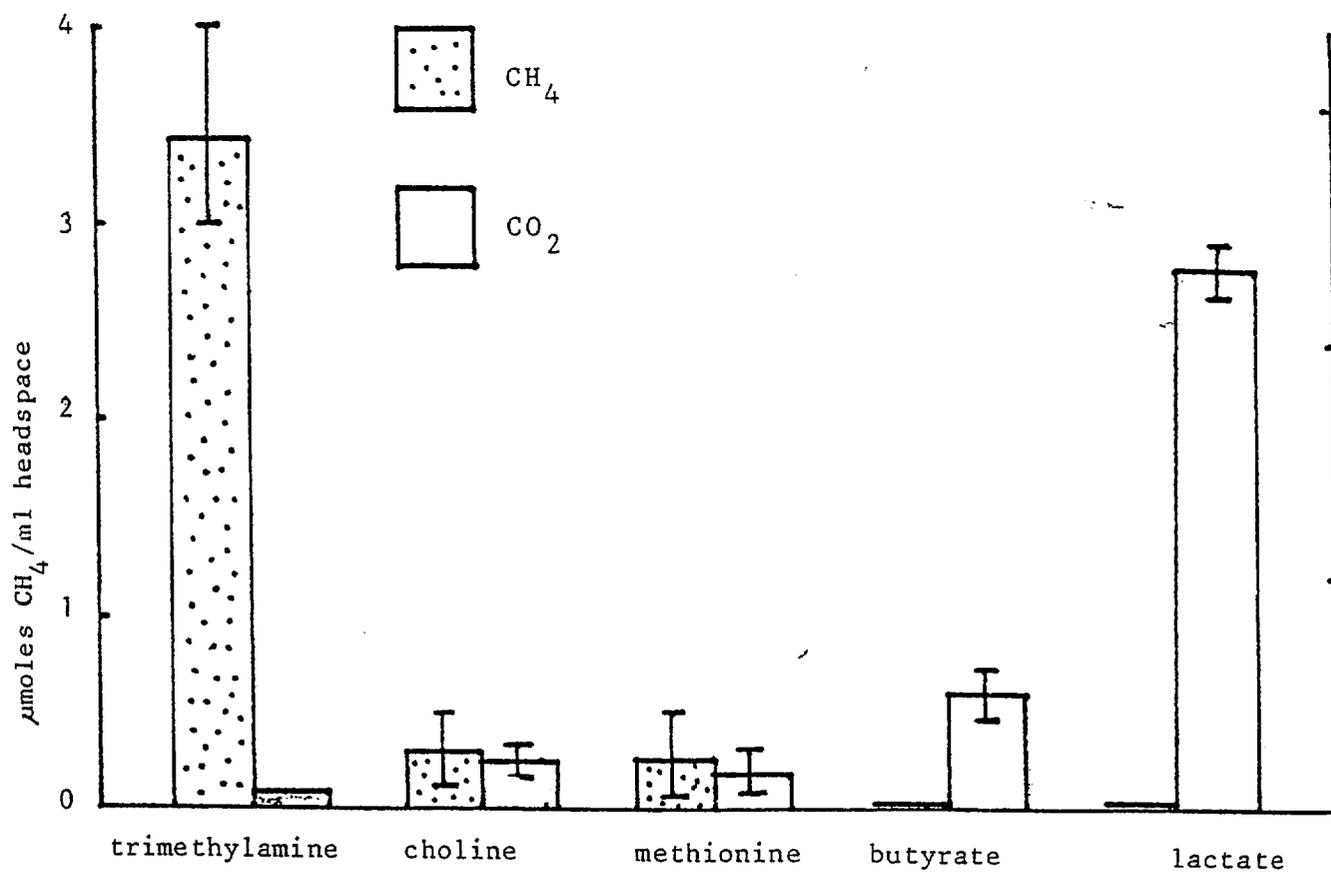


Fig. 2. Methanogenesis and sulphidogenesis in enrichment cultures of Shark Bay sediment.

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CHARACTERISTICS OF GROUNDWATER SYSTEMS RELEVANT TO
GEOCHEMICAL STUDIES OF HYPERSALINE TIDAL FLATS, SHARK BAY,
W.A.

Lyn Plumb, James Ferguson* and Ian Johns.

Abstract: IEER Meeting on Water Research, Melbourne,
Dec 3 and 4, 1984.

The association of stromatolitic carbonate sequences with both base metal and hydrocarbon prospective basins has directed research to the Holocene and Pleistocene carbonate environment in Shark Bay, as a modern analogue. Pertinent studies demand an assessment of the hydrologic regime and its influence on early diagenetic reactions whose products - evaporites, cements, teepees etc. - are often salient fundamentals in models of the palaeoenvironments.

The strategy of investigation at Shark Bay is to characterise and differentiate between marine and continental contributions to groundwaters in the marginal marine environments. Surveyed transects have been established from the hinterland to subtidal environments and include redbed dune terrain and Pleistocene and Holocene marine sequences. Highly permeable coquina beach ridges make a special contribution to the hydrologic regime.

Waters from along these transects have been subjected to extensive geochemical assays, including deuterium and oxygen isotope analyses.

Important environmental data (wind run and direction, solar radiation, precipitation, tide-height, water and air temperatures and barometric pressure) are being continuously recorded by a custom-designed remote-monitoring system which utilises satellite transmission to access the information. Monitoring of peizometer levels along the main transect is also linked to this system.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
MAY, 1985

GEOBIOLOGICAL CONTROLS ON PETROLEUM
FORMATION AND ACCUMULATION

ABSTRACT

In the wide-ranging studies at Shark Bay relationships between brine generation, bacterial sulphate reduction, iron sulphide distribution, organic matter preservation and carbonate diagenesis are beginning to become apparent. Moderately high concentrations of organic matter have been found in some of the sediments; the possibility that these could persist for geologically significant times is being studied. Distinctive hydrocarbon biomarkers have been found.

INTRODUCTION

The wide-ranging studies at Shark Bay are beginning to provide an understanding of the various relationships between brine generation and movement in the supratidal flats, carbonate diagenesis, the bacterial generation of sulphide, the distribution of iron sulphides in the sediments, and the formation and preservation of organic matter. Anomalously high Pb concentrations in some of the waters and sediments are not yet understood. Concentrations of organic matter in some of the sediments are in the range of 3-5%, but how much of this is likely to be preserved for geologically significant periods is not clear; it does seem that concentrations of 1-2% persist at least well back into the Holocene, in some areas. Distinctive hydrocarbons have been found in the Shark Bay sediments; some are known from oils and oil-shales elsewhere.

ORGANIC GEOCHEMICAL STUDIES IN SHARK BAY

R.E. Summons, R.W. Dunlop (University of W.A.) and R.V. Burne

Table 2 give, total organic carbon analyses (Robert et al., 1973) for Shark Bay sediment cores, the locations of which are given in Figure 2. These results show the following trends.

- (a) Highest organic carbon values are recorded in the surface sediments of the southern end of Hamelin Pool (sites 3A and 4)
- (b) There is a decrease in organic carbon value with depth in the sediment column

(c) Approximately 25% of organic carbon is in a water soluble form.

Organic carbon concentrations correlate positively with microbial anaerobic hydrogenase activity measurements (see Fig. 12). One lipid class (aliphatic hydrocarbon) has been analysed with the highest values of total hydrocarbon being found in the surface sediments. There was a general trend toward decreasing total hydrocarbon with decreasing organic matter and increasing depth. The dominant types of hydrocarbons are irregularly branched isoprenoids of 20 and 25 carbon atoms (Fig. 3). The combined results of the present analyses and a previous study (Dunlop, 1985) are summarised as follows:

1. The C₂₀ compounds II(C₂₀H₄₀) and III(C₂₀H₄₀) occur in trace amounts in most surface samples but are not detectable at depth. They are most abundant (13% of total) at site 4. Compound III is the second most abundant component of the alkane fraction of the Rozel Point crude oil (Utah, USA) and its biological source is presently unknown (Yon et al., 1982).
2. Compound I(C₂₅H₅₀) occurs in all surface sediments; concentration decreases with depth and it is most abundant at station 4 (9% of total).
3. Compounds IV and V always occur in an approximate ratio of 2 : 1 (which suggests they have the same source) and are present only in low concentration in surface sediments. They maximise in concentration at somewhere between 20cm and 100cm (where the quantity may be > 90% of the total) below which they decrease in concentration.
4. A newly found hydrocarbon (C₂₅H₄₈) is confined to the surface sediments of the southern basin sites 3A and 4 and adjacent sublittoral platform sites 3 and 6. This and compounds II, III and I are the major hydrocarbons of the microbial community constituting the fluid floc just above the sediment surface at sites 3A and 4.

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Table 2 Organic Carbon Distribution, Shark Bay

SAMPLE ID	SITE	DEPTH (cm)	ORGANIC CARBON (% dry wt.)		
			ACID INSOLUBLE	ACID SOLUBLE	TOTAL
1/1	1	0-5	0.39	0.16	0.54
2/1	1	45-50	0.56	0.11	0.67
3/1	1	95-100	0.52	0.08	0.60
1/2	2	0-5	1.40	0.27	1.67
2/2	2	45-50	0.26	0.16	0.42
3/2	2	95-100	0.46	0.09	0.55
1/3	3	0-5	0.82	0.24	1.06
2/3	3	7-10	0.15	0.22	0.37
3/3	3	15-20	0.80	0.16	0.96
4/3	3	37-40	0.62	0.24	0.86
5/3	3	95-100	0.78	0.30	1.08
6/3	3	125-130	1.06	0.21	1.27
7/3	3	140-145	1.10	0.65	1.75
1/3-5	3A	0-2	3.75	ND	3.75
2/3-5	3A	2-5	3.20	0.22	3.44
3/3-5	3A	7-10	2.20	0.66	2.86
4/3-5	3A	15-20	0.98	0.11	1.09
5/3-5	3A	25-30	0.72	0.21	0.93
1/4A	4	0-2	3.55	0.68	4.23
2/4A	4	2-5	4.05	1.32	5.37
3/4A	4	7-10	4.70	0.74	5.44
4/4A	4	15-20	0.63	0.46	1.09
5/4A	4	35-40	1.55	0.37	1.92
1/4B	4	95-100	0.42	0.12	0.54
2/4B	4	145-150	0.17	0.05	0.22
1/5	5	0-5	0.42	0.36	0.78
2/5	5	25-30	0.29	0.20	0.49
3/5	5	85-90	0.24	0.09	0.33
1/6	6	0-5	1.06	0.69	1.75
2/6	6	7-10	0.81	0.33	1.14
3/6	6	15-20	0.69	0.59	1.28
4/6	6	40-45	1.18	0.46	1.64
5/6	6	95-100	0.50	0.12	0.62
6/6	6	145-150	0.34	0.29	0.63
7/6	6	240-250	0.27	0.08	0.35

Table 2 contd

SAMPLE ID	SITE	DEPTH (cm)	ORGANIC CARBON (% dry wt.)		TOTAL
			ACID INSOLUBLE	ACID SOLUBLE	
1/9	9	0-2	2.10	0.37	2.47
2/9	9	2-5	1.16	0.24	1.40
3/9	9	7-10	1.01	0.19	1.20
4/9	9	15-20	1.73	0.14	1.87
5/9	9	25-30	2.05	0.18	2.23
1/10	10	0-2	0.89	0.27	1.16
2/10	10	2-5	0.87	0.25	1.12
3/10	10	7-10	0.71	0.34	1.05
4/10	10	15-20	0.57	0.22	0.79
5/10	10	25-30	1.24	0.18	1.42

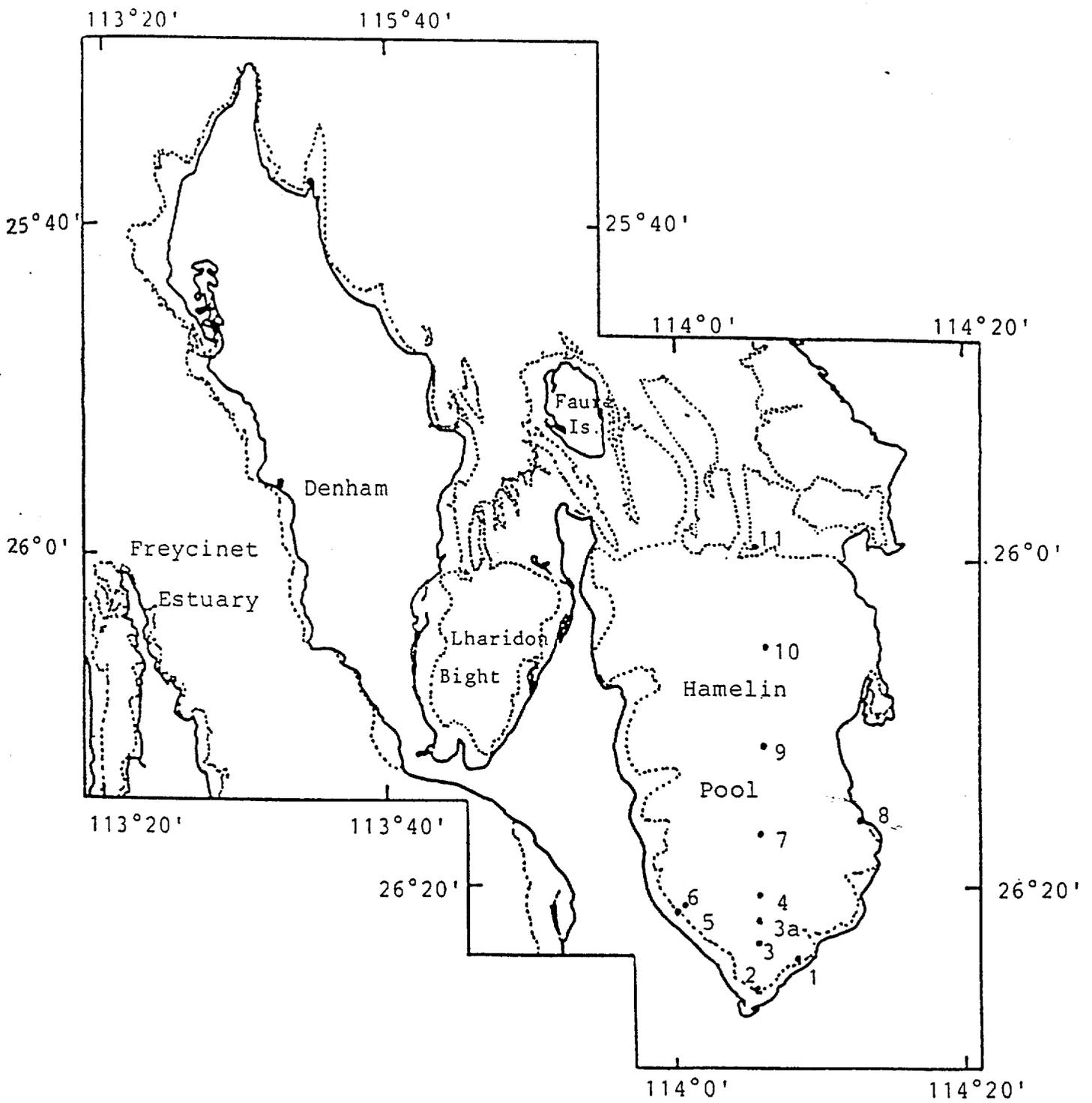
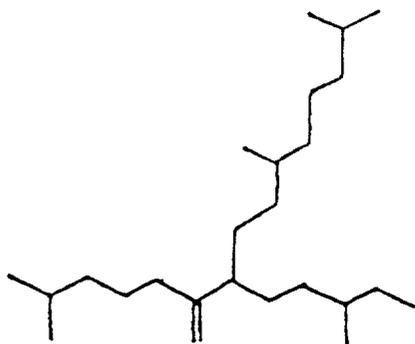
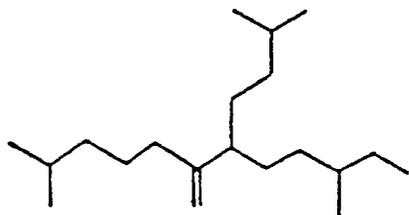


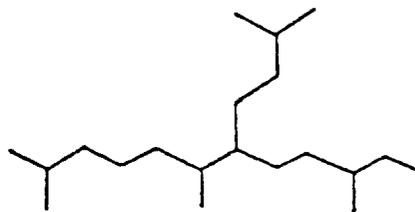
Figure 2 Map of Shark Bay showing sample sites



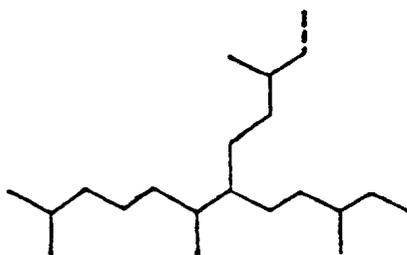
I (I.2112)



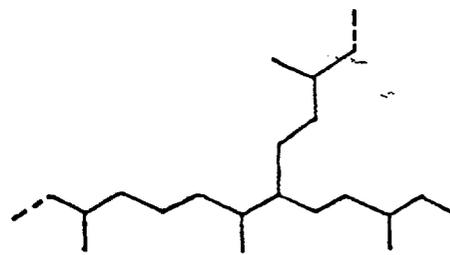
II (I.1703)



III (I.1708)



IV (I.1803)



V (I.1903)

Figure 3 Structures of distinctive Shark Bay hydrocarbons.

PHOTOTROPHIC ACTIVITY BY ENTOPHYSALIS MATS IN SHARK BAY

J. Bauld, D.T. Ho

Introduction

Entophysalis major is a coccoid, colonial cyanobacterium (blue-green alga) which constructs benthic mats referred to variously as cinder (Kendall and Skipwith, 1968), mammillate (Golubic, 1973) or pustular (Logan et al., 1974). The coccoid cells, ca 5-8µm in diameter, are encased within concentric, lamellate sheaths and produce irregular contiguous colonies which form mats. Extensive areas of the intertidal zones in Shark Bay and Abu Dhabi are covered by *Entophysalis* mats (Table 3). The mats are usually dark brown to black in appearance, of a firmly gelatinous to rubbery texture, and generally favour coarse, porous, well-drained sediments. In addition *E. major* has been invoked (e.g. Golubic, 1983) as the constructing organism for domal, lithified stromatolites which are unique to the intertidal zone of Hamelin Pool, Shark Bay. Both types of structure have been described at length (e.g. Kendall and Skipwith, 1968; Golubic, 1973; Logan et al., 1974; Golubic, 1983) with little or no attention to the metabolic processes carried out by the constructing cyanobacteria or their responses to environmental constraints. An understanding of such processes is clearly of relevance in view of:

- 1) the extensive area of intertidal sediment covered by this mat (it appears to be the dominant intertidal colonizer in Hamelin Pool but quantitative data are not yet available)
- 2) its probable role in the formation of the unique domal lithified stromatolites
- 3) the resemblance of these Recent stromatolites to certain Proterozoic stromatolites e.g. those found in the Belcher Supergroup (Hofmann, 1976)
- 4) the resemblance of modern *Entophysalis* to the dominant microfossil (*Eoentophysalis*) in the Proterozoic forms (Table 3).

Methods

Phototrophic activity was routinely measured using ¹⁴C-labelled substrates during short-term incubations of *Entophysalis* under field conditions of temperature and light intensity. Due to the irregular nature of the mat (a consequence of *Entophysalis* morphology and growth habit) the previously employed technique, of removing small (0.5cm²) cores for experimental work, was found to be unsatisfactory. *Entophysalis* is, in addition, much less cohesive than e.g. smooth or tufted mats and it proved

exceedingly difficult to obtain the required uniformity of sample size. Consequently, there was high variability between replicate treatments with attendant difficulties of data interpretation.

The field method was modified such that a "large" area of mat, equivalent to the surface area of a known number of cores, was excised and homogenized to produce a slurry. Aliquots of this slurry, sufficient to provide a final biomass concentration equivalent to a single core, or selected multiples thereof, were then transferred to standard incubation vials. Additions of seawater, ^{14}C -isotope and potential inhibitors followed.

Figure 4 shows that photosynthesis is linear with respect to biomass over a 4-fold concentration range (where 1.0X is equivalent to a single core). $^{14}\text{CO}_2$ uptake is linear with respect to incubation time for up to 90 min (Fig. 5). Slurries of the top 3-4mm were routinely used in the experiments described below, unless otherwise stated in the text and/or figure captions.

Response to light intensity

Entophysalis cells in the upper ca 1-2mm of the mat ("surface") are surrounded by sheaths which are deep brown due to an as yet uncharacterized pigment referred to as scytonemine. In contrast the cells from deeper within the mat ("subsurface"), presumably shaded from above by the pigment screen, have paler, yellow to clear sheaths. The two populations were separated in the field by shaving off the top 1-2mm with a sharp razor blade. Microscopic examination showed that separation was imperfect but that the "surface" fraction was dominated by cells with deeply stained sheaths whereas, in the subsurface fraction, these were much less prevalent.

In this experiment (Fig. 6) it is shown that cells taken from different levels within the mat exhibit distinctive responses to light intensity as measured by photosynthetic $^{14}\text{CO}_2$ -fixation. At low light intensities (\leq ca $100 \mu\text{E m}^{-2} \text{s}^{-1}$), the responses of the two populations are similar, but at higher light intensities differences are detectable. The "subsurface" fraction shows only a slight increase of photosynthetic activity in response to increasing intensity between ca 100 - $1000 \mu\text{E m}^{-2} \text{s}^{-1}$, indicating that light saturation occurs in the range ca 100 - $700 \mu\text{E m}^{-2} \text{s}^{-1}$. At light intensities greater than ca $1100 \mu\text{E m}^{-2} \text{s}^{-1}$ photosynthesis is inhibited such that at ca $2300 \mu\text{E m}^{-2} \text{s}^{-1}$ (intensity of sunlight arriving at the sediment surface) photosynthetic activity is only ca 30% of the maximum rate measured at $700 \mu\text{E m}^{-2} \text{s}^{-1}$, at which point the cells appear to be

light-saturated. The "surface" fraction shows only slight photoinhibition - at full sunlight photosynthesis is still ca 85% of the maximal rate. If the photosynthetic rates shown in Figure 6 are standardized to either protein (estimate of total biomass) or chlorophyll *a* (estimate of phototrophic biomass) in order to compensate for the slightly different biomass concentrations of the two fractions, the two response curves shown in Figure 6 retain their shapes. However, the "subsurface" fraction exhibits much greater photosynthetic activity than the "surface" fraction at light intensities \leq ca 500 $\mu\text{E m}^{-2} \text{s}^{-1}$, a situation which reverses above ca 1100 $\mu\text{E m}^{-2} \text{s}^{-1}$. These data are consistent with a benthic phototrophic community, composed of non-motile cells, and employing screening pigments to attain sun-or shade-adaptation and hence optimize their photosynthetic efficiency.

Response to salinity

The response of *Entophysalis* to various salinities is shown in Figure 7. As measured by short-term photosynthetic $^{14}\text{CO}_2$ -fixation the highest activity occurred at 35‰, a salinity considerably lower than that of Hamelin Pool (58‰ at this time). The response to increasing salinity between 2.5‰ and 35‰ appears to be linear. Photosynthetic activity at 60‰ and above is less than half that of the maximal activity. The response of *Entophysalis* to salinity is thus distinctly different to that exhibited by other intertidal mats, e.g. smooth and tufted, examined earlier. The latter mats have broader response curves with maximal activity at higher salinities.

Possible explanations for this difference include (1) the salinity response curve for growth differs from that for short-term $^{14}\text{CO}_2$ fixation, (2) rapid physiological adaptation may overprint genetic capacity leading to a general plasticity of response (the mats used in this experiment were collected after heavy rainfall during which the mats were not covered by Hamelin Pool water), and (3) as a consequence of mat topography and porosity the effects of desiccation are apparent before those related to increasing salinity during "normal" inundation-exposure cycles ("ponding", and subsequent salinity increases caused by evaporation characteristic of e.g. tufted mat, are effectively precluded).

Recovery from desiccation

These experiments were performed in Canberra using *Entophysalis* samples air freighted from Shark Bay. Small, intact "cores" were dried at 45°C mimicking summer mat-surface temperatures. Water loss was approx. linear for $t=0-60$ min, after which the rate slowed (data not shown). Constant weight

was attained after 2.5h. Cores were then transferred to seawater containing $^{14}\text{CO}_2$ and incubated for periods ≤ 1 hr in order to measure the rate of recovery of photosynthetic activity during post-desiccation immersion. The rate of water uptake was measured in a parallel set of cores incubated without isotope.

Water uptake was initially rapid but slowed significantly after 20 min (Fig. 8). Metabolic activity was initially slow ($t=0-20$ min) but increased and exhibited linearity from $t=20-60$ min (Fig. 8).

Response to potential metabolic inhibitors

The effects of various treatments are compared in Figure 9. Sparging with N_2 to produce an initially anoxic environment had no effect on photosynthetic activity when compared to the untreated control, whereas the addition of ascorbate (a reductant which would scavenge O_2 and poise the redox potential at ca 60mV) significantly inhibited this activity. The effect of GeO_2 , an inhibitor of diatom activity, is uncertain due to substantial inter-replicate variability. However, diatoms are rarely encountered during microscopic examination of *Entophysalis* mats and it is conceivable that any (possible) effect exerted by GeO_2 may be caused by non-specific inhibition of *Entophysalis* (Davies et al., 1982). DCMU, a specific inhibitor of oxygenic photosynthesis, is a very efficient inhibitor of *Entophysalis* photosynthetic $^{14}\text{CO}_2$ -fixation ($> 90\%$ inhibition, Figure 9 and additional, unreported experiments). Sulphide completely blocks photosynthesis at a concentration of 1mM. These data are consistent with the habitat of *Entophysalis* i.e. growth, by oxygenic photosynthesis, on coarse, well-drained sediments which are probably oxic. Sediments beneath intact *Entophysalis* mats are very rarely sulphidic. An exception to this generalization was observed during a period of sustained water cover.

(Photo)assimilation of acetate

The ability of *Entophysalis* mat to assimilate [$1-^{14}\text{C}$] acetate was measured in both light and dark and in the presence/absence of DCMU (Fig. 10). It can be seen that photoassimilation (i.e. light-dependent uptake) is ca 25% of total acetate assimilation, a somewhat lower value than that observed for smooth mat (Quarterly Report, May, 1983). There appeared to be no significant difference between control and DCMU treatments. The experiment does not enable us to distinguish between dark assimilation by *Entophysalis* and that by associated chemoheterotrophs. However, the response to DCMU, together

with the position of the label (1-¹⁴C i.e. carboxyl group), indicates that ¹⁴C photoassimilation is not due to secondary fixation of ¹⁴CO₂ released by respiratory activity, since DCMU (see above) is an efficient inhibitor of ¹⁴CO₂-fixation by *Entophysalis*.

