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Organic matter oxidation and sediment chemistry in mixed terrigenous–carbonate sands of Ningaloo Reef, Western Australia

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Abstract

The oxidation of organic matter in relation to porewater and solid-phase element chemistry was examined in mixed terrigenous–carbonate sediments in sheltered and exposed lagoons of Ningaloo Reef, Western Australia. Rates of O_2 consumption and CO_2 release were faster in the very fine sand (41–43% $CaCO_3$ content) of the sheltered lagoon of Mangrove Bay (means = 10.5 mmol m^{-2} day^{-1} O_2 and 9.4 mmol m^{-2} day^{-1} CO_2) than in the carbonate-rich (73% $CaCO_3$) sand of the exposed back-reef lagoon of Ningaloo Reef (means = 2.1 mmol m^{-2} day^{-1} O_2 and 3.5 mmol m^{-2} day^{-1} CO_2). Rates of sulfate reduction (ΣSRR) were similarly faster in the Mangrove Bay sediments (6.1–25.3 mmol m^{-2} day^{-1} S), sufficient to account for all of the organic matter mineralization. In Ningaloo reef sands, ΣSRR rates (1.0 mmol m^{-2} day^{-1} S) accounted for a significant fraction (57%) of total organic carbon oxidation. In Mangrove Bay, in contrast to previous measurements of sulfate reduction in tropical sediments, most (mean = 64%) of the reduced ^{35}S was incorporated into the acid-volatile sulfide fraction with a buildup of iron sulfides. In contrast to most carbonate-bearing sediments, the production and accumulation of Fe sulfides (most evident in Mangrove Bay) increased pH to levels promoting carbonate precipitation.

Higher decomposition rates in Mangrove Bay are attributed to restricted water circulation, a richer benthic community, and geomorphology conducive to greater input and retention of mangrove- and macroalgae-derived detritus. At both sites, the lack of a clear zonational sequence of porewater solutes, discrepancies between depth profiles of solutes and solid-phase elements, and high core-to-core variation in conservative element concentrations and in rates of bacterial activity, suggest non-steady state diagenesis. Non-steady state conditions may be fostered by a combination of factors, such as physical disturbances, temporal changes in rates and quality of organic sedimentation, and tidal advection.

Keywords: organic matter; sediment; biogeochemistry; carbonate; terrigenous; Western Australia

1. Introduction

The lagoons of most fringing and barrier reefs and atolls are complex sedimentary mosaics consisting of a mixture of sediment types and habitats. Many lagoons are interspersed with low isles or smaller lagoons or embayments colonized by macroalgae, seagrasses and mangroves (Ogden, 1988). From the reef proper to shore, unconsolidated deposits in these lagoons usually grade from reef-derived carbonates (> 60% $CaCO_3$) to transitional (30–60% $CaCO_3$) to terrigenous (< 30% $CaCO_3$) facies (Guilcher, 1988). These carbonate–clastic transitions and adjacent habitats are common in many reef lagoons worldwide, such as in the Great Barrier Reef (Alongi,

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1995) and in reef complexes of the Caribbean (D'Aluisio-Guerrieri and Davis, 1988) and Africa (Fay et al., 1992).

Despite their prevalence in many reef lagoons, the biogeochemistry of these mixed clastic–carbonate sediments has not been extensively examined. Considering the presence of macroalgae, seagrasses and mangroves, the potential exists for sediments in sheltered lagoons and embayments to be sites of high primary productivity with concomitantly high rates of nutrient retention and organic matter decomposition. Nutrient stoichiometry and rates of oxidation of organic matter have been examined in carbonate sediments in subtidal reef lagoons (D'Elia and Wiebe, 1990), but no such studies have been conducted in intertidal reef lagoons colonized by seagrasses, macroalgae and mangroves, and composed of a mixture of terrigenous and reef-derived carbonate material (Ogden, 1988).

In the lagoonal complex of Ningaloo Reef in Western Australia, there exist vast expanses of intertidal sediment in coastal embayments and lagoons, composed of mixtures of siliciclastic and carbonate sand. As in other reef lagoon complexes, these habitats shelter rich and diverse communities of plants, invertebrates, fishes and birds. These habitats were declared sanctuary zones within Ningaloo Marine Park in 1987 (May et al., 1989).

In this paper, we compare and contrast microbial decomposition of organic matter and sediment chemistry in lagoonal sands of a sheltered sanctuary zone (Mangrove Bay) with the biogeochemistry in sands composed mainly of reef-derived carbonates in the intertidal back-lagoon of Ningaloo Reef. These data are compared with similar information obtained from other shallow-water, carbonate-rich sediments.

2. Materials and methods

2.1. *Study area (Fig. 1)*

Ningaloo Reef is a fringing barrier reef between latitudes 21°47′ and 24°S, extending nearly 240 km along the North West Cape peninsula of Western Australia (Fig. 1). The reef is discontinuous and encloses a lagoon ranging in width from 0.2 