Table 3. Reported occurrences of (*Eo*)*Entophysalis* mats

Ancient (<i>Eoentophysalis</i>)	Modern (<i>Entophysalis</i>)
Belcher Supergroup <u>ca</u> 1.8-2.5 Ga (1)	Hamelin Pool -Shark Bay (7)
Bitter Springs Fm <u>ca</u> 0.7-1.0 Ga (2)	Khor al Bazam -Abu Dhabi (8)
McArthur Group <u>ca</u> 1.6-1.7 Ga (3,4)	*Laguna Mormona -Baja California (9)
Bungle Bungle Dolomite <u>ca</u> 1.6 Ga (5)	
Gaoyuzhang Fm <u>ca</u> 1.4-1.5 Ga (6)	

(1) Hofmann (1976); (2) Knoll and Golubic (1979);
 (3) Oehler (1978); (4) Oehler et al.(1976);
 (5) Hofmann and Schopf (1983); (6) Zhang (1981);
 (7) Logan et al.(1974); (8) Kendall and Skipwith (1968);
 (9) Horodyski and Vonder Haar (1976).

* Note that the Laguna Mormona (a.k.a. Laguna Figueroa) occurrence is considered doubtful, since the organism reported is now identified as a *Pleurocapsa* sp. on the basis of ultrastructure (Stolz, 1983). I have not found *Entophysalis* mats at Laguna Mormona during 2 short field trips.

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ENTOPHYSALIS MAT (SHARK BAY)

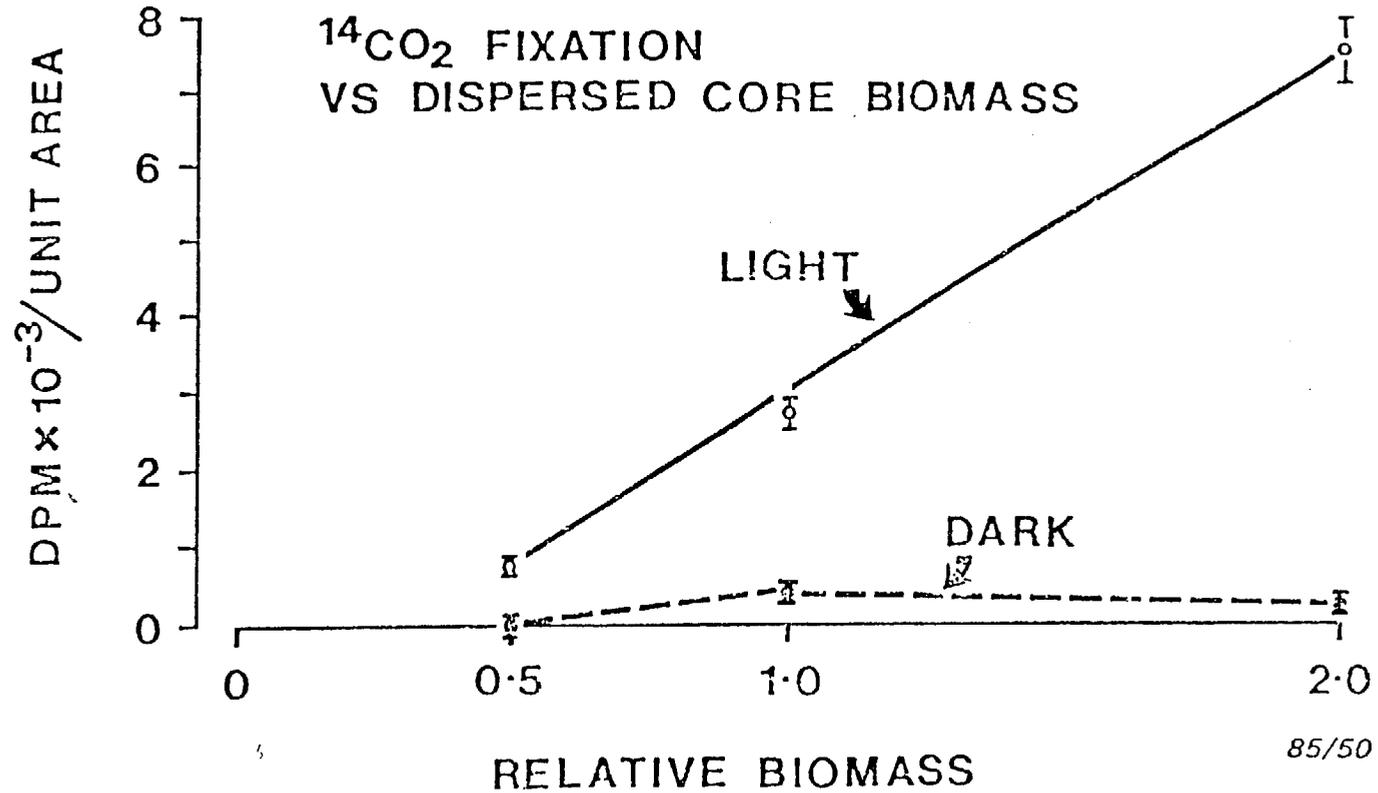


Figure 4 Relationship between biomass concentration of dispersed mat (slurry, see methods) and $^{14}\text{CO}_2$ -fixation. 1.0X is equivalent to a single core. (DPM=Disintegrations Per Minute).

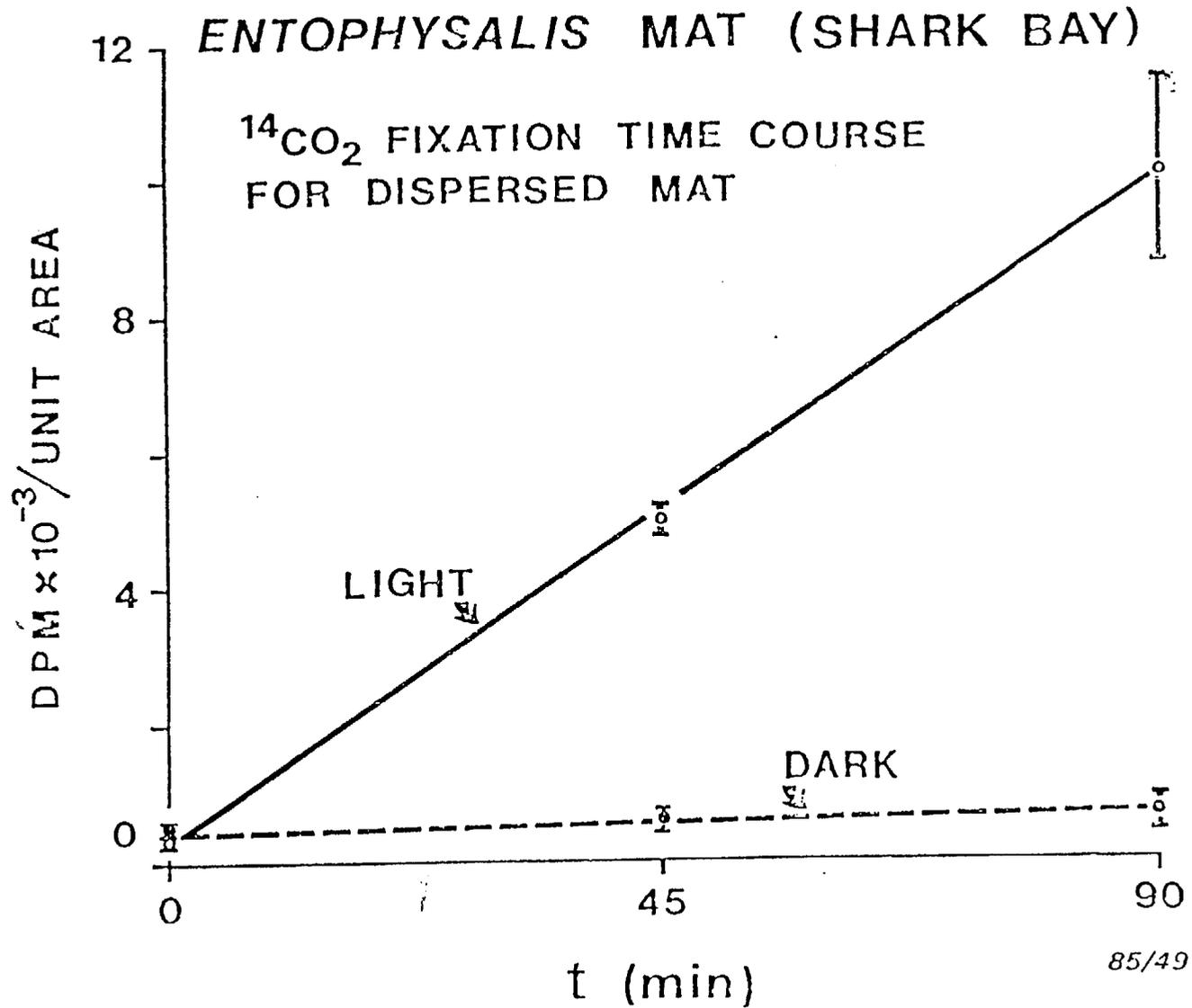


Figure 5 Time course for $^{14}\text{CO}_2$ -fixation using slurry preparation.
(DPM=Disintegrations Per Minute)

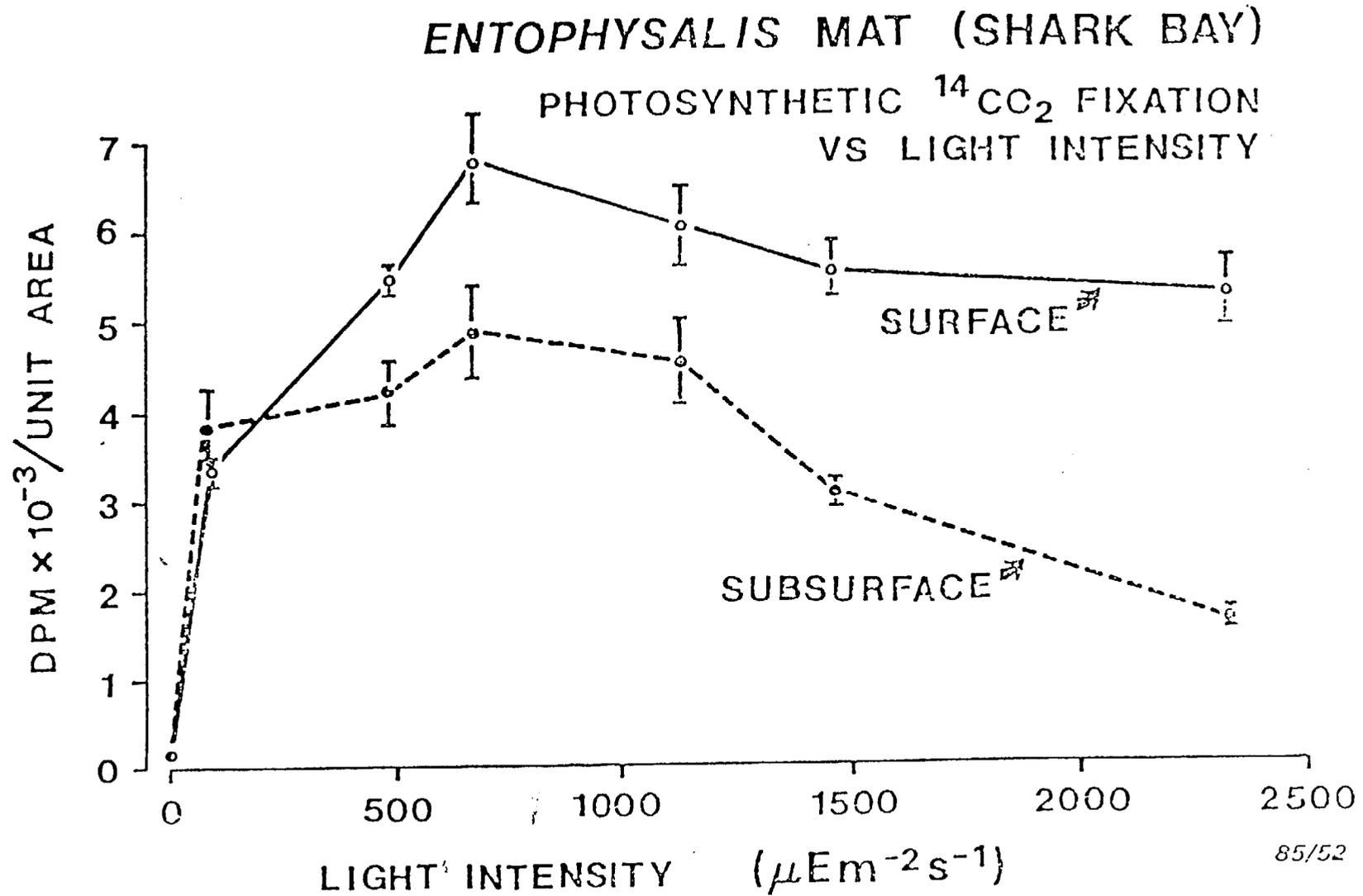


Figure 6 Response to light intensity by cells from different levels within the mat. Separation procedure is described in text. (DPM=Disintegrations Per Minute)

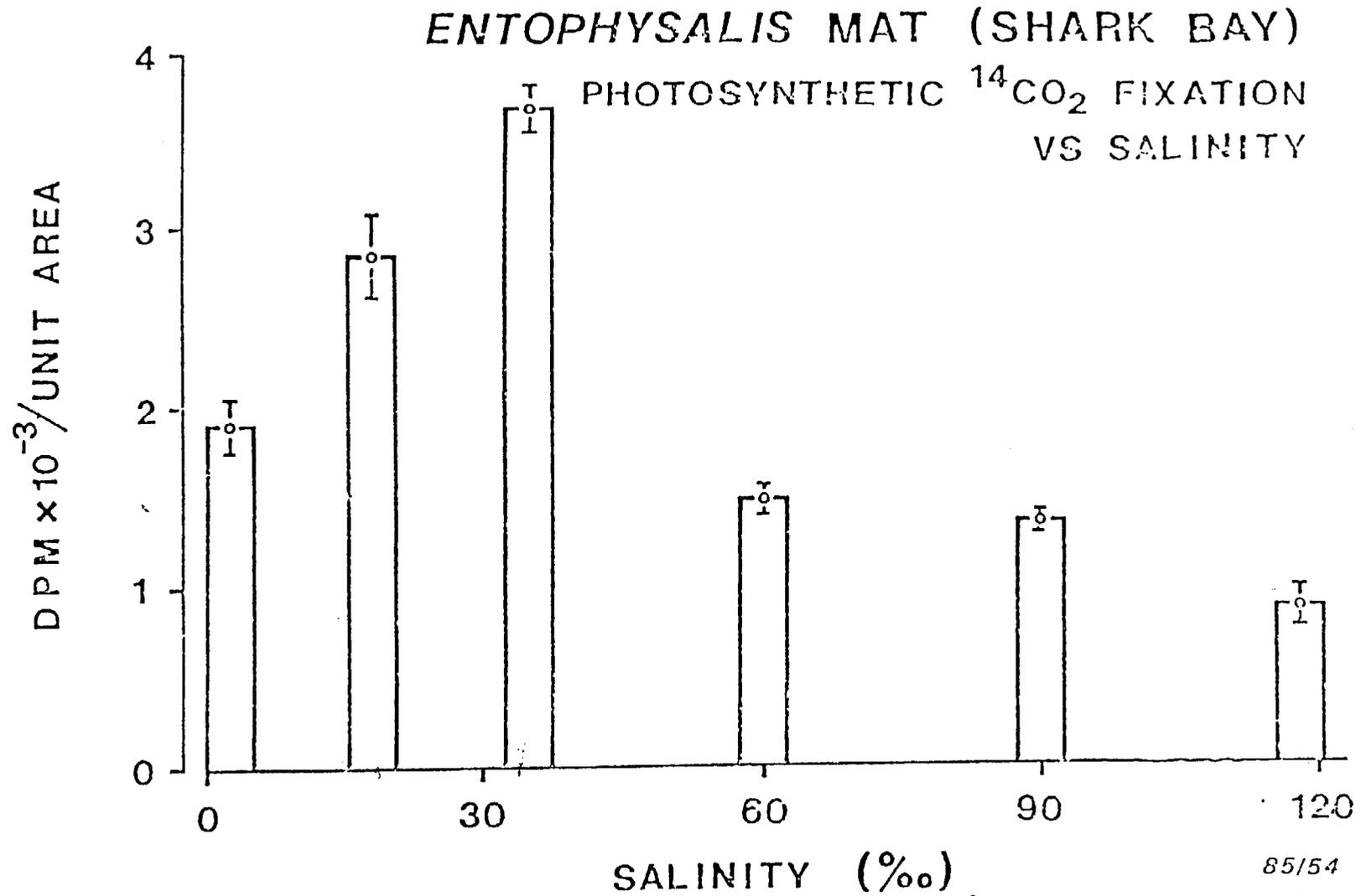


Figure 7 Response to salinity. "Normal" sea water=35‰; open water of Hamelin Pool=58‰. (DPM=Disintegrations Per Minute).

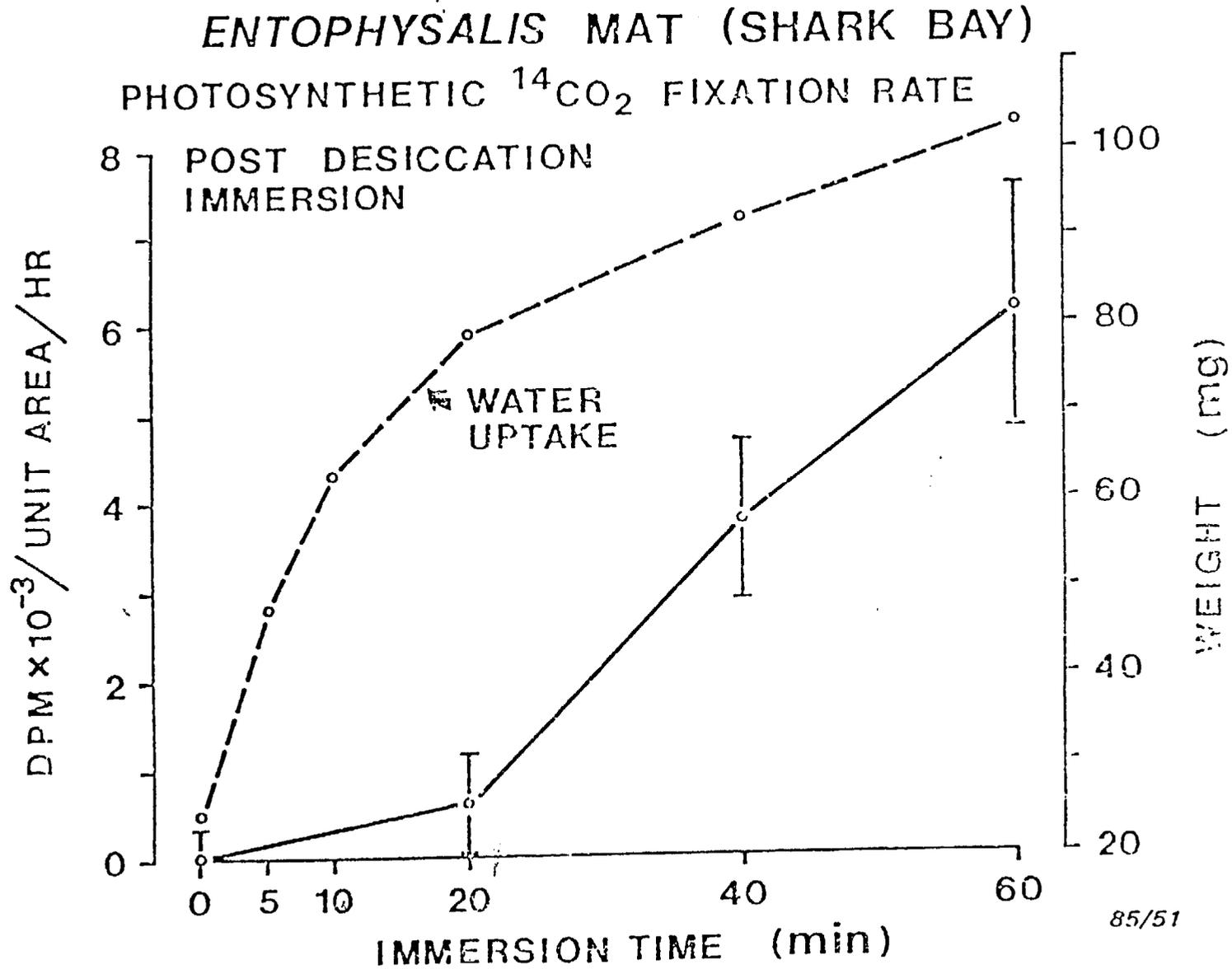


Figure 8 Recovery of photosynthetic activity after desiccation. Intact cores were dried (see text) then immersed in water. (DPM=Disintegrations Per Minute)

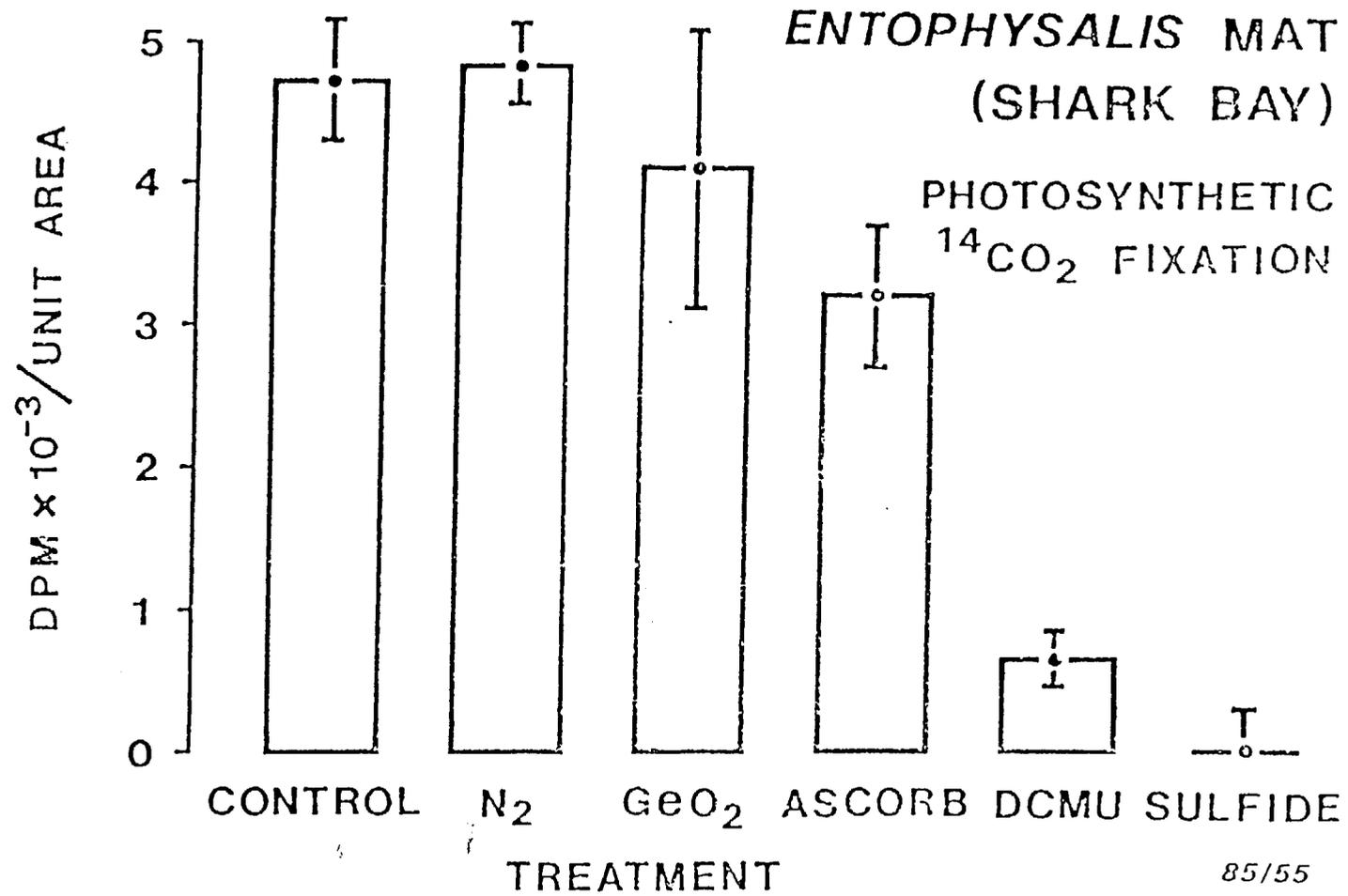


Figure 9 Response to potential metabolic inhibitors (see text for details) (DPM=Disintegrations Per Minute)

ENTOPHYSALIS MAT (SHARK BAY)

[1-¹⁴C] ACETATE UPTAKE

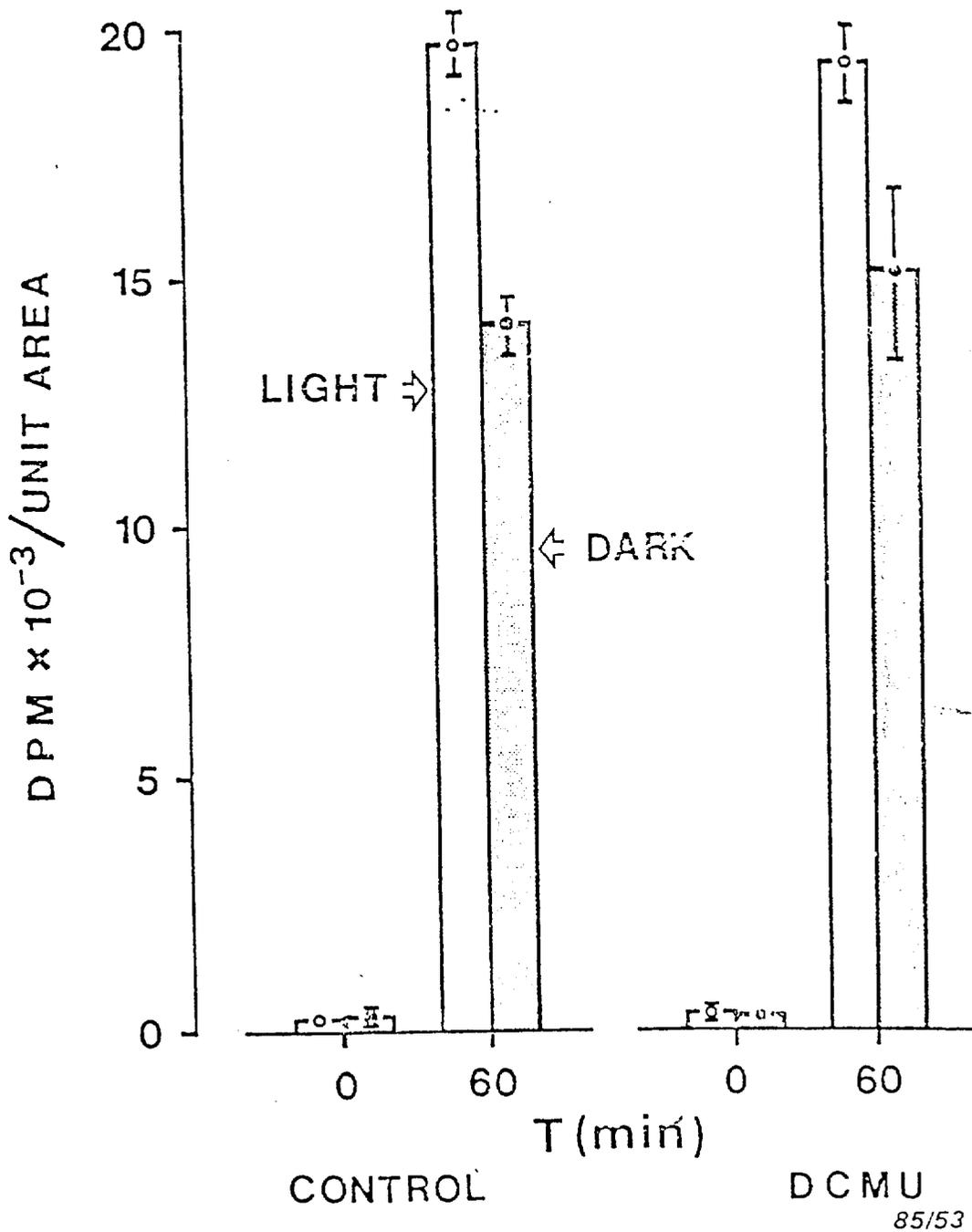


Figure 10 Assimilation of ¹⁴C-acetate in the presence or absence of DCMU, a specific inhibitor of photosynthetic CO₂-fixation. (DPM=Disintegrations Per Minute)

SULFATE REDUCTION IN HOLOCENE ENVIRONMENTS

G.W. Skyring, F.S. Lupton, S. Dibb

The data obtained from the November (1984) field trip to Shark Bay are given in Table 4. The locations in Hamelin Pool where vibrocores were obtained are given in Figure 2.

SULFATE REDUCTION IN HAMELIN POOL SEDIMENTS (Table 4)

Above 10cm

Sediments from Stations 4 and 9 had the highest sulphate reduction rates. Moderate rates were determined for sediments from Stations 2 and 7 and the rates for sediments from Stations 3 and 6 were very low.

Below 10cm

It was not feasible to determine the sulphate reduction rates for every 5cm layer from all cores. The strategy adopted was to sample from the 5cm layers at the top and bottom of the recognizable different sediment types. Black sediments, and those which were apparently organic-rich, were also sampled irrespective of their position in the sedimentary column. Previous work showed that sulphate reduction rates in subsurface sediments were likely to be low. Therefore long incubation periods (up to 14 days) under nitrogen were used.

Station 2: Although the sediments contained small quantities of acid volatile sulphide (AVS) and tin-reducible sulphide (TRS - which is presently interpreted as pyrite-S), sulphate reduction was not detectable.

Station 3: The situation was similar to that for Station 2 but there did appear to be some sulphate reduction occurring at very low rates.

Station 4: This represents a newly discovered (by R.V. Burne and R. Summons) and fairly extensive deposit of gelatinous (organic) black to grey mud about 40cm thick overlying a buff to grey, sandy sediment. About 80% of sulphate reduction occurred in the upper 10cm. However, there did appear to be a minor peak of activity between 20 and 30cm and this may be co-incident with a different sediment type. Below 40cm, sulphate reduction was not detectable.

Station 6: The sulphate reduction rates for this station were barely detectable, even in the 0-5cm layer. This was surprising

since the porewaters contained sulphide and ammonia down to 120cm and there was appreciable concentrations of TRS at all depths.

Stations 7 and 9: Sulfate reduction was not detectable below 10cm at both of these locations, however, the sediments were grey and contained appreciable quantities of TRS.

THE FORMATION OF TIN-REDUCIBLE SULPHUR

(For previous discussion of "rapid pyrite formation" see Quarterly Report, Nov, 1983).

There was a positive correlation between the sulphate reduction rates calculated from the acid volatile sulphide (AVS) and tin-reducible sulphide (TRS), respectively. However, there was an inverse relationship between the AVS and the incorporation of ^{35}S into TRS (Fig. 11). Because of the variation of TRS rates among control samples and test samples the data were often difficult to interpret. From the results of various experiments, the limits of detection with respect to the TRS fraction is about $300\mu\text{mol m}^{-2}$ or 4nmol g^{-1} . This is because some of the sulphate in the sample is reduced during reflux distillation with tin and hydrochloric acid. The sulphate reduction rates in most of the sediments from below 10cm were so low that activity was not detected even after 14 days incubation.

ANAEROBIC HYDROGENASE AND SULPHATE REDUCTION

Anaerobic hydrogenase activity is a measure of the capacity of the microbial population to use or evolve hydrogen. As with sulphate reduction, the highest rates occurred in the surface layers. However, there was not a simple correlation between sulphate reduction and hydrogenase activity. For example at Station 4 sulphate reduction rates decrease rapidly below 10cm whereas hydrogenase activity decreased slowly to 40cm (Table 4). One interpretation of this result is that the sulphate-reducing bacteria are of minor importance in the oxidation of organic matter in subsurface layers. Whatever the reason, it is not immediately obvious why the sulphate reducers are so inactive in the subsurface layers when the hydrogenase analyses indicate that other hydrogen-metabolising organisms are apparently active.

MICROBIAL ACTIVITY AND ORGANIC MATTER

Over the wide range of sulphate reduction rates which were determined, there was a positive but complex correlation between the rates and the concentration of organic matter.

One of the reasons for examining sediments from various parts of Hamelin Pool was to search for locations where organic matter and sulphide was preserved. Sediments from Station 4, down to 40cm, were sulphidic and gelatinous. However, high organic carbon concentrations were characteristic of the upper 10cm only. Subsurface sediments from Stations 3, 6 and 9 also had organic-C concentrations in excess of 1% down to 40cm. From the present work it seems that sulphate reduction virtually ceases when the acid insoluble C is around 1% or less, even if this situation occurs in surface sediments such as Stations 3, 6 and 7. Although sulphate reduction rates were undetectable in most subsurface sediments it is not possible to conclude that it had ceased. Clearly some process must be responsible for the TRS which increases with depth at all locations and the most likely cause is sulphate reduction. For example, the very low rates of reduction found for Station 3, would be interpreted as zero if taken individually. However, there did appear to be a trend for slightly higher sulphate reduction rates in the 100-145cm layer and this corresponded with slightly higher organic carbon contents. If this interpretation is correct, it might be expected that the TRS from subsurface layers would be highly enriched in ^{32}S . On the other hand the sulphide in Station 3 sediments may have not formed as a result of in situ reduction but as a result of lateral movement of waters from areas where sulphate reduction is active.

Hydrogenase activity correlated more simply and significantly with the acid soluble organic-C concentration which may be a better indicator of "available" organic carbon than is total organic-C (Fig. 12).

More detailed analyses of these data will be given subsequently.

PLAYFORD'S TRANSECT

Studies on the intertidal, organic deposits of Playford's Transect (Hamelin Pool) were continued during the November, 1984 field trip. Other data on these sediments are given in previous Quarterly Reports.

Table 5 shows the results obtained for analyses of samples of this black sediment at various stages of diagenesis. It is evident from the chemical properties of the porewaters the AVS concentrations of the sediments and the relatively high sulphate reduction rates that anaerobic processes were very active in these sediments. From the high alkalinities it is also apparent that sulphate reduction was a significant component of microbial activity. The age of the sediment at 30cm is not known. It must be at least several decades old but still supports sulphate reduction at appreciable rates.

TABLE 4 Porewater and sediment analyses, Hamelin Pool, Nov. 1984.
(See foot notes for column codes)

DEPTH cm	%	pH	POREWATER				GRAIN DESCRIPTION OF SEDIMENTS	SULFIDE		REDUCTION RATE DAY-1				ORGANIC C %		HYDROGENASE nmolH ml-1 day-1
			SO4 mM	S2- mM	NH4 mM	ALK meq l-1		AVS μmol g-1	TRS μmol g-1	AVS μmol m-2	TRS μmol m-2	TOT nmol g-1	AT	AS	TOC	
STATION 2								STATION 2								
0-5	79	8.03	46	0	423	3.98	Coarse shell grit	0.55	3.35	415	246	12.08	1.40	0.27	1.67	1.44
20	88	7.82	42	0	585			-								
40	90	7.81	43	0	1210	3.42	Fine shell grit, grey	0.48	28.5	8	?	?	0.26	0.16	0.42	0.41
60	96	7.71	44	0	683			-								
80*	93	7.44	47	0	682	3.6	Coarse sand, shell grit, grey	0.46	51.6	0	?	?	0.46	0.09	0.55	0.49
STATION 3								STATION 3								
0-5	69	7.55	47	34	560	4.61	Soft sandy mud, grey	0	56.7	63	539	12.3	0.82	0.24	1.06	1.15
35-40	69	7.67	44	0	1087	4.90	Shell fragments, grey	0	50.2	14?	107?	2.7?	0.62	0.24	0.86	0.43
75-80	80	7.62	56	0	1358	4.25	Start of carbonate mud, grey	0	60.3	0	0	0				0.37
100-105	79	7.66	59	128	1208	3.87	Carbonate mud, shell grit, grey	0	72.3	0	135?	4.3?	0.78	0.30	1.08	0.25
145	82	7.91	64	0	1127	4.10	End of carbonate mud	0	130.0	0	249	6.5	1.10	0.65	1.75	0.27
165	80	7.76	55	0	1071	4.10	Brown organic debris; old soil?	0.85	259.8	0	0	0				0.12
180	85	7.38	59	0	1208	3.6	Calcrete,* tube casts, grey	0.61	50.5	0	0	0				0.15
200	84	7.78	33?	0	1168	2.8		0	30.6	0	0	0				
220	84	7.49	60	0	1287	2.7		0	-	0	0	0				
240	85	7.83	60	0	1168	3.2	Calcrete, grey	0		0	0	0				0.09
STATION 4								STATION 4								
0-5	60	7.91	40	0	222	4.58	Gelatinous ooze, black	1-25	10-43	4844	1995	622	3.80	1.0	4.8	2.00
5-10	60	8.28	35	9	286	4.10	Gelatinous ooze, grey	24	21	3806	1000	326	4.70	0.74	5.44	1.40
10-15	59	7.91	39	11	286	4.10	Gelatinous ooze, grey	3	10	268	347	14				1.20
15-20	59	8.05	36	105	384	3.92	Gelatinous sand, tube casts	9	17	294	527	14	0.63	0.46	1.09	1.23
20-25	61	7.53	40	29	449	3.92	Gelatinous sand, shell grit	7	20	808	1043	113				1.09
25-30	60	7.83	39	66	533	4.2	Gelatinous sand, shell grit	7	33	486	590	91				1.13
30-35	64	7.90	43	117	579	4.5	Gelatinous sand, shell grit	8	70	97	382	29				1.39
35-40	62	7.36	44	220	675	6.7	Gelatinous sand, light grey	0	68	130?	634	32				0.43
60-65	73	7.84	-	0	872	4.33	Not gelatinous, grey	0	43	0	0	0				0.40
80-85	76	7.77	-	0	1190	4.47	Shell grit, buff coloured	2	122	0	0	0?				0.55
100-105	66	7.76	-	0	986	3.81	Fine grit, grey-buff	12	141	69?	92?	4?	0.42	0.12	0.54	0.22
130	74	7.48	-	0	920	4.28	Tube casts, calcrete	-								
140	61	7.76	-	0	950	3.85	Calcrete	0	498	0	0	0	0.17	0.05	0.22	0.36

Table 4 contd

STATION 6							STATION 6									
0-5	64	7.97	42	117	564	3.94	Shell grit, black	0	13.4	277	1447	47	1.06	0.69	1.75	1.30
15-20	65	7.80	42	22	590	3.89	Shell grit, grey	0	10.5	0	1157	37	0.69	0.59	1.28	1.12
40-45	68	7.91	44	62	775	4.23	Shell grit, grey	0	75	0	1057	27	1.18	0.46	1.64	1.17
80-85	71	8.12	45	220	677	6.02	Shell grit, grey	0	8.5	0	0	0				1.83
115-120	74	8.14	52	1066	870	3.89	Sand, buff coloured	0	121	0	0	0	0.50	0.12	0.62	0.60
120-125	74	7.90	52	15	840	3.89	Sand, buff coloured	1.3	181	0	0	6	0.31	0.29	0.63	0.60
145-150	76	7.85	56	36	759	3.52	Sand, buff coloured	0	92	0	0	0				0.24
150-155	79	7.91	52	0	791	3.39	End of buff layer	0	101.5	0	0	0				
190-195	74	-	54	0	726	3.27	Shell grit, grey	-								
200-205	77	7.73	51	0	759	2.84	Shell grit, grey	0	48.5	0	0	0				
235-240	74	7.86	56	0	837	3.56	Mud, buff coloured	0	73.8	0	0	0				
250-255	74	7.74	55	0	742	2.96	Mud, buff coloured	0	52	0	0	0	0.27	0.08	0.35	
STATION 7							STATION 7									
0-5								6.4	9.6	839	425	29	0.42	0.36	0.78	
30								0	18.9	0	767	27	0.29	0.20	0.49	
80-85								0	21.6	0	0	0	0.24	0.09	0.33	
STATION 9							STATION 9									
0-2	58	8.09	39	0	175	5.02	Shell grit, buff coloured	6.3	9.7	10483	3032	430	2.1	0.37	2.47	1.04
2-7	61	-	36	0	266	-	Shell grit, grey, amine smell	1.9	7.4	3850	1843	151	1.16	0.24	1.4	0.83
20-25	63	7.97	44	36	435	3.93	Sand, grey	0	6.5	0	0	0	2.05	0.18	2.23	0.64
35-40	61	7.96	44	90	613	3.70	Sand, grey	0	8.8	0	0	0				0.64

Footnotes: Column Codes

% - Salinity in ppt as NaCl

pH - These data have not been corrected for the effect of salt

SO4- Sulfate concentration, mM

S2 - Sulfide concentration, μ M

NH4- Ammonia concentration, μ M

AVS- Acid volatile sulfide

TRS- Tin-reducible sulfide

TOT- AVS+TRS expressed as μ mol g⁻¹ day⁻¹

AI - Acid-insoluble organic carbon

AS - Acid-soluble organic carbon

Both AI and AS data were kindly supplied by Dr R Summons

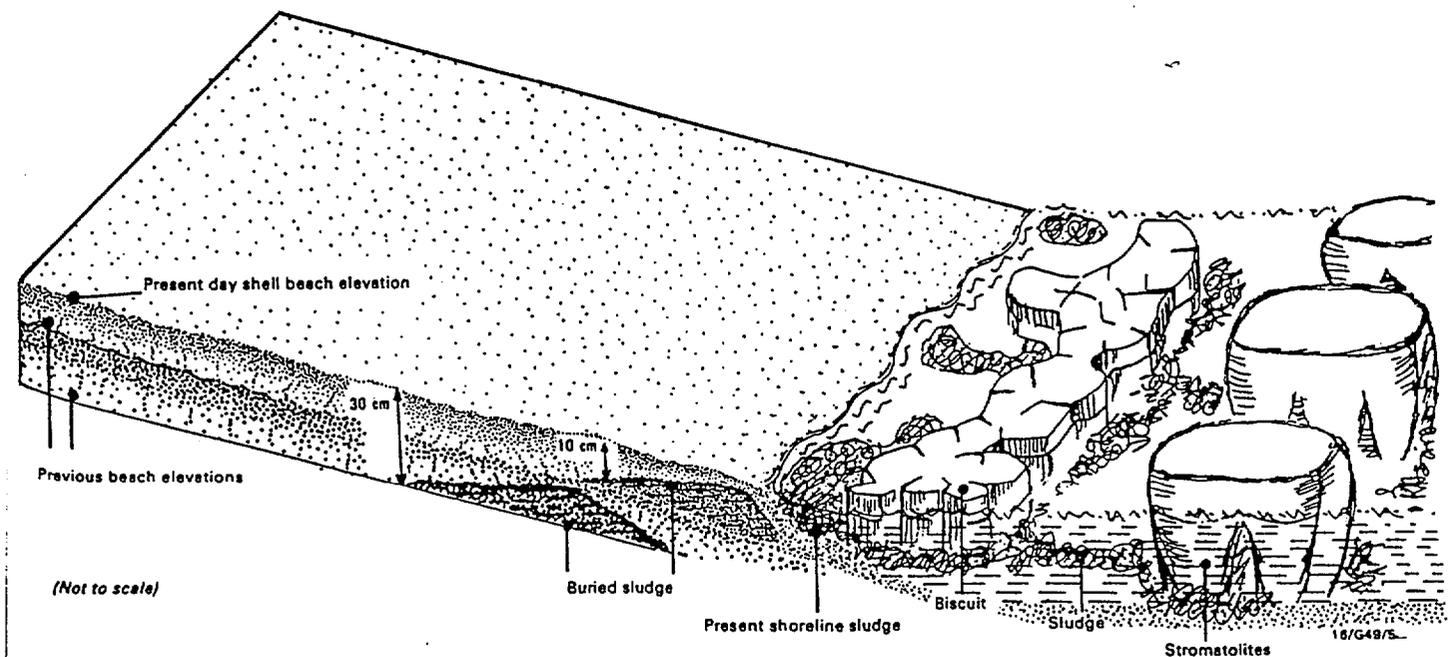
The brief descriptions of the sediments are guides only. They are subject to alteration by more definitive descriptions.

*Calcrete is used as a synonym for lithified carbonate.

TABLE 5 Porewater and sediment analyses, Playford's Transect. Nov. 1984

	%	pH	POREWATER				SEDIMENT			
			SO4 mM	S2- µM	NH4 µM	ALK meq l-1	SULFIDE		REDUCTION RATE	
							AVS µmol g-1	TRS g-1	AVS .mmol m-2 d-1	TRS m-2 d-1
BISCUITS*	70	7.74	29	1580	5404	22	13	51	49718	7488
SLUDGE	65	7.59	38	2224	2975	9	15	37	14722	4036
BURIED 10cm	56	-	15	3125	6241	-	11	46	123879	1389
BURIED 30cm	44	7.85	33	71	1763	7	4	10	11500	5695
SHORELINE SLUDGE	121	7.66	70	882	5990	11	17	35	11526	4751

* These are brief descriptions of the varieties of black sediment in the intertidal areas of Playford's transect. The biscuit material results from the desiccation and cracking of organic sludge which is stranded during low tides. The sediment consolidates and provides a barrier which prevents newly settled organic sludge from being carried back into Hamelin Pool with tidal water. The following drawing is a simplified representation of the sedimentary environment at this location of Playford's Transect.



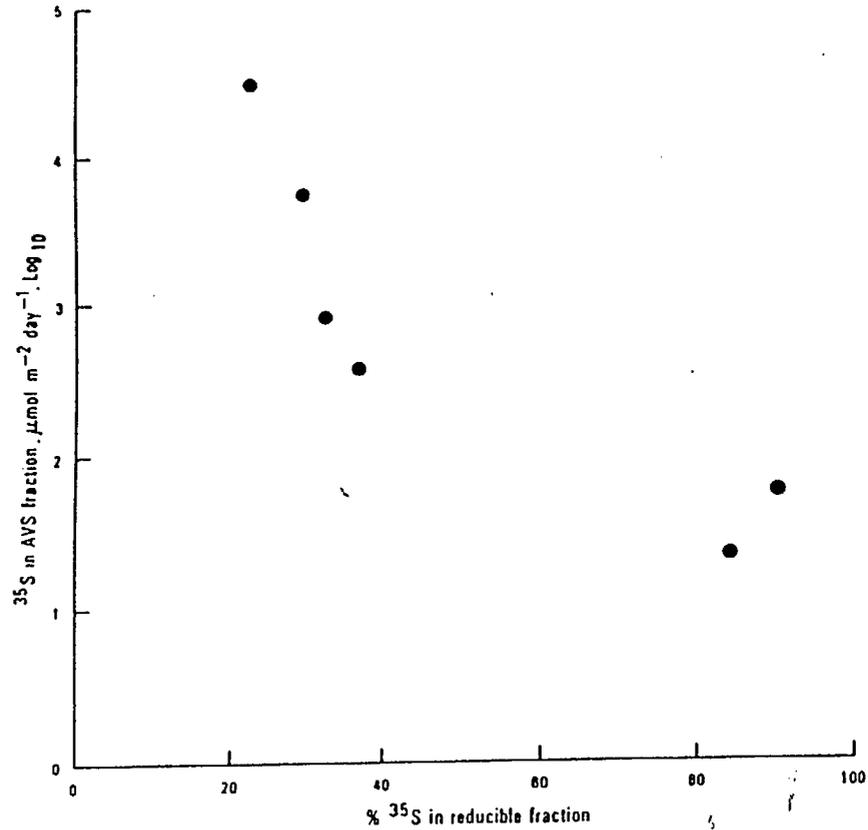


Fig. 11 Relationships between the sulfate reduction rates as AVS and the % of S appearing in the tin-reducible fraction; data from the 0-5cm layer from Hamelin Pool stations 2, 3, 4, 6, 7 & 9.

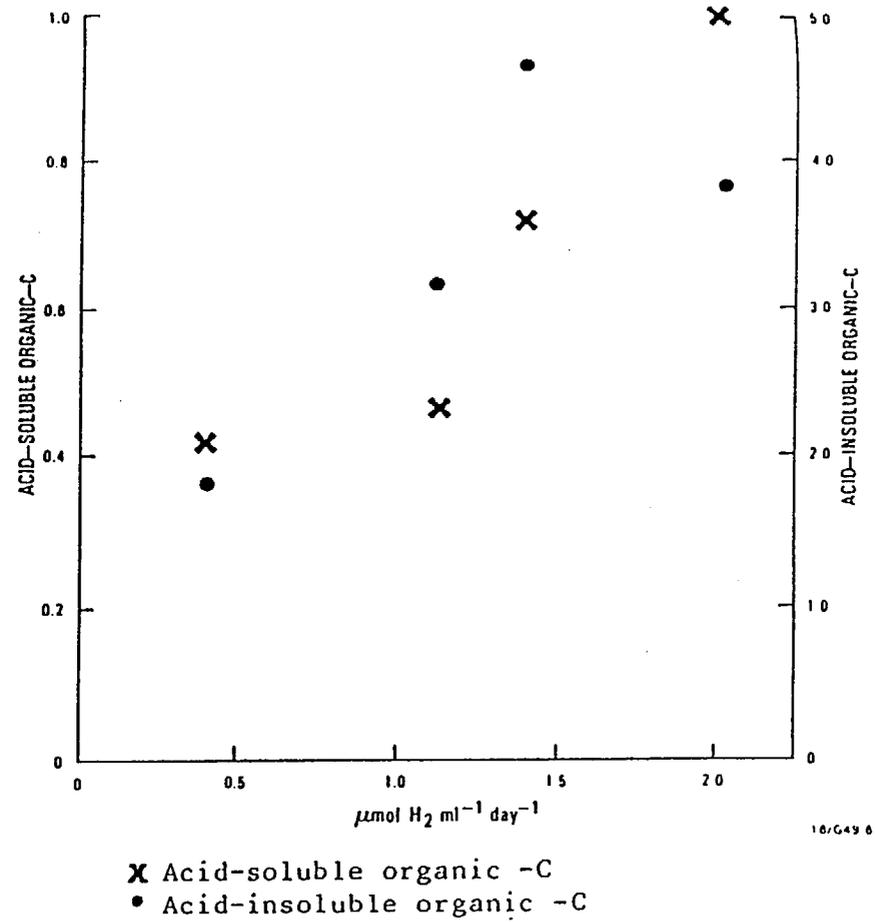


Fig. 12 Relationships between hydrogenase activity and organic carbon in Hamelin Pool sediments from Station 4.

HYDROLOGIC INVESTIGATIONS AT NILEMAH EMBAYMENT, HAMELIN POOL

L.A. Plumb, James Ferguson, B. Simeonovic, I.C. Reichstein

Isotopic data for groundwaters in the tidal flats at Nilemah Embayment have indicated an overprinting of typically marine waters by meteoric water. This is likely to arise from either regional groundwaters or freshwater lenses which result more immediately from local rainfall. The highly permeable character of the Holocene beach ridges which are formed predominantly from *Fragum* shells and which overlie much less permeable Pleistocene strata, may be a contributing factor. In any case, ponding in topographic lows after heavy rainfall is an observed feature.

Two aspects have been considered in attempting to identify the meteoric contribution in the groundwaters. The first is the isotopic composition of the precipitation in the region. This approach has revealed major variations between rainfall events. The limited data available are given in Table 6. When plotted on a deuterium vs oxygen-18 diagram, the winter rainfall events fall on a regression line of slope +7.5 and intercept +14.1. The slope is close to that of the meteoric water line (MWL) (slope = +8) governed by the ratio of the equilibrium isotope fractionations for hydrogen and oxygen between liquid and vapour. The intercept is referred to as the "deuterium excess" and can exhibit considerable deviation from the worldwide average value of +10‰. This deviation is most notable for oceanic vapour sources.

The summer rainfall events do not fall on the local precipitation line, but show evidence of enrichment by evaporation of the rain falling through the dry air of an arid zone. This process involves kinetic factors which reduce the deuterium enrichment relative to that of oxygen-18 and result in evaporation lines with slopes less than 8. Humidity is a major influence and correlates positively with the slope. The samples which show the greatest departure from the MWL are from a series of storms (Nov. 15th, 1983). They also show the influence of what is called "the amount effect" whereby initial or limited rainfall exhibit heavier isotopic compositions.

Effective use of the isotopic composition of rainfall as an end-member in assessment of groundwater isotopic composition thus requires continual monitoring so that an amount-weighted estimate can be achieved. Nevertheless, the data to hand provide important constraints on interpretation of porewater isotopic

data, particularly if there is other evidence of rainwater infiltration.

The second approach to characterise the meteoric component of the Nilemah groundwaters has been to identify the isotopic composition of waters evolving in the back flats where the sediments are Pleistocene-Pliocene aeolian quartz dunes and marine carbonates with horizons of calcrete and clay of lower permeability. Holocene beach ridges of high permeability overlie these strata at the boundary of the back flats and the tidal flats.

Isotopic compositions of waters from this area are given in Table 7. If these waters are evolving by evaporation, there should be a linear relationship between the deuterium and oxygen-18 values which defines the evaporation line. In very arid climates the slope may be as low as 2 for water evaporated in the vadose zone. Whether the quantity of such evaporated waters could substantially influence the isotopic composition of groundwaters in the phreatic zone is, however, open to question. Groundwaters associated with the beach ridges (NBR and some NM) show a deuterium vs oxygen-18 correlation with a slope of 2.4. Inclusion of data from BF3, 4 and 5 in the regression produces no change in slope. These latter sites are in alluvial material derived from the aeolian dunes in which evolution of local recharge could be expected to emulate that in the beach ridges. Extrapolation of this line intersects the local MWL about δD , -29; $\delta^{18}O$, -6.

The remainder of the data is for waters in the Back Flat immediately landwards of the Holocene Beach ridge. Here, the alluvial veneer is thin and at one location the relatively impermeable late Pleistocene marine sediments are exposed and a small salina has formed. The deuterium vs oxygen-18 relationship for these waters falls on a line of slope 3, but at the lowest site (BF15) there is considerable scatter from this line. Consideration of both oxygen-18 and salinity increases suggest that the latter is not simply a result of evaporation but is enhanced by re-solution of salts, or mixing with more highly saline waters. Data for a depth profile of waters from BF15 (included in Table 7) also indicate the presence of different waters.

The available data cannot distinguish precise sources for different waters because of the variety of parameters influencing their evolution. Local recharge appears to have a significant influence and as a result of its isotopic variability the water which evolves may also show considerable scatter. The samples taken at depth

from BF15 may be representative of the meteoric waters likely to influence the tidal flats.

Table 6. Deuterium and oxygen isotope analyses of rainfall at Hamelin Pool.

DATE	TIME	AMOUNT	δD	$\delta^{18}O$	$\delta D - 7.5\delta^{18}O$ (deuterium excess)
		mm	‰	‰	
June 1982		*	-9.0	-3.10	14.3
1-2 June 1983	OVERNIGHT	*	-29.7	-6.02	15.5
2 June 1983	0730	*	-39.6	-7.09	13.6
2 June 1983	1230	*	-1.1	-2.01	14.0
15 Nov 1983	0830-0900	0.5	-9.4	+1.40	-19.9
15 Nov 1983	1230-1730	6.0	-39.3	-3.25	-14.9
15 Nov 1983	1730-2200	20.0	-68.7	-9.09	-0.5
5 Nov 1984	0800-1000	1.0	+23.2	-2.83	2.0
5 Nov 1984	1000-1400	1.5	+18.0	+0.42	14.9

* Not known

Table 7. Deuterium and oxygen isotope analyses of rainfall salinities of groundwaters from the Back Flat, Nilemah Embayment.

SAMPLE+	SALINITY‰	δD ‰	$\delta^{18}O$ ‰
PS4a 5.6M	74	-18.9	-1.22
NBR1 5.4M	88	-15.4	-0.89
NBR2 4.46M	89	-16.8	-0.80
NBR3 6.6M	100	-14.0	-0.19
NBR4 5.3M	108	-12.6	0.47
NM(-3/-4)	86	-15.2	-1.29
NM(-2)	74	-18.5	-1.79
NM1 2.5M	60	-17.5	-1.24
NM2(-10) 2.6M	85	-7.5	-0.12
BF3 3M	64	-17.2	-0.95
BF4 4.2M	65	-16.0	-0.92
BF5 3.3M	78	-15.9	-0.64
BF9a 4.4M	98	-15.0	0.62
BF10 4.5M	104	-11.7	1.57
BF11c 2.6M	100	-12.5	1.64
BF12 5M	123	-8.2	2.71

Table 7. continued

SAMPLE+	SALINITY°/∞	∂D°/∞	∂ ¹⁸ O°/∞
BF 13 4.45M	128	-9.8	2.41
BF 14 2.5M	132	-7.9	2.92
BF 15 2.5M	157	-7.8	2.90
BF 15a	208	-8.9	2.30
BF 15a(bot)	192	-6.8	2.21
BF 15 3.3M	155	-9.4	2.51
BF 15(0-29)	226	-9.2	+2.19
BF 15 top	*	-24.20	-1.72
1.86-1.98M(AHD)	80	-18.60	-1.59
1.74-1.86M	120	-14.80	-0.29
1.60-1.74M	174	-13.30	1.31
1.16-1.60M	196	-11.50	2.62
0.62-1.16M	196	-12.30	2.64
0.20-0.62M	192	-12.40	2.50
-0.24-0.20M	188	-10.90	2.67
BF 16 2M	164	-9.2	2.75
BF 17 4M	138	-5.9	2.42
BF 18a 5.5M	132	-8.8	2.07
BF 19	64	-16.6	2.33

+ PS, Peron Sandstone; NBR, Nilemah Beach Ridge;
 NM, Nilemah: tidal flats; BF, Back Flat.

* Not known

CONCENTRATIONS OF Pb, Zn, Cu AND Cd IN GROUNDWATERS AT HAMELIN POOL, SHARK BAY

James Ferguson, L.A. Plumb, B. Simeonovic, Ian, Reichstein.
(In collaboration with A.W. Mann and M. Linten, CSIRO Division of Mineralogy, Perth, W.A.)

Concentrations of the metals Pb, Zn, Cu and Cd in groundwaters from 3 main types of environment at Hamelin Pool have been determined (Table 8). These environments are: (1) Holocene and Pleistocene marine sediments and adjacent and interfingering redbed sediments at Nilemah Embayment; (2) redbed sediments underlying intertidal Holocene marine carbonates at Booldah Well; and (3) sub-tidal Holocene and Pleistocene sediments beneath Hamelin Pool.

Significant metal concentrations in these environments have been detected only at Nilemah Embayment. Sub-tidal sediments sampled in this investigation usually smelled strongly of sulphide and in all cases metal concentrations were below the detection limits. Metal concentrations in highly saline waters ($S \sim 80\text{‰}$) in redbed and marine sediments at Booldah Well were also below the detection limits, indicating that significant leaching of metals from the redbed sediments is not occurring.

At Nilemah Embayment Pb concentrations are high (up to $4400\mu\text{g/l}$) and concentrations of Cu (up to $70\mu\text{g/l}$), Cd (up to $5\mu\text{g/l}$) and Zn (up to $120\mu\text{g/l}$) may be marginally higher than expected from evaporative concentration of seawater to the same salinities as the groundwaters. In this area, Continental brines of meteoric water origin flow seawards from redbed sediments on the hinterland through Pleistocene marine carbonates and interfingering redbed sequences and then into Holocene carbonates in the supratidal/intertidal zone. It is not clear to what extent the brines associated with the Pleistocene units contribute to the groundwaters in the Holocene carbonate part of the aquifer system where input of seawater and surface runoff of meteoric water may be high. However, a graph (Fig. 13) of Pb concentrations in groundwater samples taken along transects at Nilemah Embayment shows that high values occur in brines in both parts of the aquifer system.

Although the groundwaters associated with the redbed sediments at the landward margin of the embayment are enriched in Pb (e.g. PS3, $840\mu\text{g/l}$) there is no well-defined pattern showing an increase of the Pb concentration with evaporative increases in salinity from landwards to seawards across the Pleistocene

marine carbonate environment (the "back-flats"). In fact, the highest Pb concentrations were detected at BF18 where the salinity (138‰) is less than that of the more landward sample BF17 (172‰). This pattern of Pb concentrations raises the possibility that some of the Pb in the groundwaters in the Pleistocene marine carbonate part of the aquifer system is being leached from the marine carbonates themselves. High Pb concentrations in the sediments have been detected at NM2(-10) (up to 170mg/1000g) but not at NM8 or BF15. Possibly there are high Pb concentrations in both the groundwaters and sediments between NM8 and BF15. They would not have been detected because of limitations on drilling and the large dilution of the brines by meteoric waters in the Holocene beach ridge system which overlies this area.

The Pb concentrations in the brines associated with the Holocene sediments decrease seawards. The Pb concentrations in the Holocene marine carbonates are very low, which suggests that the Pb originates in the seawards-flowing continental brines and that these brines enter the Holocene marine sediment system in significant amounts. Surprisingly, however, the Pb concentrations in the near-surface waters in the Holocene sediments are higher than those in their deeper counterparts.

Clearly, the origins of the Pb in the groundwaters and the processes controlling its mobilization, transport and precipitation are not yet evident. However, the high Pb concentrations in the groundwaters and the high probability that these groundwaters flow to, and interact with, strongly sulphidic intertidal and subtidal environments, indicates that these processes could be analogous to those involved in the formation of some types of low temperature, marginal marine ore deposits.

Table 8 Concentrations of Pb, Zn, Cu & Cd in Surface & Groundwaters at Hamelin Pool

All metal concentrations in µg/l

<u>Classification & Description</u>	<u>Sample Designation</u>	<u>Salinity</u> ‰	<u>Pb</u>	<u>Zn</u>	<u>Cu</u>	<u>Cd</u>
<u>Seawater</u> : Near-shore, Nilemah	M4, filtered & M5 not filtered	65	<5	<50	<5	<5
<u>Nilemah Embayment:</u>						
Peron Sandstone (redbeds)	PS3	52	840	<200	<10	1.3
	PS1	49	260	<200	40	3.9
Back flats (Pleistocene marine carbonates/redbeds)	BF5	78	60	120	50	2.2
	BF11a	113	960	40	30	0.5
	BF12	121	280	<200	20	1.5
	BF13	122	560	<200	30	0.9
	BF14	136	380	<200	<30	0.6
	BF15	155	1900	<100	70	0.5
	BF16	172	560	<100	10	0.9
	BF17	147	1700	<100	35	3.4
	BF18	138	4400	<100	<100	2.1
Holocene Beach Ridge (Holocene/Pleistocene marine carbonates)	NM(-3/-4)	85	340	<100	40	1.4
	NM(-2)	70	60	<100	20	0.7
	NM1	77	580	60	20	3.2

Table 8 contd

<u>Classification & Description</u>	<u>Sample Designation</u>	<u>Salinity</u> ‰	<u>Pb</u>	<u>Zn</u>	<u>Cu</u>	<u>Cd</u>
High Supratidal (Pleistocene marine carbonates/ redbeds)	NM8 (shallow)	~225	2000	<50	<5	10
	(deep)		1600	<50	<5	5
Supratidal (Holocene marine carbonates)	NM15/16 (shallow)	136	1400	<50	<5	<5
			1100	<50	<5	5
			600	<50	<5	<5
	(deep)	150	450	<50	<5	<5
	NM19 (shallow)	168	130	<50	<5	<5
		(deep)	154	30	<50	<5
Holocene Beach Ridge (Holocene marine carbonates)	NMR (deep)	172	120	<50	<5	<5
?Pond at end of Holocene beach ridge	Ponded water	186	60	70	60	1.3

Table 8 contd

<u>Classification & Description</u>	<u>Sample Designation</u>	<u>Salinity</u> ‰	<u>Pb</u>	<u>Zn</u>	<u>Cu</u>	<u>Cd</u>
<u>Booldah Well</u>						
Intertidal Holocene marine carbonates	BW1(1) 0-11 cm	78	<5	<50	<5	<5
Underlying redbed sand	BW1(2)50-61 cm	78	<5	<50	<5	<5
Underlying redbed sand	BW1(3)	82	<5	<50	<5	<5
Intertidal Holocene marine carbonates	BW2 marine	67	<5	<50	<5	<5
Underlying redbed sand (reduced)	BW2 reduced sand	81	<5	<50	<5	<5
Underlying redbed sand (oxidized)	BW2 oxidized	81	<5	<50	<5	<5
<u>Subtidal, Hamelin Pool</u>						
Offshore, Nilemah	St2, 2 nd core 80-85 cm	100	<5	<50	<5	<5
	St3, (275) 40-50 cm	78	<5	<50	<5	<5

Table 8 contd

<u>Classification & Description</u>	<u>Sample Designation</u>	<u>Salinity</u> ‰	<u>Pb</u>	<u>Zn</u>	<u>Cu</u>	<u>Cd</u>
	St3,(275)					
	120-135 cm		<5	<50	<5	<5
	260-280 cm		<5	<50	<5	<5

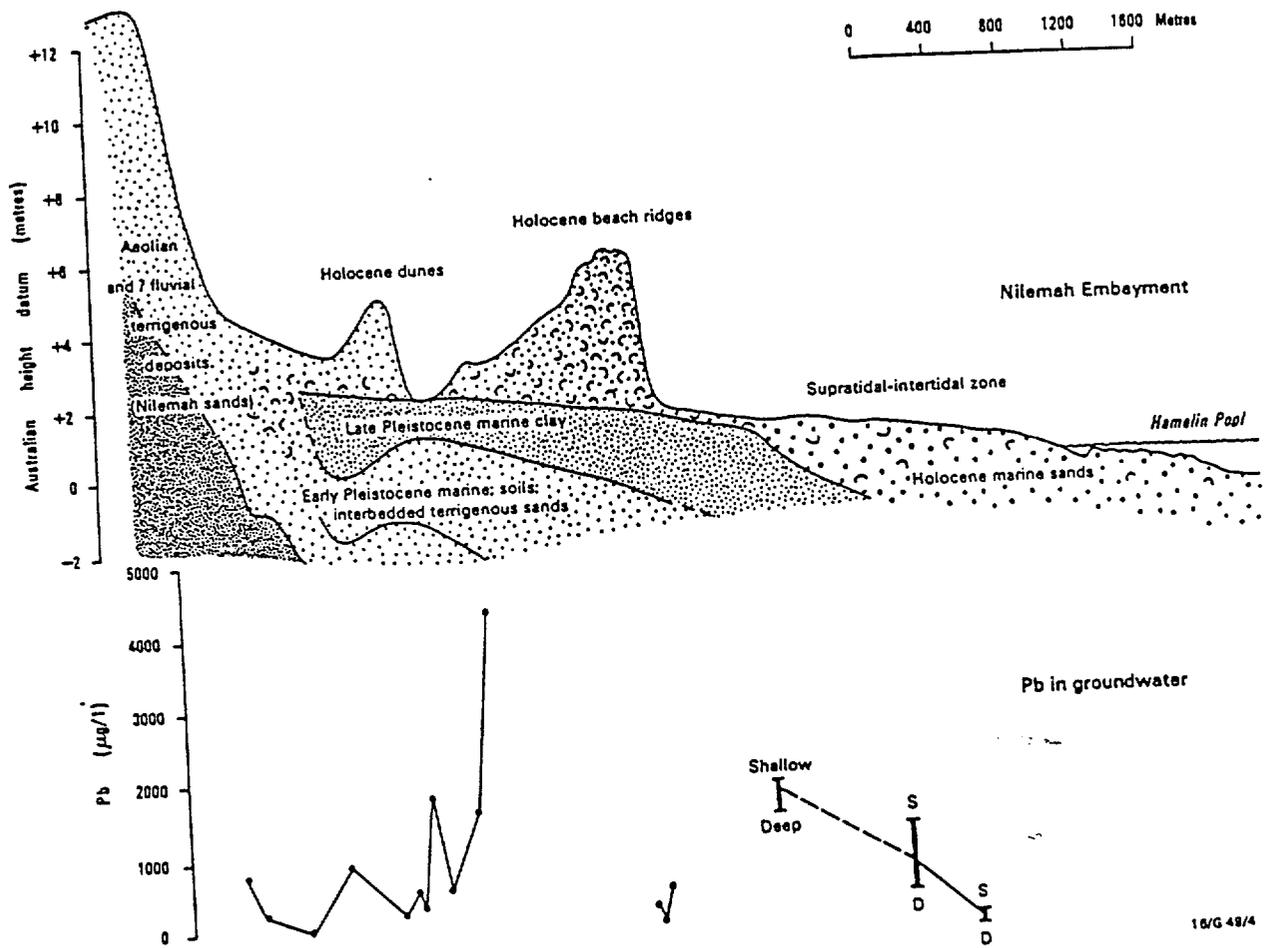


Figure 13 Pb concentrations in groundwaters at Nilemah Embayment

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
AUGUST, 1985

GEOBIOLOGICAL CONTROLS ON ORE FORMATION

ABSTRACT

Rates of sulphate reduction in Hamelin Pool, Shark Bay, are commensurate with those required for the genesis of stratiform copper ore deposits such as the Kupferschiefer (Mansfeld).

GEOBIOLOGICAL CONTROLS ON PETROLEUM
FORMATION AND ACCUMULATION

ABSTRACT

Algal and bacterial dominated environments at Shark Bay and in coastal lagoons serve as models of Proterozoic and younger source and reservoir rocks. At Hamelin Pool, Shark Bay, the major sources of organic matter are the benthic microbial communities: hydrocarbon biomarker patterns show positive correlations with depth and total organic carbon. A model is presented for the formation of high-grade oil shales (torbanites) by the hydrocarbon-rich alga, *Botryococcus*.

HAMELIN POOL, SHARK BAY, AND COASTAL LAGOONS AS
MODELS FOR STUDIES OF PROTEROZOIC AND YOUNGER
SOURCE AND RESERVOIR ROCKS.

R.V. Burne, J. Bauld, D. Ho

Algal and bacterial dominated environments are of particular geological significance as the sites of primary production and degradative modification of organic matter that produces rich Type I and II kerogens. In addition, many Proterozoic and Phanerozoic limestones appear to have been deposited in environments strongly influenced by algal and bacterial ecosystems. The decline in the relative importance of microbial systems with the evolution of higher life forms through the Phanerozoic is well documented, and microbial systems dominate today only in specialised environments such as carbonate tidal flats, saline lakes, and hot springs. These are not direct analogues of ancient holomarine microbial environments. They nevertheless provide vital information for the interpreting of ancient sequences.

Intermittently exposed cyanobacterial mats are found in intertidal zones and along seasonally exposed lake margins. A number of factors influence their distribution, the most important probably being frequency and duration of inundation. They are important producers of organic carbon, but the intermittent exposure typical of their environment assists the diagenetic destruction of the organic material. Conditions favourable for the preservation of organic carbon in mat deposits are encountered in Lake Eliza, where the mat sediments occur along a saline groundwater seepage zone. The positive head of water together with the porous but impermeable mat sediments provide an interstitial environment that inhibits complete degradation of the organic material.

Subaqueous environments provide a setting more favourable for the preservation of organic matter. In the southern basin of Hamelin Pool a benthic organic mat comprising diatoms, cyanobacteria, as well as other organisms exists in 5m of water at salinities of about 68‰. Despite an active fauna of shrimp and fish, organic material is preserved beneath this mat to a depth of 20cm.

Microbial communities play a vital part in the formation of lithified stromatolites in several lakes as well as in Hamelin Pool. Mineralogies range from gypsum through monohydrocalcite, calcite, and aragonite to protodolomite. Textures vary from laminated, through thrombolitic to travertine. Morphologies also show great variety, with club-shaped forms in the high energy oolitic environments of Hamelin Pool, large mound structures in the relatively quiet deeper waters of Lake Inneston, and small columnar colonies in the shallow marginal waters of Slereford Mere.

Studies of these present day systems are providing information of direct significance for the interpretation of Proterozoic and younger source and reservoir rocks.

ORGANIC GEOCHEMICAL STUDIES IN HAMELIN POOL

R. Summons, V. Grey

Organic matter in surface sediment of Hamelin Pool is generally in low abundance (1-2% T.O.C.). The exception is a moderately organic-rich deposit at the southern end of the basin plain (~5% T.O.C.). On the sublittoral platform the T.O.C. values decrease rapidly down the sediment column. Organic matter is present at depth in cores from the basin plain.

The major source of Hamelin Pool organic matter is considered to be subtidal benthic microbial communities. These communities shows interesting variations in biotic composition and are generally dominated by diatoms with some cyanobacteria. The organic-rich deposit in the southern end of the basin plain contains diatoms not previously recognised in this basin. As well, a live community of *Fragum* was observed.

Hydrocarbon biomarker patterns show consistent positive correlations with depth and with T.O.C. Benthic mat communities which can be visually distinguished by their microbial components can also be differentiated by their very distinctive hydrocarbon distributions. Biomarker profiles indicate a large component of heterotrophic bacteria in the benthic communities.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
NOVEMBER, 1985

GEOBIOLOGICAL CONTROLS ON ORE FORMATION

ABSTRACT

Additional detailed work in Shark Bay has defined the rates of sulphate reduction in several extensive areas and has provided some evidence for possible lateral migration of sulphide.

GEOBIOLOGICAL CONTROLS ON PETROLEUM
FORMATION AND ACCUMULATION

DIAGENETIC PRODUCTS OF MARINE AND CONTINENTAL
GROUNDWATER SYSTEMS

L.A. Plumb, James Ferguson, B. Simeonovic, I.C. Reichstein

Stable isotope distributions in diagenetic products can be used to elucidate formation mechanisms within the modern environment and to establish an association in particular environments between sedimentological features and isotopic distribution patterns. These can then serve as a basis for interpretation of ancient environments.

Carbon and oxygen isotope distributions in waters, dissolved carbonates and carbonate minerals are considered relative to those of standard mean ocean water (SMOW) for oxygen, and Peedee Belemnite (PDB) for carbon. Positive or negative permil deviations from these zero points means increased or decreased heavy isotope content.

Carbonates (excepting dolomite) precipitated in equilibrium at 25°C will differ by approximately +28‰ from the oxygen of the parent water. Dolomite will tend to be an additional 3-6‰ heavier. Under the same conditions there is about +2‰ fractionation for carbon between dissolved bicarbonate and the precipitated carbonate except for dolomite which is at least 2‰ heavier. Oxygen isotope fractionation decreases with increasing temperature by about 7‰ from 0 to 30°C while carbon isotope fractionation increases by only 1‰. In the parent solution evaporation causes heavier oxygen and carbon values because of the loss of the light isotopes. Photosynthesis within waters depletes the bicarbonate reservoir of light carbon thus creating a

tendency for precipitated carbonates to be heavier in such an environment. Also, if the produced organic matter (-7 to -34‰) is subsequently oxidised in another environment a localised reservoir of light bicarbonate occurs. An example of this is seen in soil horizons with resulting light carbonates being formed.

At Nilemah Embayment a 12m drill-hole (NM2B) at the landward fringe of the present-day supratidal zone intersects sediments of a marginal marine environment from the Pleistocene. Marine units are interbedded with soils formed during phases of regression and interfringed with underlying and laterally equivalent terrigenous sands and sandstone. Calcrete, gypsum and dolomite are present. Table LAP1 lists geochemical and petrological data for the sediments in relation to depth and sedimentary environment. There is additional drill-core (PS2) data from an area of the sandstone immediately landwards of the marine sediments.

The sulphur isotope compositions of gypsum from different levels is a simple illustration of overprinting of the original depositional environment. They show no correspondence with the primary environments since values less than 21 are indicative of continental influence for gypsum. Calcretes and dolomites show at least two generations but although spatially related a genetic association is doubtful on the basis of the separation of the oxygen isotope contents. The brine causing the dolomitisation has been highly evaporated to raise the oxygen value to around 38‰ . Present-day meteoric waters are not quite heavy enough to produce such oxygen values. The dolomites are also unusual in having comparatively light carbon contents. The most likely explanation for these values is in the oxidation of organic matter producing light carbonate in solution.

SAMPLE IDENTIFICATION	FORMATION/AGE	XRD major	XRD minor	DEPTH (M)	PERCENT CO2	PERCENT Ca	PERCENT Mg	PERCENT SO4	PERCENT Ca as CO3-	RATIO Mg/Ca as CO3-	PPM Sr	RATIO Sr/CO2	13 & Cpdb	18 & Osmow	34 & Scdt	87 /86 Sr
NM 28 /42	Bibra/l Pleist	Q,4-16MgCO3	dol,arag	1.15	34.20	26.90	3.04	0.81	26.562	0.1144	2100	61.403	2.448	32.834		
NM 28 /41	..	Q,4-12MgCO3,dol	arag	1.30	29.00	23.30	2.43	0.83	22.954	0.1058	1550	53.448	1.095	31.485		
NM 28 /40	..	Gyp,4-12MgCO3,dol	arag	1.40	30.00	22.40	2.82	0.72	22.100	0.1276	1250	41.666	1.876	32.532		
NM 28 /39	..	Gyp,Q,dol,2-12MgCO3		1.55	27.00	20.70	2.98	3.84	19.100	0.1560	3800	140.740	1.873	33.020		
NM 28 /38	..			1.80	24.80	21.10	2.72	9.88	16.983	0.1601	940	37.903				
	..	Gyp		1.90												22.30
NM 28 /37	..	Gyp,Q,dol,2-12MgCO3	arag	1.95	24.90	20.20	2.91	6.94	17.308	0.1681	980	39.357	1.274	32.759		
NM 28 /36	..	Q,2-16MgCO3,dol	arag	2.10	25.50	18.40	3.16	2.07	17.537	0.1801	860	33.725	0.600	31.707		16.80
	..	Gyp		2.20												22.00
NM 28 /35	..	2-8MgCO3,gyp,dol		2.30	22.70	17.00	2.67	2.91	15.787	0.1691	740	32.599	0.500	32.573		
NM 28 /34	..	Gyp,Q,dol,2-16MgCO3		2.50	19.70	15.80	2.34	4.26	14.025	0.1668	610	30.964	0.217	32.356		
NM 28 /33	..	2-12MgCO3,Q,dol	arag	2.60	26.90	25.30	2.45	0.91	24.920	0.0983	2100	78.066	1.703	31.854		
NM 28 /31	Dampier/e Pleist	Cal,gyp,Q,dol		2.75	15.10	12.80	1.29	1.86	12.025	0.1072	450	29.801	-3.187	29.543		
NM 28 /30	..	Q,2MgCO3,gyp,dol		2.95	17.40	15.70	1.16	4.59	13.787	0.0841	530	30.459	-3.407	29.799		
NM 28 /29	..	Q,2MgCO3,dol		3.15	20.80	16.00	1.91	0.41	15.829	0.1206	710	34.134	-3.626	29.668		
NM 28 /28	..	Q,2MgCO3	dol	3.30	22.10	16.90	2.26	0.44	16.716	0.1351	800	36.199	-3.367	30.186		
	..	Gyp		3.40												21.90
NM 28 /27	..	Gyp,Q,dol,4MgCO3		3.60	19.50	14.60	2.97	4.90	12.558	0.2364	690	35.384	-2.753	31.245		
NM 28 /26	..			4.00	18.60	15.30	4.84	13.80	9.550	0.5068	590	31.720	-1.347	35.883		19.90
NM 28 /25a	..	Q,gyp,2-8MgCO3,dol,arag		4.20	21.40	17.50	2.29	2.61	16.412	0.1395	2300	107.476	-0.498	32.018		
NM 28 /25b	..	2-12MgCO3		4.20	35.00	27.90	2.81	0.83	27.554	0.1019	1250	35.714	1.994	32.678		
NM 28 /24	..	Q,dol,2-16MgCO3	arag	4.40	32.40	25.20	3.01	1.20	24.700	0.1218	1900	58.641	1.567	32.217		
NM 28 /22	Peron Ss/Plioc-Pleis	Dol,Q,gyp	tr.cal	4.50												21.30
	..			4.55	23.10	15.90	5.54	9.14	12.091	0.4581	630	27.272	-1.152	36.003		
NM 28 /21	Dampier/e Pleist	Cal,Q	Gyp,dol,arag	4.85	32.90	27.20	1.91	1.75	26.470	0.0721	2200	66.869	0.664	32.463		
	..			4.90												21.90
NM 28 /20	..	Dol,gyp,Q		4.95	18.90	11.30	4.90	5.08	9.183	0.5335	360	19.047	-1.601	37.659		21.20



SULFATE REDUCTION IN SEDIMENTS FROM NILEMAH EMBAYMENT, SHARK BAY

G.W. Skyring, J. Luck

There is an extensive volume of sediment at Nilemah embayment which is grey and contains tin-reducible sulfide, presumed to be indicative of pyrite. The colour change from buff to grey occurs near the groundwater table. In previous studies active sulfate reduction was not demonstrated, however, sampling this environment was difficult and the data were equivocal. In the present series of investigations, several experimental procedures were used to improve the methodology and increase the chances of observing microbial activity. None of the following procedures resulted in observable sulfate reduction:

- * rapid sampling and incubation for long periods under high purity nitrogen
- * addition of sulfide to maintain a low Eh during the preparation of the samples
- * addition of acetate and lactate, known to be readily oxidised by the sulfate reducers
- * careful determination of experimental error to facilitate the detection of very low sulfate reduction rates.

From other studies on sediments, sulfate reduction has been measured at very low rates of $2-3 \text{ nmol g}^{-1} \text{ day}^{-1}$ which is the lower limit of detection. Thus if sulfate reduction occurs in the grey surface sediments at Nilemah Embayment, the average daily rate is probably $<2 \text{ nmol g}^{-1} \text{ day}^{-1}$.

Although the sulfate reduction rates are not detectable, the pore water of this grey sediment is characterised by a low Eh and a low but detectable sulfide content. Also, ammonia which is indicative of anaerobiosis in sediment porewaters, was detected (Figure 1).

Either the pyrite, sulfide and ammonia associated with these sediments are relics of some previous seasonal or historical event, or the ammonia and sulfide have been transported from other locations.

Because of the important geochemical implications of this extensive anoxic environment, subsequent investigations will be directed to resolving this question.



Sulfate reduction in a solar pond

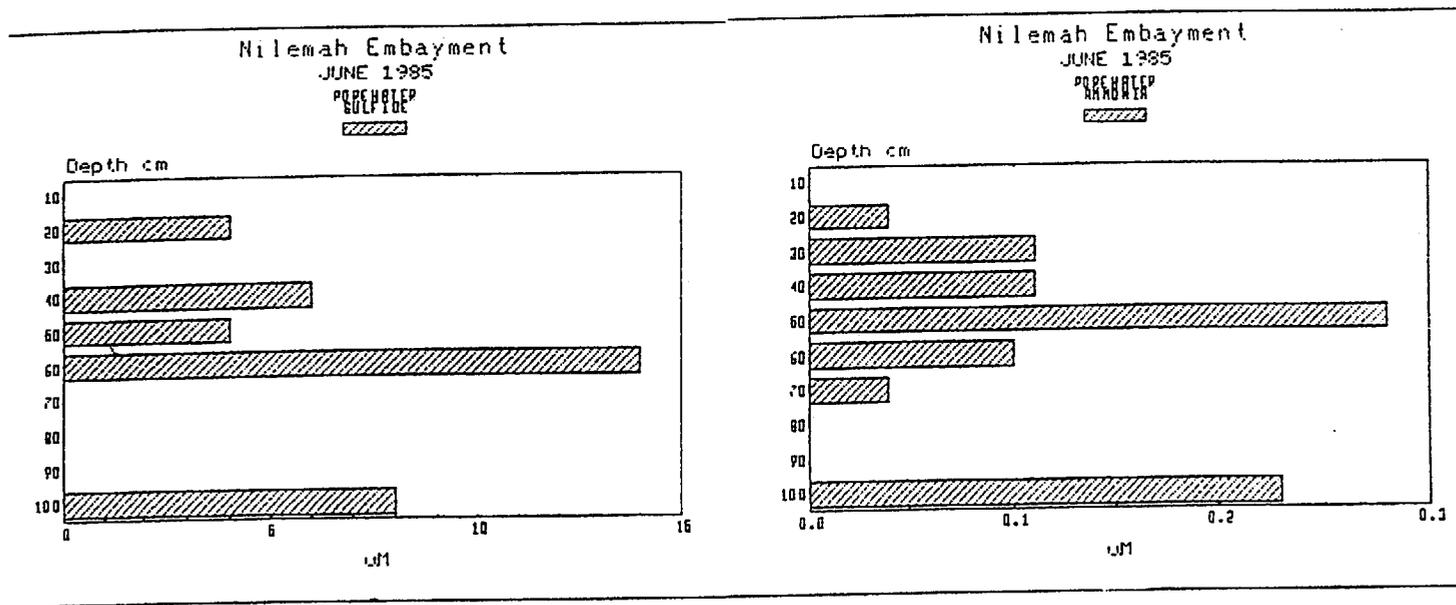
A solar pond on the western shore of Hamelin Pool north of Booldah Well, is representative of one of the many environments where anaerobic microbial processes in sediments are predominant. The pattern of sulfate reduction with depth was normal being maximal in the surface layers and decreasing rapidly with depth. However, contrary to expectation, the salinity of the porewater decreased from 143‰ in the upper 5cm to 29‰ in the 35-40cm layer. These data indicate that the lake is being replenished with water from the bottom. Acid volatile sulfide decreases and below 5cm, tin-reducible sulfide increases with depth (Figure 2).

Sulfate reduction in Lake Eliza sediments

Previous investigations showed that sulfate reduction occurred in the subsurface layers of the organic rich layers of Lake Eliza sediments at two stations, 350m and Water Spring in November 1983 and 1984 but it was not detected at other times of the year. Subsurface samples taken during March of 1985 were incubated under nitrogen for longer periods (up to 17 days) than previously and as a result, very low sulfate reduction rates from 2 to 3 nmol g⁻¹ day⁻¹ were measured.

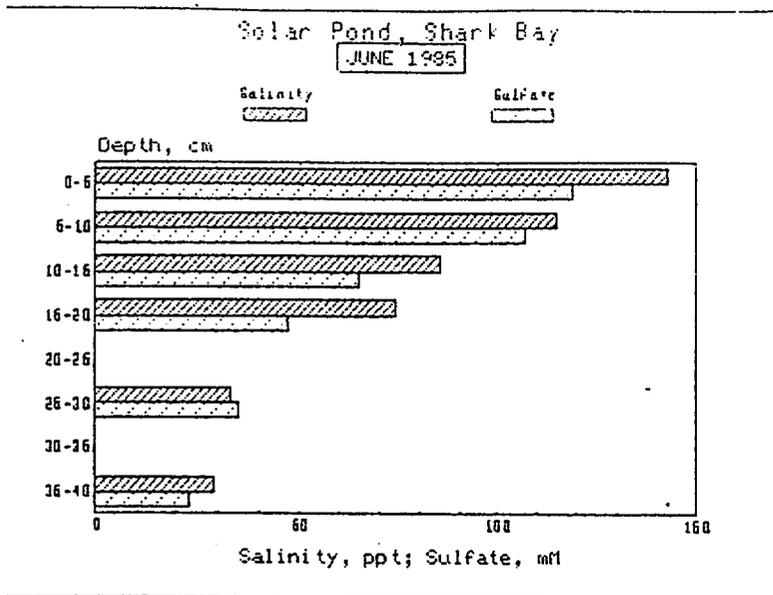
Some samples were incubated in the presence of molecular hydrogen which is used by most of the sulfate reducers to reduce sulfate. Hydrogen is a preferred substrate, inducing fast reduction rates thus providing some relative measure of the sulfate reducing capacity of the sediments from various layers. As might be expected, stimulation of sulfate reducing activity occurred in the 0-5cm layers from both the 350m and Water Spring stations. Slightly higher sulfate reduction rates were measured in the subsurface layers from the Water Spring station but stimulation was not observed in the 350m sediments below 5cm. In a slurry of sediment from the 0-5cm layer of the Spring station, sulfate reduction was increased by about five times the rate observed in samples incubated under nitrogen. In intact samples, the rate in samples under hydrogen was increased 25 times over that measured for samples under nitrogen. The data from these various experiments indicate that sulfate reducers are active in the sediment down to around 50cm but below that depth the sulfate reducers must be very sparse with a very low aggregate activity.

Figure 1

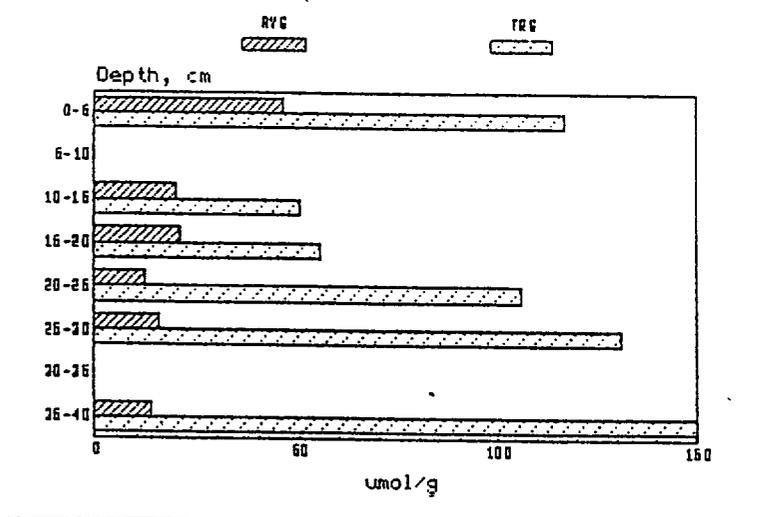


Sulfide and ammonia concentrations in porewaters from sediments of transect NM (at NM22.5).

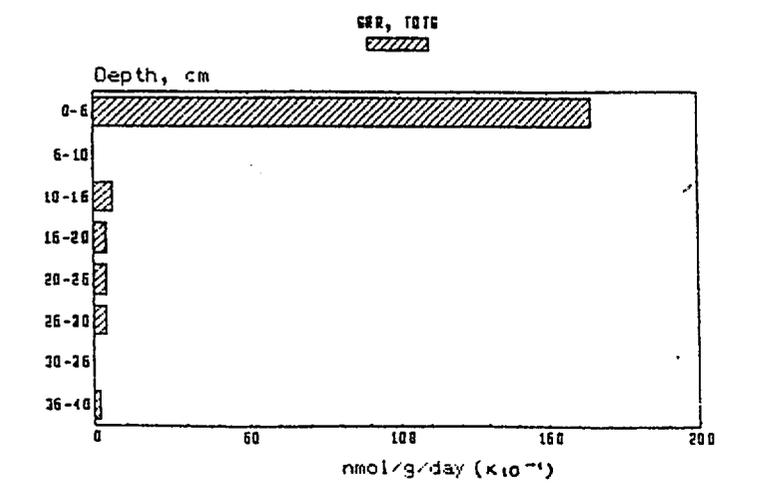
Figure 2 --



Salinity and sulfate concentration of the Solar Pond porewater.



Acid volatile (AVS) and tin-reducible sulfide (TRS) of the Solar Pond sediments.



Sulfate reduction rates in Solar Pond sediments.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
JANUARY, 1986

GEOBIOLOGICAL CONTROLS ON PETROLEUM
FORMATION AND ACCUMULATION

INTRODUCTION

Continuing field work in Shark Bay has produced new insights on the distribution of the columnar stromatolite lithofacies, a facies that can be considered as a potential petroleum reservoir and which in fact is comparable to some such reservoirs.

SULPHUR OXIDATION IN SHARK BAY SEDIMENTS

P.A. Trudinger and L.-E. Hogle

One of the objectives of the Shark Bay research program is to determine the relative importance of various environmental factors in controlling the preservation of sulphide in sediments.

In broad terms, in the absence of hydrothermal inputs, sulphide accumulation in sediments is governed by:

- . the rate and extent of bacterial sulphate reduction,
- . the supply of metals,
- . the rate and extent of sulphide diffusion, and
- . the rate and extent of sulphide oxidation.

Sulphide can be oxidised anaerobically by certain photosynthetic bacteria and cyanobacteria (blue-green algae). Alternatively, oxygen-linked oxidation can occur either chemically or catalysed by chemolithotrophic sulphur bacteria - i.e. bacteria that utilise the energy derived from the oxidation of reduced sulphur compounds for growth.

Morphologically distinct chemolithotrophic sulphur bacteria have been isolated from surface sediments from Gladstone Embayment and Site 4 of Hamelin Pool. Enrichment cultures on thiosulphate developed within 1 to 2 days indicating that the organisms play an active role in sulphur cycling in these sediments.

The organism from Gladstone Embayment is a small motile rod that oxidises thiosulphate completely to sulphate. It is a strict autotroph i.e. it is unable to utilise organic compounds but obtains its carbon for growth from carbon dioxide. It grows optimally in

6% NaCl which is close to the salinity of Hamelin Pool water. It is unable to oxidise polythionates: its ability to oxidise sulphide has not yet been tested.

The sulphur bacteria are to be examined for the presence of unique markers detected in Hamelin Pool sediments.

FACTORS INFLUENCING STROMATOLITIC DEVELOPMENT IN HAMELIN POOL

R.V. Burne

Work undertaken elsewhere in Shark Bay by U.W.A. has demonstrated several areas of groundwater resurgence around the coastline. Few data are available for Hamelin Pool, and so, since many occurrences of lacustrine stromatolites are in areas of groundwater discharge, attempts were made to detect evidence of groundwater discharge in areas of active stromatolite growth.

A seepage flux device modified by L.S. Moore (U.W.A.) from the design of Lee (Limnology and Oceanography, 1977) was installed consecutively at Carbla Point, Booldah Well, and in the solar pond onshore of Snake Bank. A positive flux was recorded at all locations, though reliable rates and groundwater character could not be measured because of the short period available for the experiments. The occurrence of groundwater seepage in the solar pond is particularly interesting, and supports our earlier suggestion that these features may have been created by spring sapping.

Work in co-operation with Prof. N. James (Memorial University, Newfoundland) was undertaken on the subtidal stromatolites off Carbla Point and south of Flagpole Landing. The lithified subtidal platform south of Flagpole Landing is petrographically similar to the columnar stromatolites, and this platform forms the foundation for columnar stromatolite growth. A series of intertidal mound-like stromatolites at Carbla Point were excavated and proved to be partially buried columnar stromatolites rising from a lithified sheet. It is concluded that these stromatolites were of sub-tidal origin and grew from an old sub-littoral lithified platform. They have since been stranded by falling sea level and partially buried in intertidal deposits.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
APRIL, 1986

GEOBIOLOGICAL CONTROLS ON ORE FORMATION

ABSTRACT

In the research on Shark Bay, evidence suggesting lateral transport of sulphide in the groundwaters continues to accumulate.

GEOBIOLOGICAL CONTROLS ON PETROLEUM
FORMATION AND ACCUMULATION

ABSTRACT

The organic geochemistry of the Holocene sediments of Shark Bay has been shown to be distinctive. In addition to the presence of some unusual compounds, bacteria from these sediments produce hydrocarbons with an even over odd carbon number preference. This will be of sedimentological and geochemical significance.

ORGANIC GEOCHEMICAL STUDIES IN SHARK BAY -
OBSERVATIONS OF BACTERIAL HYDROCARBONS WITH
STRIKING EVEN OVER ODD PREDOMINANCE

R.E. Summons, J. Bauld, T. Hiesler, V. Grey and D.T. Ho

Progress on this project was last reported in May 1985 where we recorded quite high T.O.C. values in the surface sediments of an extensive topographic low in the basin plain of Hamelin Pool. We also reported dominance of the sediment-hydrocarbon distribution by a previously unknown C₂₅:₂ isoprenoid alkene. These particular sediments can be distinguished from those of the remainder of the basin plain by the abundance of C₂₅:₂ relative to the C₂₅:₁ hydrocarbon identified by Dunlop et al. (1985). Since then, we have found numerous literature reports of the occurrence of these highly unusual and distinctive compounds in water column particulates, sediments and grab samples of benthic algae. Only in 1986 publications have some chemical structures been correctly assigned and in no case has the specific source organism been unambiguously identified. There is world-wide interest in the distribution and origin of these hydrocarbons and several of the above mentioned occurrences have similar characteristics to Shark Bay including the carbonate shelf sediments of the north-eastern Gulf of Mexico and a series of hypersaline ponds (Los Monegros) and

lagoons of the Ebro Delta in Spain (Albaignes et al., 1984). A major aim of this project, therefore, is to correctly determine the structures of all C₂₅ hydrocarbons and ascertain, if possible, their relationships to specific source organisms and depositional environments.

A large number (ca. 80) of aerobic heterotrophic bacteria, cyanobacteria and diatoms were cultured from Shark Bay sediments in order to identify the specific source(s) of the C₂₅ hydrocarbons. Initial work has been directed towards study of the aerobic heterotrophs of which about 50 have been isolated into axenic culture. These cultures were extracted, chromatographed and the n-alkane distributions studied by GC and GC-MS. Thus far, none of the C₂₅ hydrocarbons have been observed in these organisms. However, of the 50 samples investigated, about 20 show a remarkable even-to-odd predominance in the C₁₆-C₂₀ range and a slight odd-to-even predominance in the higher carbon number distribution.

Previous studies of n-alkanes in modern and Holocene sediments indicate that a predominance of odd carbon number alkanes in the C₁₅-C₃₅ range is common. Odd over even predominance of long-chain n-alkanes is also the hallmark of many ancient terrestrial and lacustrine organic-rich sediments and petroleums. Even over odd predominance in n-alkanes is therefore highly unusual although it has been observed in several recent marine sediments and a Miocene evaporite in the Mediterranean. Nishimura and Baker (1985) recently reported a striking even to odd predominance (C₁₆-C₂₄) in some recent marine surface sediments and by a process of elimination, speculated that the source could be marine bacteria. They discounted the possibility of formation by diagenetic reduction processes or direct marine planktonic origin.

Welte and Ebhardt (1968) have proposed diagenetic reduction of the corresponding n-fatty acids as a source of these even carbon number n-alkanes. However, these reduction processes are unlikely to occur in modern marine sediments and hence the data suggest that the even-predominant n-alkanes originate, without modification, from the marine biota. Our work supports this interpretation, since the same even-to-odd predominant n-alkane distribution was observed from our cultures of Shark Bay bacteria.

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SULFATE REDUCTION IN SUPRATIDAL, SURFACE SEDIMENTS AT NILEMAH EMBAYMENT : (HAMELIN POOL, SHARK BAY)

G.W. Skyring, J. Luck

Introduction

Previous reports on microbial activity in the pyrite-containing subsurface sediments of the supratidal zone of Nilemah Embayment are given in Quarterly Reports August and November, 1984, November 1985. These studies indicated that sulfate reduction was not occurring at measurable rates in these sediments. Thus there remained the problem of explaining the persistence and origin of the sulfide. A possible explanation was that the method for measuring sulfate reaction rates was insufficiently sensitive to measure very low rates. Another possibility was that sulfate reduction in these supratidal sediments was seasonal and that the time most conducive to active sulfate reduction was during the winter when tidal waters, containing nutrients, flood the supratidal plains of Nilemah Embayment.

Therefore, sulfate reduction rates were measured in 35 subsurface sediment samples representing several environments along the NM transect and transects 30 and 31 collected in July 1985 (see p. 13 Quarterly Report, May 1984). In this series of experiments the samples were incubated in an atmosphere of high purity N₂ for 24 days.

Results and Discussion

There was no sulfate reduction detected in any of the subsurface sediments even in those supplemented with acetate and lactate - containing growth media. It is possible that sulfate reduction has not yet been measured at the appropriate season. However, it seems from the data that has been obtained for the last three years that microbial productivity is non-existent or extremely low for most of the year in these supratidal, subsurface sediments (Dr. F.S. Lupton measured very low levels of microbial activity in these sediments by a sensitive tritium incorporation method, Quarterly Report, November 1984).

TABLE - Chemical and physical properties of porewaters from Nilemah Embayment, TRANSECT NM 19 (STATIONS 2 TO 33) and Hamelin Pool (STATIONS HP 2 to 4)

STATION	← SUPRATIDAL →						← INTERTIDAL →		← SUBTIDAL →				Hamelin Pool Water
	2	5	7	15/16	19	21	27	30/31	33	HP2	HP3	HP4	
DEPTH (cm)	180	140	120	106	100	105	25	60	80	80	100	100	0
SALINITY ‰	98	188	228	139	161	168	142	118	108	99	79	66	68
Eh* (mV)	238	252	184	78	158	110	22	-23	-7	ND	ND	ND	370
SULFIDE (μM)	0	6.4	3.7?	17	8	8	44	89	212	47 [∅]	59 [∅]	-	0
AMMONIA (μM)	0	9	9	12	0	0	45	45	63	96	170	139	0

* Eh vs a standard redox solution at 440 mV.

[∅] Probably low because porewater samples were prepared from vibrocores : some oxidation probably occurred during separation of the porewater and sediment.

An analysis of the distribution and seasonal variations of acid volatile sulfide (and Eh), pyrite, ammonia, bicarbonate and fatty acids in the porewaters and sediments of the subtidal, intertidal and supratidal environments of Nilemah Embayment is proceeding. All of these substances are products of anaerobic microbial metabolism and a knowledge of the zones of high production rates and spatial distributions is essential to models the dynamics of the environment system.

A preliminary analysis of porewaters from the subsurface sediments along NM transect indicated that the effects of anaerobic microbial metabolism became more evident from landward to seaward (Table). Because there is no conclusive evidence which suggests that the sulfate reducing bacteria are active enough to maintain the in situ reducing environment in the landward supratidal sediments, the origin of the "anaerobic products" may be in the more active intertidal and subtidal environments.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
AUGUST, 1986

GEOBIOLOGICAL CONTROLS ON ORE FORMATION

INTRODUCTION

Studies of the hydrology, hydrogeochemistry and bacterial sulfate reduction in Shark Bay are now nearing completion, allowing the construction of a comprehensive model for the origin of particular forms of base metal sulfide mineral deposits.

GEOBIOLOGICAL CONTROLS ON PETROLEUM
FORMATION AND ACCUMULATION

BIOGEOCHEMISTRY OF HOLOCENE ENVIRONMENTS
HOLOCENE CARBONATE ENVIRONMENTS, SHARK BAY (W.A.)

HYDROLOGIC INVESTIGATIONS AT NILEMAH EMBAYMENT
HAMELIN POOL

L.A. Plumb, James Ferguson, B. Simeonovic

During the previous quarter, isotopic data from groundwaters in the tidal flats at Nilemah Embayment have been interpreted to determine the relative contribution from three potential sources - seawater, rainwater and regional groundwaters.

In summary, it appears that the tidal-flat groundwaters at Nilemah Embayment have a predominantly meteoric component in the landward zone but that this is principally from immediate recharge and run-off rather than being a contribution from evaporated waters (regional groundwaters) evolved in the back flats. There is an ill-defined and irregular evaporative and seawater-mixing evolution in the more landward sediments which produces a reasonably homogeneous ("tidal-flat") brine at depth. This is probably reflecting tidal mixing of seawater since it is most fully developed at the two sites for which peizometric heights show the most immediate correlation with tide-height. Finally, at the seaward margin of the tidal zone the "tidal-flat" waters are dominated by seawater.

These conclusions have been reached on the basis of the following discussion. Isotopic data for rainwater and the regional

groundwaters which evolve in sediments landward of the peritidal zone have been discussed previously (May 1985, Quarterly Report) and are shown on a deuterium - oxygen-18 plot in Fig. 1. In addition, values for seawater samples of salinities up to 146‰ are included. Hamelin Pool seawater ranges in salinity from 48‰ at the Faure Sill to 60-65‰ at the southern extremity offshore

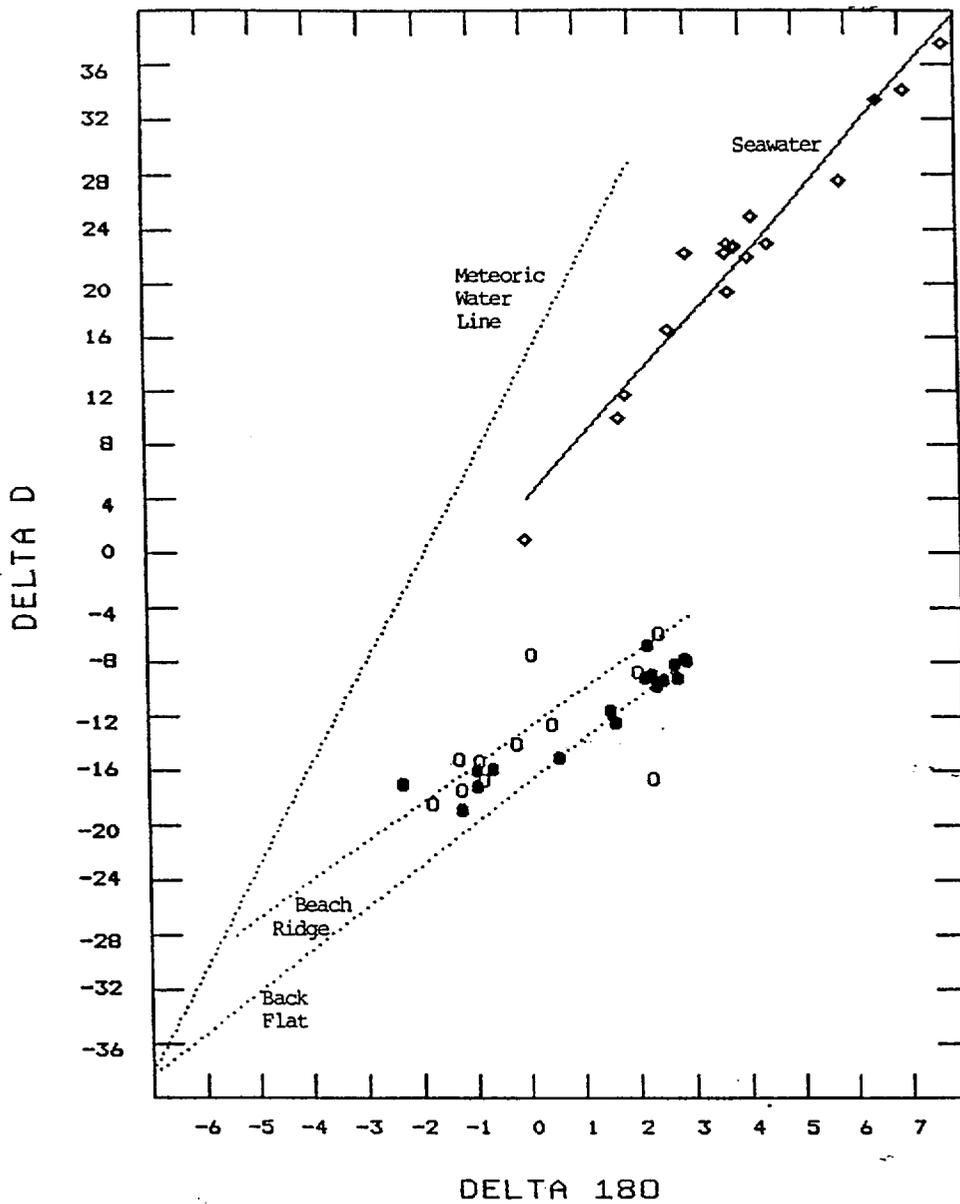


Fig. 1. Deuterium - oxygen-18 plot for groundwaters from the Back Flat and beach ridges at Nilemah Embayment compared to the seawater evaporation line and the local Meteoric Water Line (MWL). The intersection of the regression lines for groundwater data with the MWL gives a likely mean-weighted range for the isotopic composition of local rainfall.

from Nilemah Embayment. This occurs as a consequence of evaporation and the restricted flow imposed by the seagrass sill.

The isotopic composition of the tidal flat groundwaters will be determined by the relative contributions from different sources and the effect of evaporation either prior or subsequent to mixing. Fractionation of deuterium and oxygen-18 in evaporating water involves both equilibrium and kinetic effects. At 25°C equilibrium separation factors between vapour and condensed liquid water are of the order of 9.3‰ and 76.5‰ for oxygen-18 and deuterium respectively.

Kinetic effects arise because of the differential diffusion of isotopic species from the evaporation surface to the atmosphere. These effects are therefore particularly sensitive to changes in conditions at the evaporating surface and kinetic fractionation in sediments is higher than that for evaporation from an open water surface. However, the additional effect is of the same magnitude for both deuterium and oxygen-18 and thus produces a proportionately greater change in the oxygen-18 distribution. This variation in kinetic effect is most readily observed in the lower slope of deuterium versus oxygen-18 plots for subsurface groundwaters. Humidity is also a controlling factor in the kinetic fractionation, producing greater increases at lower humidity and therefore contributing further to the lower deuterium - oxygen-18 slopes in sediments of arid, low humidity environments. However, this may be alleviated somewhat in the case of brines developing in tidal flat sediments because increased salinity increases the effective humidity.

Isotopic variations of evaporating waters are also commonly considered in relation to their salinity changes. As a brine evaporates, the increasing salinity causes an increase in effective humidity and progressively decreasing fractionation. The effect is most marked for oxygen-18 because of its smaller equilibrium fractionation compared to that for deuterium.

Groundwaters from the tidal flats at Nilemah Embayment have been sampled on three transects, two of which (NB and N31) traverse zones of gypsum-accumulation. The third transect (NM) traverses the broadest expanse of tidal flat in which there is also the greatest topographic diversity and the greatest potential for varied recharge from both rainfall and seawater.

Isotopic distributions in relation to salinities for groundwaters from transects N31 and NB are presented in Figures 2a and 2b. The

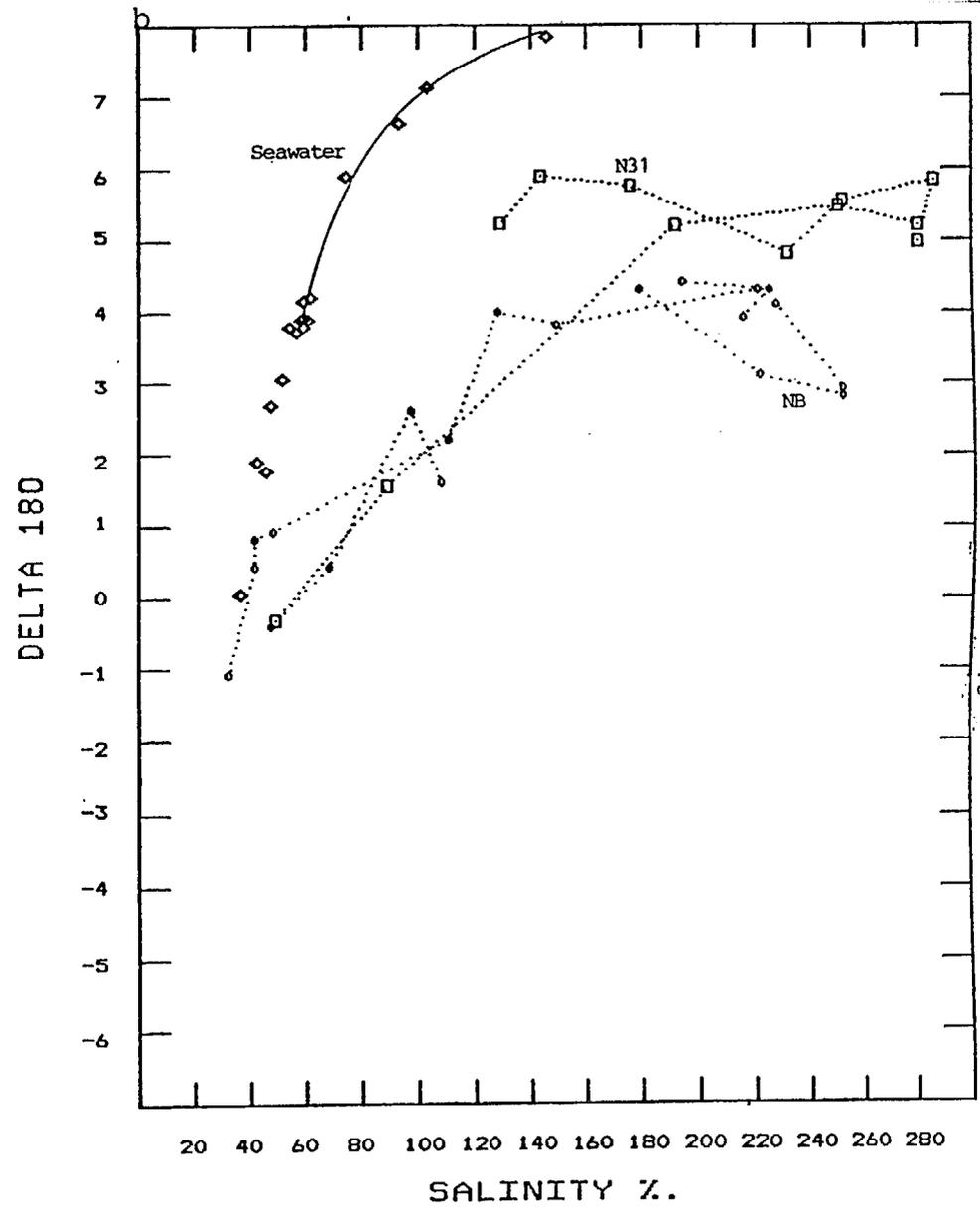
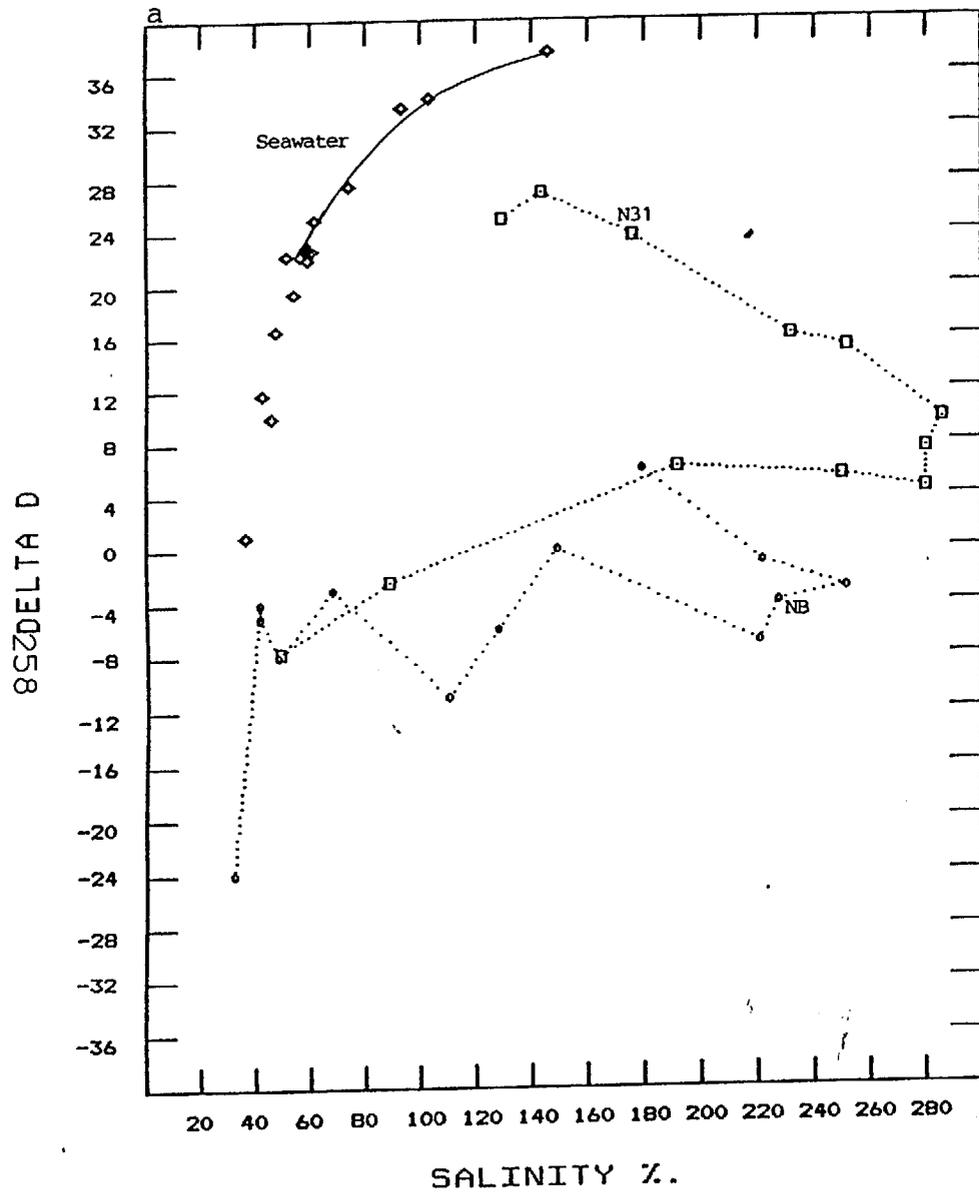


Fig.2. Changes in deuterium (2a) and oxygen-18 (2b) distributions versus salinity for evaporating seawater and groundwaters from transects NB and N31.

evaporation curve for surface seawater samples is included and represents the free surface evaporation which could be expected from seawater influencing Nilemah Embayment. The plots for each transect are presented as sequences from landward to seaward with the most landward point being at the base of a beach ridge.

There appears to be a general similarity in the pattern for each transect which is most clearly seen in the deuterium plot (Fig. 2a). For the data from N31 the most saline samples correspond to the area in which abundant gypsum is found and the lack of corresponding increase in δD suggests that the salinity increase is due to resolution of salts rather than from evaporative concentration. Indeed the curve produced from selected sampling points may not represent an evaporative process at all because of the possibility of solution of additional salts or mixing with another water.

This latter possibility may be illustrated in the plot of data from NB transect. Water emanating from the beach ridge has a salinity of 33‰ and isotopic distributions of δD , -24‰ and $\delta^{18}O$, -1.1‰ while Nilemah seawater with a salinity of 60‰ has isotopic compositions δD , 21.9‰ and $\delta^{18}O$, 4.15‰ . Is it feasible that the isotopic distributions of the next three samples (δD , -6‰ ; $\delta^{18}O$, 0.6‰ ; $S\text{‰}$, 44) are the result of mixing between these two waters? The resulting deuterium value would require 39‰ seawater which would yield a salinity of 44‰ while calculations using the $\delta^{18}O$ values suggest 33‰ of seawater producing a salinity of 42‰ . In addition, ion ratios for these samples (Mg/Cl, SO_4/Cl , Mg/Br, Na/Br) appear to have a seawater contribution. The apparent simplicity of the landward end of the N31 transect, compared to a comparable area on NB, may be a fortuitous consequence of fewer samples. It is also worth noting that additional data for $\delta^{18}O$ on waters sampled at a different time show some variability. The difference between the two transects in the extent of isotopic increase landward of the gypsum zone is probably influenced by the greater breadth of tidal flat at N31 allowing more evaporative effect in the predominantly meteoric component. The seaward end of the salinity plots represents a mixing and dilution by seawater, of the brines associated with the zone of gypsum accumulation.

The isotopic data can also be considered on a deuterium - oxygen plot, and is shown in Figure 3 with the seawater and meteoric water data for comparison. The seawater line is the higher end of that in Figure 1 and represents the free surface evaporation of seawater from nearshore Nilemah. The shaded area for meteoric

waters is taken between the regression lines for beach ridge and back flat data (Fig. 1). The solid section of the Meteoric Water Line represents the likely mean-weighted range for isotopic composition of local rainfall, and is derived by extrapolating the regression lines for the meteoric waters (see Fig. 1).

Plotted in this way, the data for NB suggest meteoric-like waters which mix at some points with seawater, although on this diagram exact calculations may demand that the seawater be modified by mixing with rainfall. The data available for N31 could be

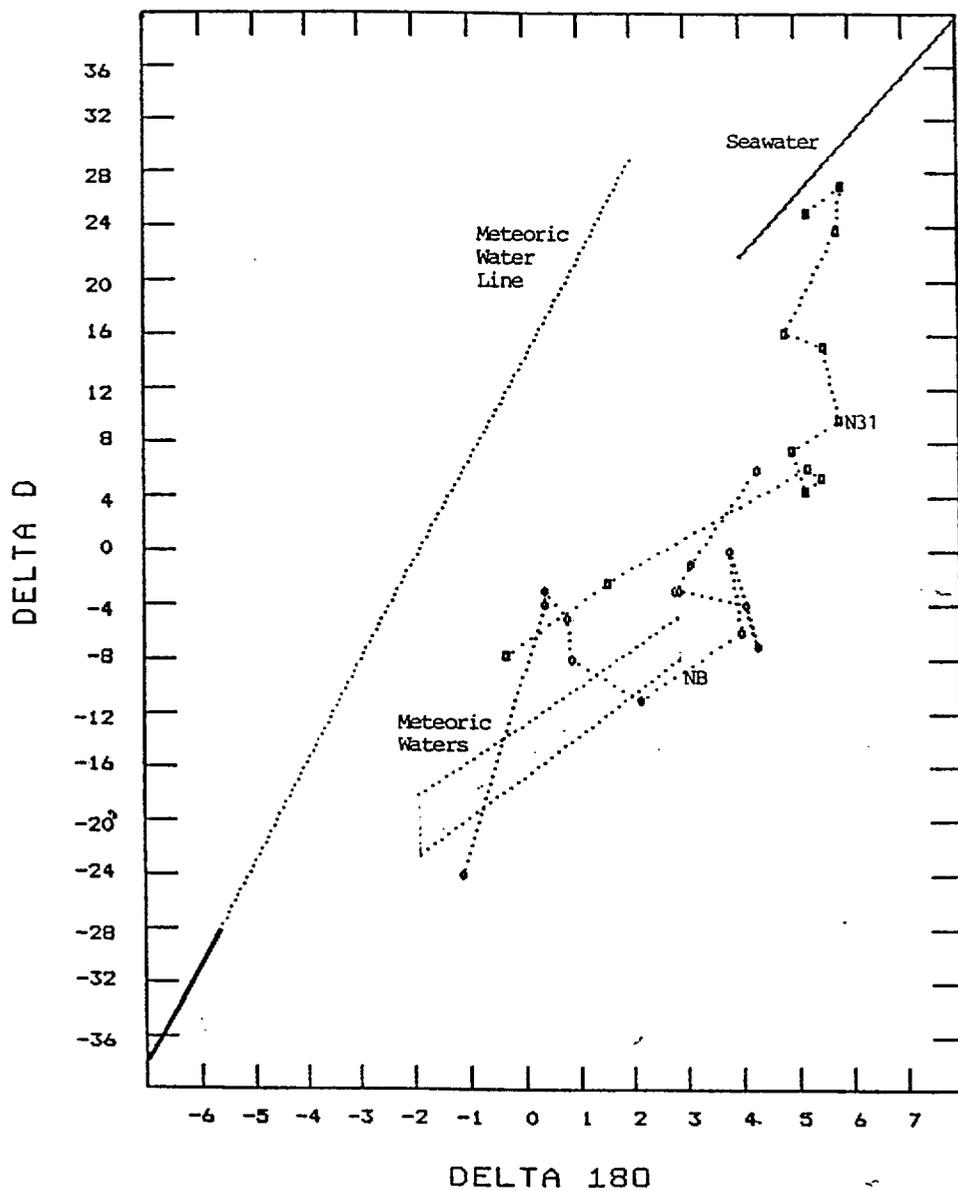


Fig. 3. Deuterium - oxygen-18 plot for groundwaters from transects NB and N31 relative to meteoric waters and seawater.

interpreted as the evaporative concentration of a water which emerges from the beach ridge with a more positive isotopic composition than meteoric water. However, as has already been argued in relation to the salinity diagrams, comparison with the greater number of data points on the topographically comparable NB transect (in terms of slope elevation above AHD) raises the possibility that waters on N31 are also mixtures of meteoric water and seawater. The lack of regular progression in the isotopic values of the porewaters landwards to seawards on the NB transect may also reflect the small-scale topographic variability which results in the watertable being relatively close beneath the sediment surface at some sites. Waters from these locations have a greater evaporative potential. In addition, where there is a deeper vadose zone, samples taken in the usual way from augered holes may be selecting the topmost water and this may not be representative of the deeper and more homogenised brine.

Beyond the gypsum zone, the more clear-cut influence of seawater in the isotopic compositions along transect N31 could mean either that the meteoric component was subjected to more extensive evaporation or that waters at the landward end of the transect had a greater seawater contribution than those from an equivalent position along NB.

Along the third transect (NM) it is most convenient to consider the waters in terms of their isotopic composition in three groups:

- (i) NM 1 to NM 8
- (ii) NM 9 to NM 19
- (iii) NM 20 to NM 26

The first group is associated with an area in which only a thin bed of Holocene sediments overlies the Pleistocene marine carbonates which are exposed in the back flats. This area is thought to be particularly subject at the surface to recharge from rainfall, and the groundwaters appear to be essentially meteoric-like (Fig. 4). A suite of four samples at NM8 represent a depth profile to approximately -1 m AHD and indicates that these waters are also predominantly meteoric.

The next group are from Holocene sediments where the elevation (AHD) from NM16-NM19 is comparable to that of the other transects and the isotopic compositions are similarly more positive than the meteoric waters. Brown and Woods (1974) have, in fact, defined an intertidal zone for this area which would include all sampling points in this group, and piezometric increases at NM19 and NM15/16 correlate with tidal influence. The former is more pronounced than the latter. The final group (NM20 -

NM26) from the seaward end of the transect have compositions within the same range as a similar section of transect N31, as a result of the mixing of the "tidal-flat" water with seawater.

A plot of salinity versus $\delta^{18}\text{O}$ for these data is shown in Figure 5a for comparison with Figure 2b. There are also additional data for NM7 and NM8 showing a disparity with the waters sampled in depth profile. The complex relationship between sequential samples in the second group of waters appears to include mixing and dilution

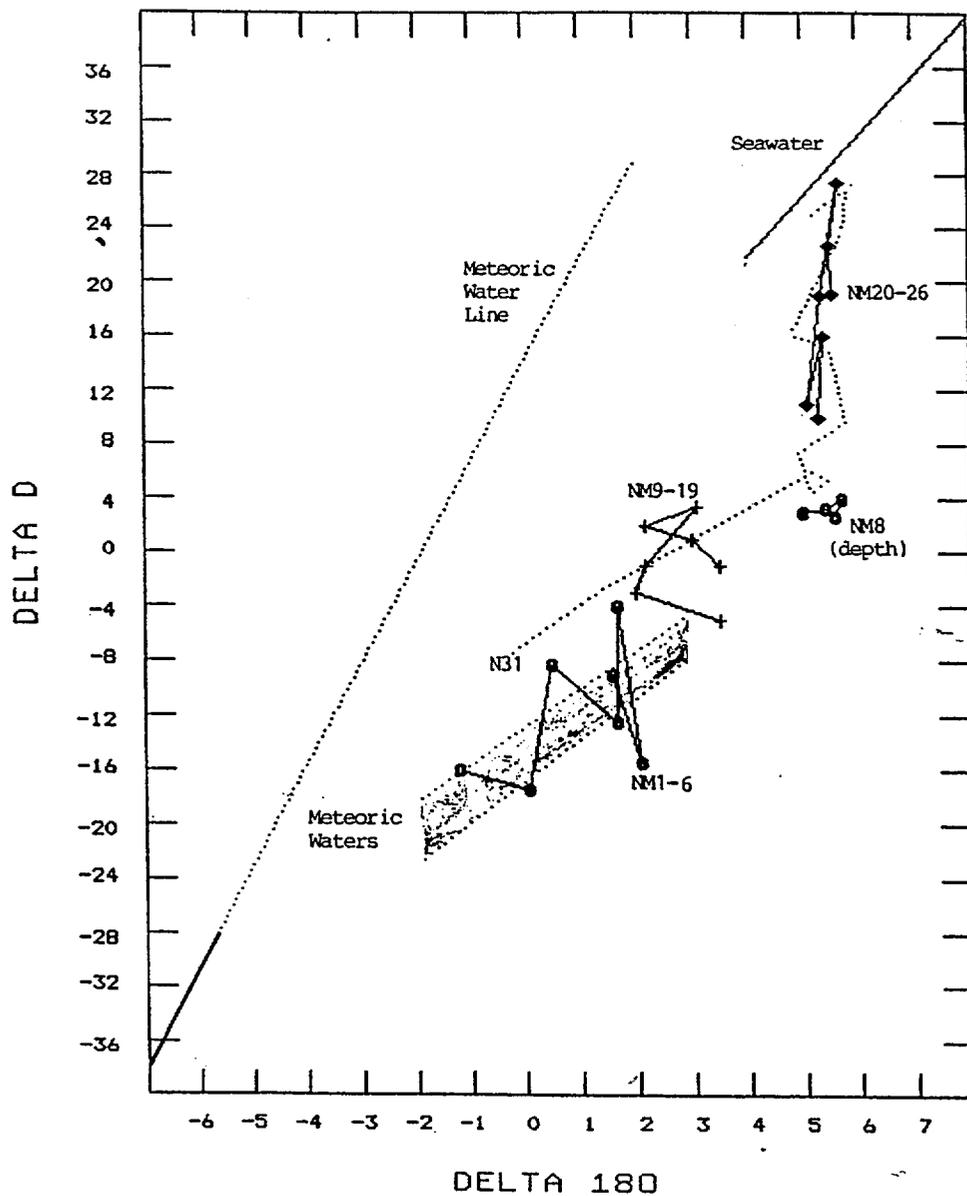


Fig. 4. Deuterium - oxygen-18 plot for groundwaters from transect NM compared to meteoric waters, seawater and groundwaters from transect N31.

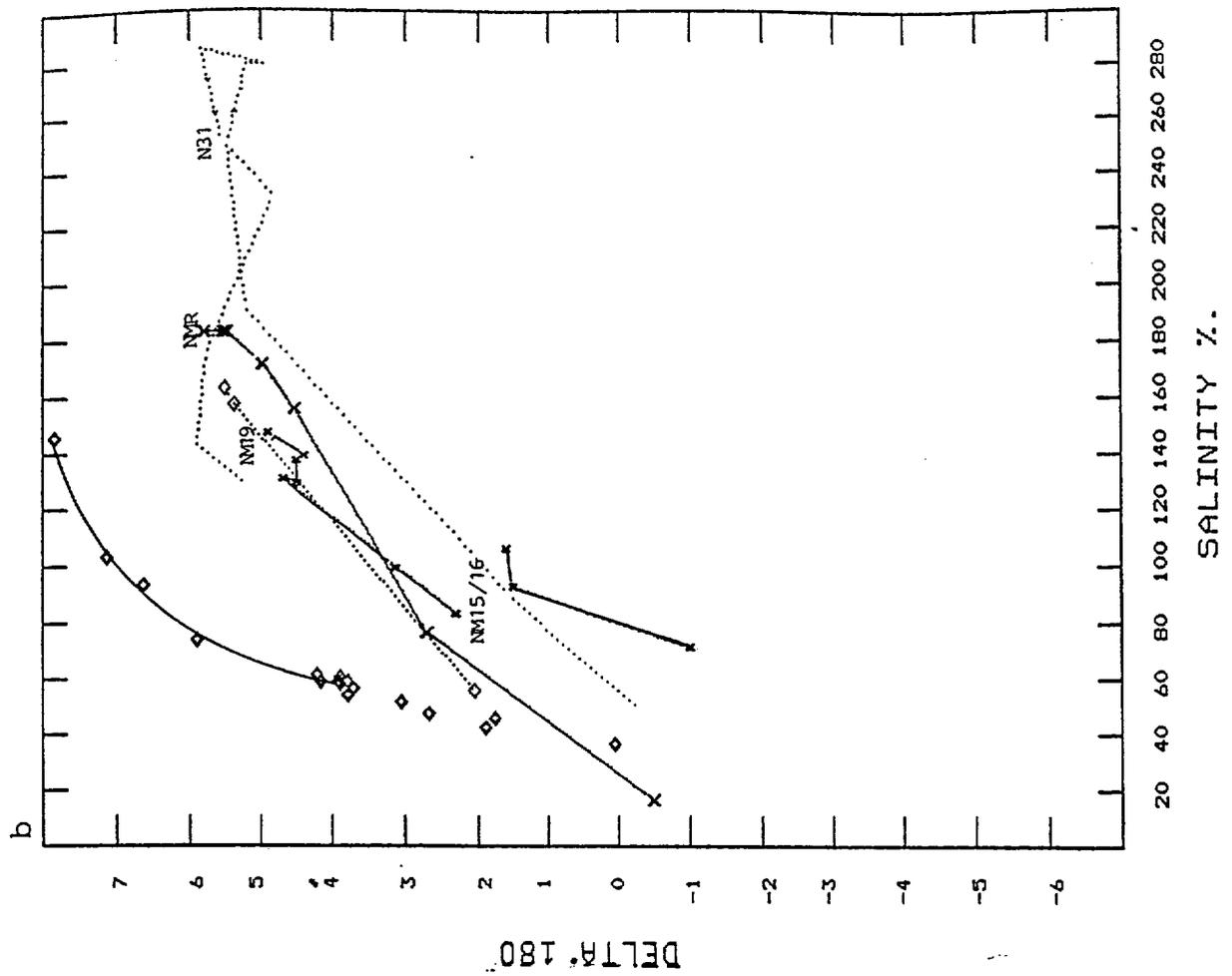
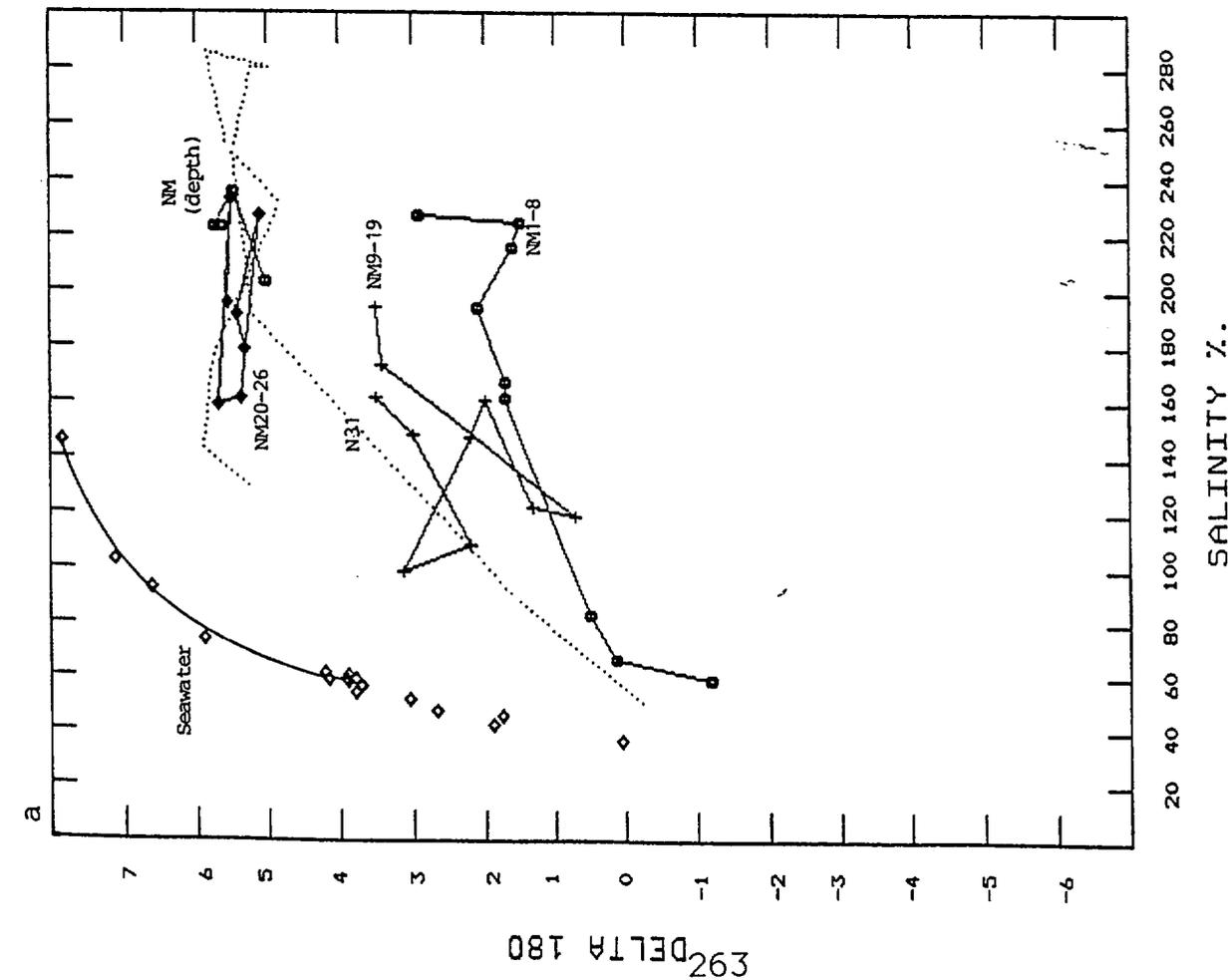


Fig.5. Oxygen-18 distribution versus salinity for (a) groundwaters along transect NM and for (b) groundwaters in depth profile compared to seawater and groundwaters from transect N31.

by meteoric water and seawater.

Figure 5b shows the change of $\delta^{18}\text{O}$ and salinity for waters from depth profiles at three sites. At each location lower salinity surface waters exhibit more negative and more meteoric-rich oxygen-18 values. With depth, both salinity and $\delta^{18}\text{O}$ increase to values similar to those evolved when the "tidal-flat" waters mix with seawater as in the comparative trace for the seaward end of transect N31. This can also be seen in the deuterium-oxygen plot in Figure 6.

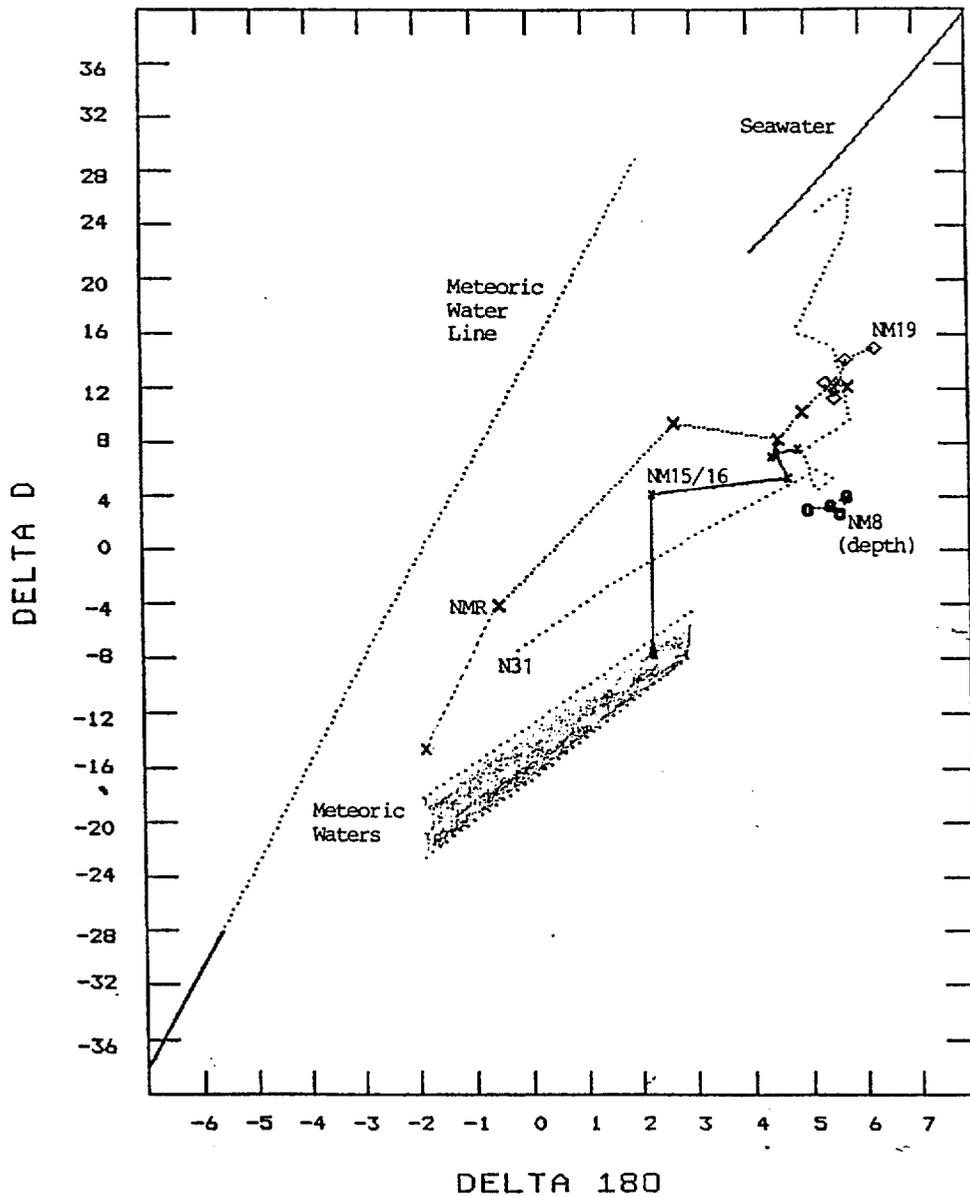


Fig. 6. Deuterium - oxygen-18 plot for groundwaters from depth profiles compared with meteoric waters, seawater and groundwaters from transect N31.

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SULFATE REDUCTION RATES IN SEDIMENTS COLONIZED BY DIATOMACEOUS MATS

NILEMAH EMBAYMENT (SHARK BAY) NOVEMBER, 1985.

G.W. Skyring, A. Blanks

The data in this report Table 1 complements and expands the data base on sulfate reduction in the different ecosystems of Hamelin Pool, especially in the Nilemah Embayment area (see also Quarterly Reports May, August, November, 1985, April 1986). The sulfate reduction rates in the surface sediments and mats were moderately high compared to other ecosystems that have been examined. The reduction rates in the subsurface sediments were very low.

This is an important zone for modelling ore-formation in a sabkha-type environment because it has the highest potential for metalliferous brine to react with biologically produced sulfide. For example if the average daily sulfate reduction rate in the upper few centimetres was 400 n mol g^{-1} it would take only 1 year to produce a sediment with around 2‰ Cu (as the sulfide), assuming that there was sufficient Cu entering the ecosystem.

Nilemah Transect

(November 1985)

CM*	Station 30/31		Station 31/32	
	Sulfate reduction rate n mol g ⁻¹ day ⁻¹	Sulfide μ mol g ⁻¹	Sulfate reduction rate n mol g ⁻¹ day ⁻¹	Sulfide μ mol g ⁻¹
0 - 1)) diatomaceous mat			437	10
0 - 2)	83	13		
0 - 5 sediment & mat	470	13	296	13
5 - 10 (above lithified plate)			0	8
10 - 15 (below lithified plate)	64	11		
20			0	39
30			0	21
40	0	13		

* A lithified carbonate plate occurred around 10cm below the surface in these sediments.

TABLE : Sulfate reduction rates and sulfide concentrations
in subtidal sediments colonized by diatomaceous mats;
November 1985, Nilemah Embayment, Transect NM

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
NOVEMBER, 1986

GEOBIOLOGICAL CONTROLS ON ORE FORMATION

INTRODUCTION

Our research on the Holocene environments of Shark Bay provides information for both the project reported here, and that on petroleum. We are gaining new information on sedimentary and geochemical facies in a marine barred basin, controls on the distribution of sulfidic, organic-rich sediments, and the transport of base metals in such an environment (the groundwaters of Nilemah Embayment are saturated, or nearly so, with lead).

GEOBIOLOGICAL CONTROLS ON PETROLEUM
FORMATION AND ACCUMULATION

INTRODUCTION

Our research on the Holocene environments of Shark Bay is drawing to a close, with the last major field trip to be held this November. This work provides information for both the project reported here and that on ore genesis. We are gaining extensive new information on benthic microbial communities as sources of organic matter, the organic geochemical characteristics of various such communities, the processes of preservation of organic matter in anaerobic, hypersaline sediments, and the features of sedimentary and geochemical facies in a marine barred basin.

Biomarkers in oils and source rocks are an enormously rich source of biological and environmental information. More accurately, they have the potential to be such a source, but to date few such compounds have been confidently identified and their biological sources determined. We have invested considerable effort in studies of biomarkers in Holocene, Ordovician, Cambrian and Proterozoic sediments. This effort is now beginning to bear fruit, with significant information on sources of organic matter. This is information that in most examples has not been available from other approaches such as conventional palaeontology.

BIOGEOCHEMISTRY OF HOLOCENE ENVIRONMENTS
HOLOCENE CARBONATE ENVIRONMENTS, SHARK BAY (W.A.)

SULFATE REDUCTION IN SUPRATIDAL, SUBSURFACE
SEDIMENTS AT NILEMAH EMBAYMENT: (HAMELIN POOL, SHARK
BAY, WA)

G.W. Skyring and A. Blanks

Introduction:

Characterization of the porewaters and measurements of rates of sulfate reduction in the supratidal, intertidal and subtidal zones along two transects, (NM and transect 31) at Nilemah Embayment, Hamelin Pool (Quarterly Report, May 1984) have shown that the activity of anaerobic micro-organisms in near surface sediments becomes more evident from land to seaward (Quarterly Report, April 1986). However, it has been more difficult to define the processes which are responsible for the extensive deposit of reduced subsurface sediments (as indicated by the presence of iron sulfide) of the intertidal and supratidal zones. For example, several attempts to demonstrate active sulfate reduction in the subsurface, reduced sediments failed (the limit of detection is a very low $2-3 \text{ n mol g}^{-1} \text{ day}^{-1}$). Also, the collection of porewaters, which, by their chemical composition, indicate biogeochemical processes was difficult. This problem has been obviated by the development of a sampler which pumps porewaters from the sediment (at rates from 20 to 200 ml min^{-1}) over specific electrodes in gas-tight, flow-through cells. The following characteristics were measured in the field in July/August 1986 and the results are given in Figure 1: temperature, dissolved oxygen, dissolved sulfide, Eh, pH.

The sulfide-specific electrode was cleaned with H_2O_2 between samples and the pS data in Figure 1 have been corrected for the effect of salt. The height of the water table and the depth of the oxidized/reduced interface was also measured. Samples were also immediately filtered through 0.45 and 0.22 μ filters and returned to the laboratory for the following analyses: salinity, ammonia, phosphate, bicarbonate, fatty acids and dissolved organic matter and iron.

Results and Discussion:

The success of the sampler for obtaining porewaters rapidly from discrete layers in the sediment was evident from some of the large changes that occurred in the sulfide and oxygen concentration within 10 cm, and also in the various, but distinctly different depth profiles in salinity, oxygen, pS (sulfide) and Eh. The new

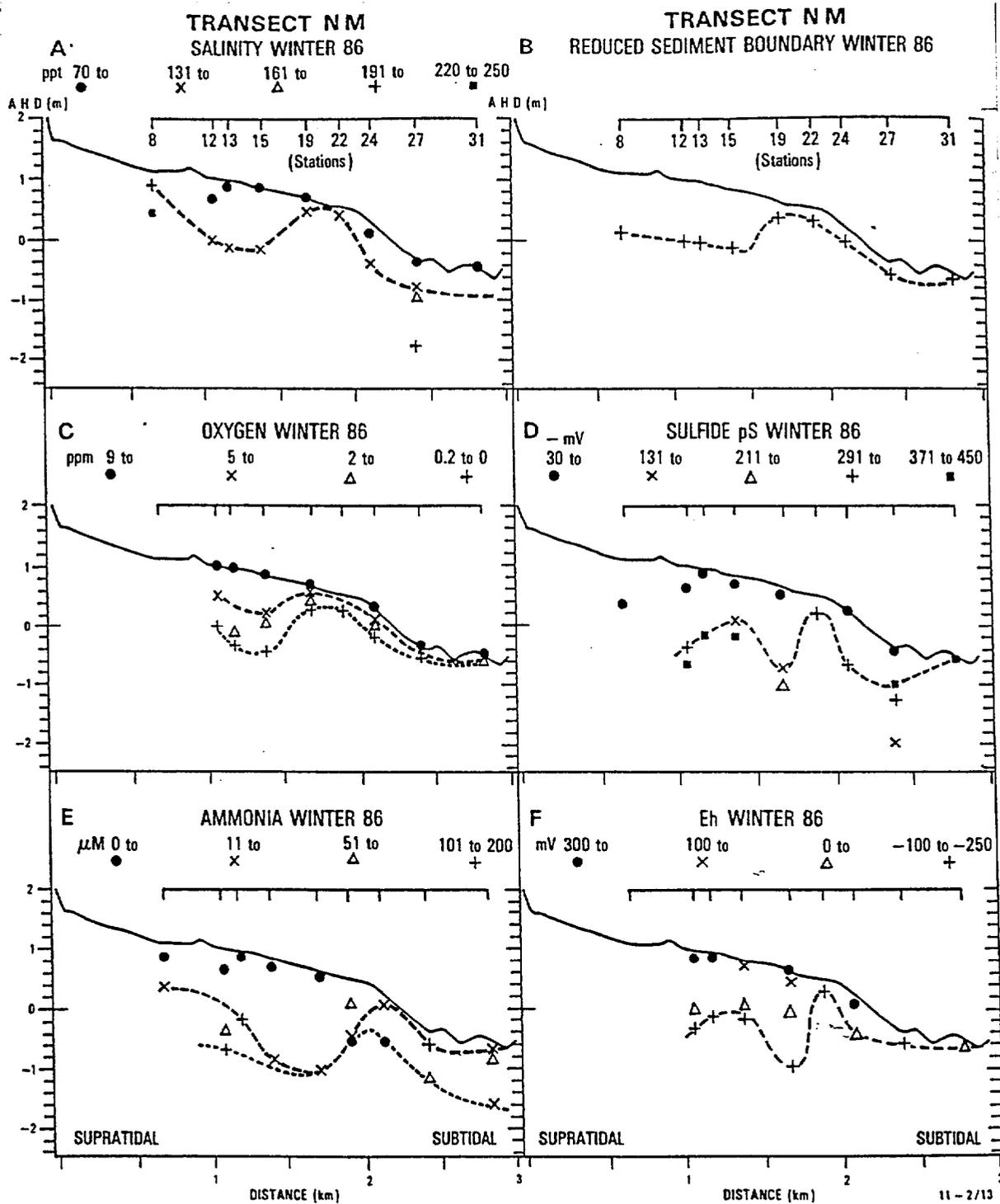


Figure 1. Shows the distribution of dissolved salts, oxygen, ammonia, sulfide and oxidation-reduction potential in the porewaters from NM transect during the winter of 1986. The boundary between the oxidized and reduced sediments (as indicated by the transition from buff to grey colour) is also given.

Several ranges of each characteristic have been plotted and the position of major boundaries are indicated by a drawn line to assist in interpretation.

The surface relief of the transect is marked to indicate the positions of the sampling stations. The line across the middle of each illustration represents the Australian Tide Height Datum.

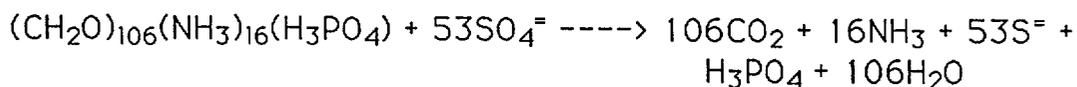
Footnotes:

1. The pS values were measured with a sulfide specific electrode vs. a double junction, saturated calomel electrode. The pS values have also been corrected for the effect of salt.
2. The Eh values were measured with a combination Pt/Ag:AgCl electrode.
3. The oxygen concentrations were measured with an oxygen specific electrode and the ammonia concentrations were determined colourimetrically.

data have also shown that previous sulfide and Eh measurements may have been affected by even brief exposure to air but, ammonia and bicarbonate alkalinity concentrations would not have been significantly altered.

A detailed interpretation of the data is not yet available however, the sulfide and ammonia profiles indicate that, progressing from landward to seaward, the zone of microbial anaerobic metabolism occurs (or occurred) deeper below the surface and occupies a narrower portion of the sediment. (Cf NM8 and NM27)

The larger quantities of ammonia in the porewaters of stations between NM8 and NM15/16 may originate from organic matter of the stand of sparse *Salicornia* bush that colonizes this area of the supratidal zone. On the other hand, the differently distributed but substantial concentrations of ammonia and sulfide in the porewaters of the seaward stations NM22 to NM30 indicate that the organic matter may be brought in by tidal waters or may be produced in situ by cyanobacterial mats. The distribution of sulfide and ammonia in the "brine" porewaters of stations NM15/16, 19 and to some extent station NM22, is difficult to interpret. For example, sulfate reduction (to sulfide) with naturally occurring organic matter is accompanied by the production of ammonia according to the general equation (1):



Applying this to the Nilemah situation, either the organic matter which is oxidized by the sulfate-reducing bacteria in the subsurface sediments, is depleted in nitrogen or the sulfide is a relic of some past sulfate reduction episode. The very low to zero ammonia concentrations may also be indicative of low to zero anaerobic microbial metabolism and this is also indicated by the sulfate reduction rate measurements. If the sulfate reduction rates are low then the substantial sulfide concentrations in the subsurface brines are enigmatic. Future research on this ecosystem will be directed at the explanation for the free sulfide but low ammonia in the sediments associated with the subsurface brines.

Soluble, reduced iron was present in the subsurface porewaters from 150-190 cm at stations NM8, PEG27 and transect 31.200. The soluble iron occurred in porewaters which were reduced but depleted in sulfide. This is a new observation and it is not yet

known if the iron originates from the Holocene or underlying Pleistocene iron-rich sediments.

Reference

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HYDROLOGIC FRAMEWORK OF A SEMI-ARID COASTAL AND MARINE/CONTINENTAL SABKHA

J. Ferguson, L.A. Plumb and B.A. Simeonovic

Marine carbonate sedimentation during the Pleistocene and Holocene has resulted in the development of a 4 km broad playa-tidal flat (marine/continental sabkha-coastal sabkha) at Nilemah Embayment, on the arid to semi-arid southern coast of Hamelin Pool at Shark Bay. The playa-tidal flat slopes gently seawards but its physiography is dominated by major sediment accumulations, such as dunes and beach ridges and, in the tidal flats, areas of erosion induced by cyclonic storms.

The playa groundwaters are part of a seawards-flowing regional groundwater system in redbed sands which form the coastal plain and underlie the marine sediments. This regional system produces a gently seawards-sloping water table across the playa. Normally, this regional groundwater influence is strongly perturbed by the combined effects of local recharge by rainfall and runoff and greatly differing rates of evaporation over the playa surface. Evaporation rates are the major control on groundwater salinities and have produced a stable pattern of low-salinity lenses associated with major sediment accumulations such as beach ridges, and upwards increasing salinity gradients where the marine sediments are exposed. The rate of recharge by rainfall and runoff is the dominant influence on the groundwater levels, and not only controls the general level of the water table but induces the formation of groundwater mounds in areas of high recharge. These areas of high recharge include topographic lows, where the marine sediments can be directly recharged, and the periphery of dunes and beach ridges where runoff accumulates. These effects are relatively short-lived because evaporation rates in these enhanced-recharge areas are high, and they produce temporary perched water tables on the clayey marine sediments and thin veneers of low-salinity recharge waters in normally evaporation-dominated areas.

The tidal flat groundwater regime is almost isolated from the regional groundwater system by the adjacent and underlying clayey

Pleistocene marine sediments which form a low permeability barrier between the redbed sands and the relatively coarse-grained Holocene-Recent marine carbonates. Consequently this tidal flat groundwater is sourced predominantly by local rainfall and runoff and tidal floods of hypersaline (salinity = 65‰) near-shore seawater. These inputs have produced a groundwater system in which a slowly moving, anoxic brine formed by evaporation in the peritidal zone is flowing seawards through the subtidal sediments. The salinity pattern of this brine reflects the juxtaposition of relatively low salinity areas associated with beach ridges and very high rainfall recharge environments at the landward margin, and high salinity areas where evaporation rates are high because the sediments have been eroded close to or below the water table. Superimposed on this relatively stable brine is a considerably more dynamic recharge system. During periods of high rainfall and/or tidal flooding, the vadose zone becomes saturated and broad shallow ponds form on the sediment surface. As normal conditions return the water level drops, probably as a result of lateral flow seawards through the permeable sediments and, to a lesser extent, evaporation and infiltration to the brine system. Under drought conditions the water level at the landward side of the tidal flat may drop below that in the intertidal/low supratidal zone, thus creating conditions for landwards flow of groundwater brine.

Many of the processes effecting the groundwater systems at Nilemah are similar to those operating in the sabkhas of the Persian Gulf at Abu Dhabi but the combined effects of the wetter climate, the topographically highly variable physiography of the playa/tidal flat, and the stratigraphic arrangement of high-permeability surface sediments and an underlying lower permeability unit produces a markedly different groundwater regime. In the Abu Dhabi sabkhas a strong regional groundwater input is a dominant feature of the hydrologic regime and is considered necessary for the sabkha to resist the effects of aeolian deflation. The Nilemah playa is subject to this type of groundwater regime and this may have been a factor in its preservation. In contrast, the Nilemah tidal flat is an example of a group of sabkhas and tidal flats with little regional groundwater input, but in this case the sediments are sufficiently coarse grained to provide some resistance to the effects of aeolian deflation. In this group, the Nilemah tidal flat is unusual in that it is not situated on a peninsula (as are some sabkhas at Qatar, Persian Gulf) or separated from the continent by a lagoon (as is a tidal flat bordering the Laguna Madre, Texas).

The Nilemah groundwater regime also contrasts strongly with the Abu Dhabi sabkhas in that local variations in the infiltration and retention of rainfall are a major influence on the groundwater regime. This contrast is most evident at the interface of the marine and continental sabkhas (the landward Holocene-Pleistocene marine carbonate boundary at Nilemah), where in both areas rainfall accumulates preferentially and produces groundwater mounds. At Nilemah this rainfall produces a low-salinity lens, but at Abu Dhabi the rainfall is rapidly lost by evaporation and lateral and vertical flow and, consequently, the marine-continental sabkha interface is a region of very high salinity. This difference has significant implications for the preservation of evaporite minerals in the Nilemah tidal flat because, as the flat progrades, tidal inundation will become less and the low salinity area at the landward margin could extend further seawards. Together with the further development of beach ridges and their associated low-salinity lenses this implies that extensive concentrations of evaporite minerals may be only an ephemeral feature of the Nilemah type of tidal flat.

BAAS BECKING GEOBIOLOGICAL LABORATORY
QUARTERLY REPORT
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GEOBIOLOGICAL CONTROLS ON PETROLEUM
FORMATION AND ACCUMULATION

MICROBIALITES: ORGANOSEDIMENTARY DEPOSITS OF
BENTHIC MICROBIAL COMMUNITIES

Robert V Burne and Linda S Moore (Department of Microbiology,
University of Western Australia)

This joint research includes data from both the Hamelin Pool study and the Saline Lake Project. The following is an abstract of a paper based on this work that has been accepted for publication in the SEPM Journal PALAIOS.

ABSTRACT

Microbialites are organosedimentary deposits formed from interaction between benthic microbial communities and detrital or chemical sediments. Processes involved in the formation of calcareous microbialites can include; trapping and binding of detrital sediment (forming microbial boundstones), inorganic calcification (forming microbial tufa), and biologically influenced calcification (forming microbial framestones). The latter process is probably the result either of chemical changes associated with photosynthesis, or the nucleation of crystals on the polysaccharide bearing sheaths of the microorganisms. Elevated $\delta^{13}\text{C}$ values in these cements may reflect isotopic fractionation associated with the biological setting of the mineralisation. Microbialites contrast with other biological sediments in that they are generally not composed of skeletal remains. Once formed, the primary framework of the microbialite becomes the locus of secondary cementation. To distinguish them from the bioherms and biostromes of skeletal origin, microbialite buildups are termed "microbial lithoherms" or "microbial lithostromes". The morphogenesis of these structures is a function of environmental influence, biological and ecological controls, and processes and rates of lithification. The internal structures of microbialites are best identified by descriptive terms that do not imply a particular origin. Consideration of the term "stromatolite" shows that it is currently used in at least three distinct ways; to refer to products of microbial sedimentation in general, to describe laminated structures of probable microbial origin, or to describe discrete laminated lithified bodies. We recommend that the term be restricted to refer to microbialites with an internal structure of

fine, more or less planar laminations. Published distinctions between thrombolites (microbialites characterised by a clotted internal structure) and stromatolites have been assessed in the light of some present-day Australian occurrences. These show that thrombolites are not always constructed by coccus-dominated BMCs, nor are stromatolites always constructed from filament-dominated BMCs. Although we have observed examples of modern thrombolitic structures forming where biogenically influenced calcification dominates, and stromatolitic structures forming where trapping and binding of either detrital sediment or seasonally precipitated carbonate dominates, both structures could be produced by other processes. Other terms used to describe internal structures of microbialites include oncolitic (concentrically laminated), spherulitic, and cryptic. It is hoped that the ability to differentiate between the processes involved in the genesis of microbialites will lead to a better understanding of factors such as the morphogenesis of microbialites, their evolution through geological time, and their potential as tools for biostratigraphical correlation.

SULFATE REDUCTION IN SEDIMENTS OF NILEMAH EMBAYMENT: (HAMELIN POOL, SHARK BAY, W.A.)

G.W. Skyring and A.M. Blanks

The objective of this investigation was to describe in three dimensions, the reservoirs of sulfide and the zones where microbial sulfate reduction occurs in the Nilemah ecosystem. The data from this and other aspects of the Shark Bay Program will be integrated to provide a comprehensive, quantitative description of the biogeochemistry of a semi-arid sabkha.

Results and Discussion:

1. Nilemah (Transects NM and 31)

An examination of porewaters from the supratidal, intertidal and subtidal zones of Nilemah Embayment was repeated in November 1986 with a rapid sampling device (see Quarterly Report, November 1986). The following characteristics were measured: temperature, dissolved oxygen, iron, ammonia and sulfide, Eh, pH and salinity. The depths of the water table and the oxidized-reduced interface were also measured.

The landward to seaward and vertical patterns of the chemistry of the porewaters for August 1986 and November 1986 were remarkably similar. A comparison of these two sets of data with

more limited data sets for 1984 and 1985 indicated that the chemical characteristics of the porewaters from various stations (3 to 32) along transects NM and 31 were extremely stable, for at least a two year period.

In this report, discussion shall be limited to the August (1986) and November (1986) records of salinity and dissolved sulfide and ammonia in the porewaters from selected stations (Nos. 8, 13, 15/16, 19, 24, 31) along Transect NM (see Quarterly Reports, May 1981 and November 1986). Salinity is used as an indicator of hydrological and evaporative excursions and sulfide and ammonia are used as indicators of microbial anaerobic metabolism. Sulfate reduction (to sulfide) with naturally occurring organic matter is accompanied by the production of ammonia according to the general equation (1):

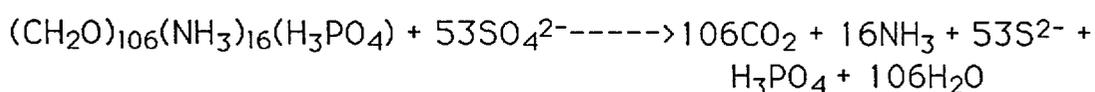


Table 1 shows in a qualitative way, the extent of changes that occurred in the vertical distribution of the concentrations of salt, sulfide and ammonia for the winter and summer of 1986. Figures 1 to 6 show the quantitative changes in sulfide (as pS) which occurred. Significant changes in ammonia occurred and concentrations fell from around 10 μM to below detectable limits. The apparent increase in the sulfide concentrations in the upper levels of the reduced zones of the sediments of stations 19 and 24 is enigmatic because concomitant increases in ammonia were not observed. If the increase in sulfide was due to biological sulfate reduction some ammonia would have been expected (see equation 1). Previous investigations have indicated that, if biological sulfate reduction occurs in the reduced, supratidal sediments at Nilemah, it occurs at extremely slow rates not detectable by a sensitive radiometric method. It is important to trace the origin of the sulfide appearing in the November samples because of the major role accorded to the sulfate-reducing bacteria in sabkha models for sulfide ore genesis.

2. Booldah Well

Similar investigations were done on an area of the intertidal cyanobacterial ecosystem at Booldah Well where a thin layer of Holocene marine sediment overlies redbed sands.

The patterns of porewater chemistry were different from those of the intertidal zone at Nilemah. Sulfate reduction was detected only in the 0-5cm layer. Sulfide occurred in the porewaters down

to 40cm where there was also a sharp change in redox potential (Figures 7 and 8). Ammonia was distributed in the same pattern as sulfide (Figure 9) and declined to zero at a depth of 40 cm. The porewaters contained no oxygen from the surface to 90cm.

Table 1. Differences observed in the vertical distribution of salt, sulfide and ammonia concentrations for the porewaters collected August (Winter) 1986 and November (Summer) 1986

TRANSECT NM (Nilemah)						
	SUPRATIDAL		INTERTIDAL		SUBTIDAL	
	Station 8	13	15/16	19	24	31
SALINITY	NC	MC	MC	MC	MC	NC
SULFIDE	-	MC	MC	SC	SC	MC
AMMONIA	SC	SC	MC	MC	SC	MC

NC = No change

MC = Minor changes

SC = Significant changes

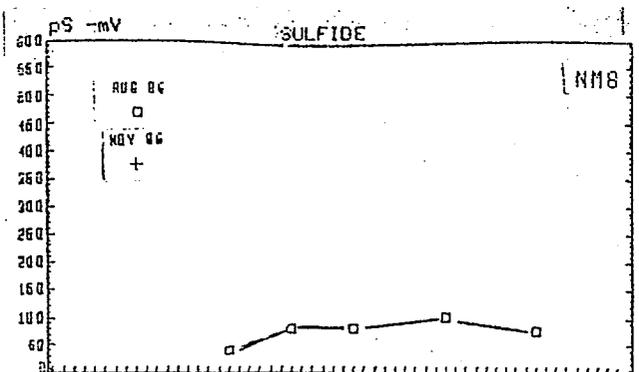


Fig. 1

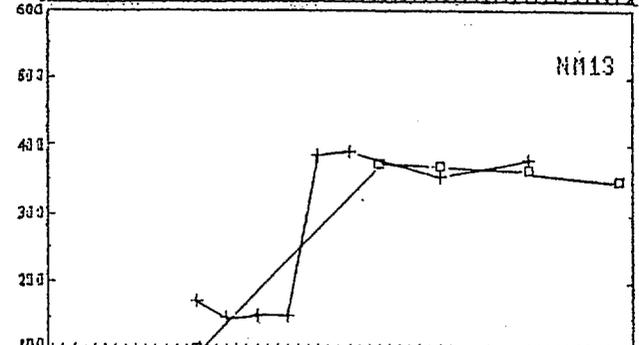


Fig. 2

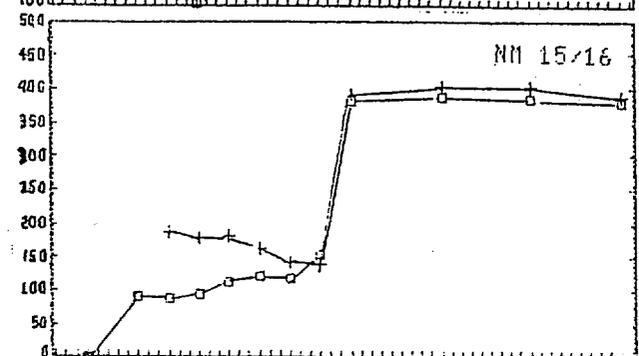


Fig. 3

Figs. 1-6 Sulfide-specific electrode recordings of the porewaters from stations along Transect NM (cf. Table 1). The more negative the mV reading the higher the sulfide concentration.

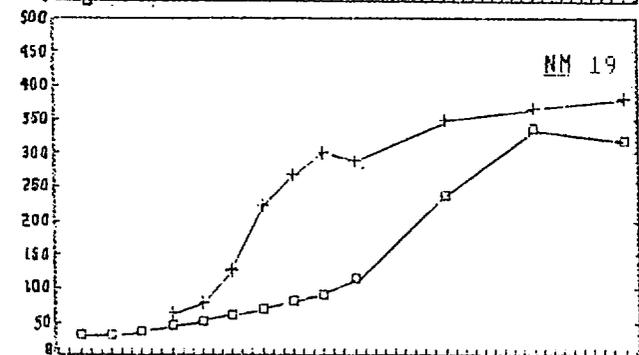


Fig. 4

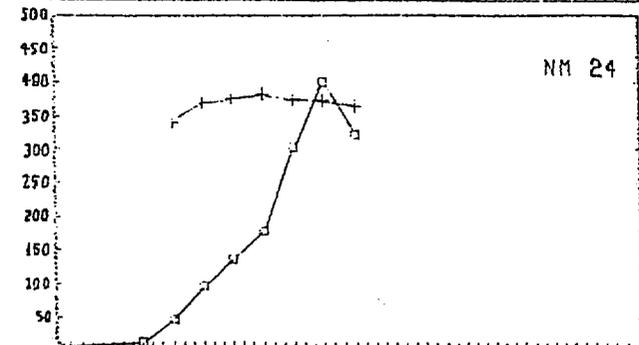


Fig. 5

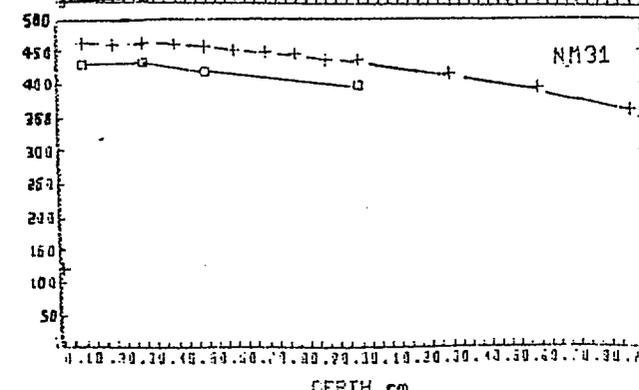


Fig. 6

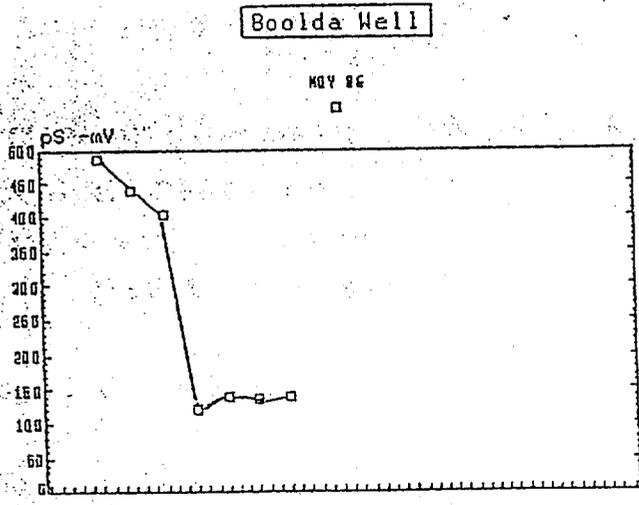


Fig. 7

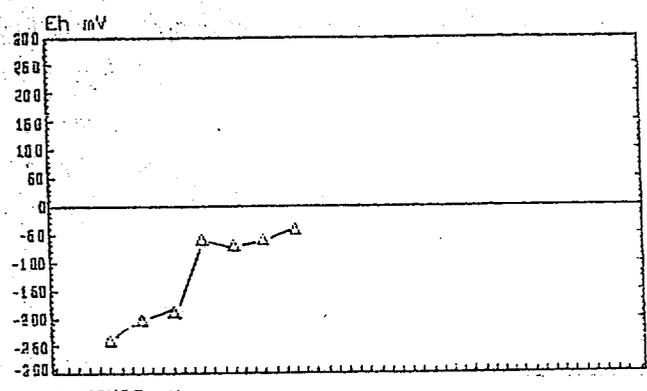


Fig. 8

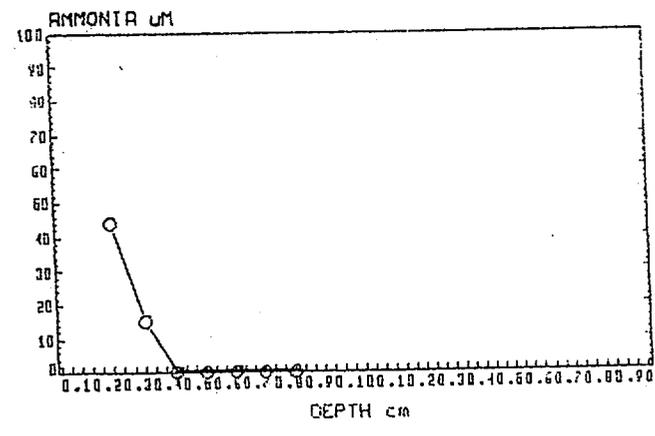


Fig. 9

Figs 7-9 Selected Chemical characteristics of porewaters from an intertidal sediment at Booldah Well.

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GEOBIOLOGICAL CONTROLS ON PETROLEUM
FORMATION AND ACCUMULATION

GROUNDWATERS AND DIAGENESIS IN SEMI-ARID SABKHAS:
ORIGINS, DISTRIBUTION, GEOCHEMISTRY AND PRESERVATION
OF DIAGENETIC GYPSUM

J. Ferguson, L. Plumb, B. Simeonovic

Holocene marine and Pleistocene marine-continental sabkhas at Nilemah Embayment contain gypsum of both marine and non-marine origins. Non-marine gypsum has low $\delta^{34}\text{S}$ values and significantly higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than its marine counterpart.

Holocene marine sabkha

Gypsum in the Holocene sabkha is formed almost entirely from seawater sulphate and non-marine gypsum occurs only at the landward fringe where non-marine groundwaters associated with beach ridges abutting continental environments intrude into the intertidal/low supratidal zone. The gypsum is present mainly as large crystals (typically 5 to 10cm, and up to 20cm long), either as single discs or complex intergrowths which form rosettes. Because the sediments are mainly grain-supported, and therefore not easily displaced, the gypsum crystals contain a large proportion of host marine carbonates and detrital quartz.

The gypsum occurs in a well-defined but restricted zone in the sabkha where the sediment surface lies from 0.4 to 0.7m above the Australian Height Datum (which corresponds to a seawater inundation index range of 23 to 5%). Within this zone gypsum is precipitating in the lower part of the salinity range while both gypsum and celestite form towards the higher part of the range. Seaward of this zone gypsum precipitation is inhibited by the high frequency of tidal flooding, which dilutes groundwater brines with seawater. To the landward the frequency of tidal flooding does not provide sufficient seawater salts to overcome the effects of low-salinity groundwaters which are associated with peripheral beach ridges, or those of accumulation of local rainfall and runoff at the landward margin of the sabkha.

The present-day occurrences of gypsum are concentrated in an area about 1km long and up to 0.5km wide where erosion by longshore currents has expanded the zone of brine development to several

times its normal width. Within this zone are two generations of gypsum, one in an horizon corresponding to the present-day groundwater regime and another in a similar, older, overlying horizon formed at a time when the sediment surface and the water table were higher. This fossil gypsum horizon is partly exhumed and appears as a broad 'pavement' whose upper surface is the former level of the water table. A further complication of the basic gypsum-forming environment has been caused by the recent deposition of an isolated beach ridge. This ridge is the locus of low-salinity waters which superimpose a local area of gypsum dissolution on the gypsiferous sediments.

The mechanism of gypsum precipitation in the Holocene sediments involves evaporation from the top of the water table, so that most gypsum is precipitated in the phreatic rather than the vadose zone. The absence of vadose gypsum is a result of the coarse-grained nature of the sediments, which limits the thickness of the capillary zone and allows ready access to recharging marine or non-marine waters. Precipitation is seasonally dependent and probably occurs mainly in the summer months. During winter and spring all but the most saline groundwaters are undersaturated with respect to gypsum because of the relatively high frequency of recharge by seawater and local rainfall/runoff. These processes produce a vertical profile showing increasing gypsum concentrations upwards to the water table; a gypsum pavement coincident with the top of the water table; and large gypsum crystals forming as a result of regular exposure to alternating solution-reprecipitation conditions.

Compared to the broad, highly arid sabkhas at Abu Dhabi, on the Persian Gulf, evaporites in the Nilemah Holocene sabkha are of limited extent and diversity. The Nilemah gypsum is analogous to the Abu Dhabi selenite gypsum facies. The gypsum mush associated with the microbial mat facies at Abu Dhabi is not present, the marine and continental gypsum associated with the high supratidal zone is absent, as is the anhydrite facies associated with the capillary zone.

Preservation of the Nilemah Holocene evaporites during progradation seems unlikely. They are vulnerable to encroaching beach ridges and their associated low-salinity waters, or, as occurs at Nilemah but which may not be common, to exhumation and dissolution by tidal seawater. If the gypsum were to survive to the stage where the marine sabkha evolved into a marine-continental sabkha then the highly permeable sediments would be particularly

favourable sites as of aquifers for potentially gypsum-undersaturated non-marine waters.

It is clear that within the general climatic spectrum where evaporation exceeds precipitation, and the potential for the formation of evaporite minerals in sabkhas and broad tidal flats is theoretically high, both the nature and extent of evaporite precipitation is highly variable. The Nilemah Embayment Holocene marine sabkha and the Abu Dhabi sabkha environments are close to opposite ends of the spectrum which can be generated in arid and semi-arid climates. In fact, the contrast in evaporite extent and diversity could be even greater because, in the absence of the erosional influence, the Nilemah Holocene sabkha may have been almost evaporite-free.

Using the Nilemah Holocene sabkha as a guide, some of the conditions antipathetic to the formation of evaporites in evaporation-dominated sabkhas and tidal flats can be deduced. They include:

- (1) limited access of potentially highly saline regional groundwaters to the landward side of the sabkha,
- (2) climatic and topographic conditions favouring high recharge of the landward parts of the sabkha by local rainfall and runoff,
- (3) the development of extensive areas of sediment accumulation, such as beach ridges, which are sites of low evaporation and low-salinity waters,
- (4) deposition of permeable coarse-grained sediments which are resistant to aeolian deflation, thus minimizing evaporation by limiting the thickness of the capillary zone and increasing the depth to the water table, and allowing removal of evaporites from the vadose zone by recharging waters,
- (5) and the development of a sharply-sloping tidal flat where the breadth of the zone of the optimum balance evaporation/recharge is minimized.

The above conditions are most likely to be met if the continental setting of the sabkha is that of a peninsula, or if the sabkha is separated from the hinterland by a lagoon, or if low-permeability sediments act as a barrier between the regional waters and the sabkha. Optimum topography and grain-size of the sabkha

sediments is most likely to result from a high-energy, prograding marine setting where most sediment deposition occurs during storms. Under these circumstances, even broad sabkhas in highly evaporative environments may not be sites of deposition of evaporites.

Pleistocene marine-continental sabkha

Gypsum in Pleistocene marine-continental sabkha occurs in the Pleistocene marine sediments and interfingering and underlying redbed sediments. Although details of the distribution could not be determined because of limited accessibility, the present-day areas of high salinity and high concentrations of gypsum coincide to some extent.

The gypsum ranges in size from about 0.5 to 11 cm in length. The larger crystals appear in bladed rather than discoidal form but they are discoidal or wedge-shaped in cross-section. They have obvious cleavage planes. Medium-sized crystals occur as both blades and as rosettes of intergrowing discs. Some crystals appear to be composites, having a central blade overgrown by small discs or by an amorphous gypsum cement. One of these crystals had different $\delta^{34}\text{S}$ values for the two morphologies which suggests that they represent more than one episode of precipitation. The smaller crystals are usually discoidal in cross-section, but not obviously so in hand specimen. The degree of occlusion of the host sediments is variable. Only the larger crystals contain areas of almost pure gypsum. There also is some dependence of the degree of occlusion on the nature of the host sediments. Gypsum in indurated sediments contains considerable amounts of host sediment whereas that in soft, clayey sediments is relatively pure. The composite crystal with the central blade and the amorphous rim has, respectively, low and high host sediment contents in the two generations. This could indicate that the sediment was indurated after the first episode of gypsum precipitation.

The gypsum has $\delta^{34}\text{S}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic signatures from both the original marine incursion and from the present-day groundwater regime. The two types of gypsum co-exist in the marine and interfingering terrigenous sediments and, as mentioned above, in at least one case they occur in the same crystal. Notably the one sample from the underlying redbed sediments has a non-marine isotopic value. Clearly, the continental groundwater regime has added new gypsum, and may have remobilized some of the original marine gypsum.

The Pleistocene sabkha groundwaters have non-marine isotopic values (both $\delta^{34}\text{S}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) at the landward fringe but within the sabkha both marine and non-marine values occur, reflecting dissolution and/or reprecipitation of the original marine sulphates. These dissolution/reprecipitation reactions may also affect the Sr content of the gypsum. These concentrations are very low and are not consistent with direct precipitation from the present-day groundwaters. Most likely they are a result of numerous dissolution-reprecipitation events leading to successive depletions in the Sr content of the gypsum. Low concentrations of Sr are also a feature of the large 'selenite' gypsum crystals of Abu Dhabi.

Specific areas of gypsum dissolution or precipitation in the Pleistocene sabkha can be identified to only a limited extent from comparison of $m\text{Ca} \cdot m\text{SO}_4$ data for the groundwaters with those for gypsum saturation because temporary undersaturation can be induced by recharge by local rainfall/runoff. Better information can be obtained from changes in $m\text{Sr}/m\text{Ca}$ ratios, which reflect gypsum, celestite and dolomite dissolution and precipitation, and the conversion of aragonite to calcite.

The latter is the dominant control on $m\text{Sr}/m\text{Ca}$ ratios in areas of high rainfall recharge at the seaward periphery of large Holocene beach ridges superimposed on the landward parts of the Pleistocene sabkha. Elsewhere, precipitation and/or dissolution of gypsum and celestite is more important. Gypsum is precipitating at the landward fringe of the sabkha as the incoming waters evaporatively concentrate. Further seawards groundwaters may be undersaturated, either intermittently as occurs in high recharge/high evaporation interdunal depressions, or in the long term in the low-evaporation environments beneath the large superimposed Holocene beach ridges. In the interdunal areas celestite precipitation is important. In high evaporation environments seaward of the Holocene beach ridges gypsum precipitation again becomes dominant.

The major control on the redistribution of gypsum in the Pleistocene marine-continental sabkha is the degree of saturation of the incoming continental waters and the extent to which they evaporate as they flow across the sabkha. Superimposed on this basic regime are the low-salinity, under-saturated environments associated with the large Holocene beach ridges deposited on the Pleistocene sediments, and high rainfall-recharge environments in depressions where the Pleistocene sediments are exposed. These superimposed environments are sites of long or short-term

dissolution of gypsum and provide focii for the remobilization and redistribution of originally deposited marine gypsum. The pronounced fluctuations in water table and salinity levels resulting from rainfall recharge provide an ideal environment for dissolution-precipitation processes and, consequently, the growth of large crystals. The effects of the type of recharge are minimized by the nature of the fine-grained Pleistocene marine sediments. They limit vertical recharge and more importantly lateral flow of waters away from the sabkha.

Mobilization and reprecipitation of gypsum appears to have been sufficient to extensively alter the original marine distribution pattern by dissolving gypsum from areas beneath beach ridges and precipitating additional gypsum in areas of high evaporation and low recharge. However, the prominence of original marine values indicates that the flow of non-marine groundwaters has not been sufficient to completely remove the original sulphate. In this respect the marine-continental sabkha may be subject to a similar continental groundwater regime as occurs at Abu Dhabi, where the incoming waters are undersaturated with respect to gypsum (Butler, 1973). However, the higher evaporation and lower recharge at Abu Dhabi may more rapidly concentrate and saturate the incoming continental waters, thus allowing greater preservation of the original gypsum/anhydrite assemblage. Both environments contrast with the situation in moister climates, where the marine-continental sabkhas can become ephemeral lakes in which the marine sediments are overlain by flat-bedded flood deposits and continental groundwater sulphate becomes the sole source of gypsum deposited at the landward margin.

Preservation of gypsum formed in marine sabkhas or tidal flats as falling sea level superimposes a continental groundwater regime on the marine sediments is favoured by a climatic and hydrologic regime which allows the development of high-salinity waters, close to gypsum saturation, in the adjoining coastal plain. These characteristics are most likely to develop in dry (arid to semi-arid) areas where the coastal plain is broad and the seawards topographic slope is low. Preservation is further favoured if the marine sediments are exposed, allowing rapid evaporation of the incoming waters and attainment of gypsum saturation a short distance into the sabkha. Under these conditions there should be minimum mobilization of the existing gypsum and new (continental) gypsum may be deposited in the marine sediments and in underlying and interfingering terrigenous sediments. This preservation/superimposition regime is disturbed by superimposition of major sediment accumulations, including beach

ridges and aeolian dunes, which act as focii for low salinity waters and dissolution of gypsum. Also, remobilization, homogenization, and recrystallization of the original and new gypsums is favoured by high local recharge, particularly in interdunal depressions. Potentially, these processes could provide a mechanism for the removal of the original marine gypsum but for this to occur there would need to be a significant seawards flow of brine. This flow can be considerably inhibited if the sediments are fine-grained, as occurs at Nilemah and in Abu Dhabi sabkhas.

NITROGEN FIXATION AND HYDROGEN EVOLUTION IN CYANOBACTERIAL MATS FROM HAMELIN POOL, SHARK BAY (W.A.)

G.W. Skyring, G.D. Smith (ANU) and R.M. Lynch

This CSIRO/ANU Collaborative Research Project will terminate on June 30th, 1987. Most of the aims and objectives of this project have been achieved (see Quarterly Report, April 1987). The following is a summary of results and conclusions:

1. Smooth mat, composed mostly of *Microcoleus* sp., exhibits light-dependent N₂ fixation.
2. Tufted mat composed of *Lyngbya* sp. and *Microcoleus* sp. exhibits light-dependent N₂ fixation. Fixation in this ecosystem appears to be due to *Microcoleus*.
3. Pustular mat, composed mostly of *Entophysalis* sp. exhibits light-dependent N₂ fixation.
4. Smooth and tufted mat ecosystems, and *Lyngbya* from tufted mat, evolve H₂ in the light and dark.
5. Pustular mat does not evolve H₂ in the light.
6. Molybdate, an inhibitor of the sulfate-reducing bacteria (SRB), stimulates H₂ evolution in the dark in smooth and tufted mat and also in *Lyngbya*. This infers that SRB are present in these photosynthetic ecosystems.
7. Molybdate has no effect on H₂ evolution in pustular mat inferring that SRB are not a significant component of this ecosystem.

8. The observations on the effects of Mo (items 6 and 7) are consistent with measurements of sulfate reduction rates and sulfide concentrations in these ecosystems (see Quarterly Report, Nov. 1984, p.49).
9. The SRB in smooth and tufted mats consume H₂ which is produced in the dark. Measurements of sulfate reduction and H₂ production in smooth mat from Spencer Gulf (SA) showed that H₂ as the reductant, accounted for about 10% of the sulfate reduction which occurred during the dark.
10. The waters of Hamelin Pool are depleted in the important nutrients of nitrogen and phosphate and this results in very low primary productivity in the water column. It is probable that the extensive benthic cyanobacterial mats which colonize the stromatolites and subtidal and intertidal sediments of the southern part of Hamelin Pool are maintained by the ability of *Entophysalis* and *Microcoleus* to fix atmospheric nitrogen. In a way that is analogous to the biogeochemical cycling of elements on a coral reef, the cyanobacterial mats and stromatolites of Hamelin Pool cycle P (as phosphate) and N very efficiently within the ecosystem.

The observations of this project are new with respect to intact cyanobacterial mat and will contribute to an understanding of the role of these ecosystems in organic diagenesis and mineral sulfide formation.

THE ISOLATION OF SULFATE-REDUCING BACTERIA FROM CYANOBACTERIAL MATS IN SHARK BAY (W.A.)

Li Yaqin and G.W. Skyring

Sulfate-reducing bacteria (SRB) are significant components of smooth and tufted cyanobacterial mats, and the objective of this project was to isolate in pure culture, SRB from these mats in Shark Bay (WA). Past experience indicated that conventional microbiological isolation methods for the SRB were tedious and time consuming. Therefore, a micromanipulator was used to isolate single bacterial cells from enrichment cultures of SRB from Shark Bay mats. Subsequently these single cell isolates were placed in a growth medium containing ferrous ions. Growth of SRB was indicated by the precipitation of black FeS in the medium. Four acetate - and five lactate - utilizing SRB have been isolated by this single step technique. The cultures are being examined for some nutritional and physiological characteristics.

of organic origin. Kevex analysis of this showed the presence of Fe. Examination of the black carbonate grains under the S.E.M. showed only an isolated organic structure which was possibly a mega-spore. Isolation of sulphide for isotopic analysis is planned.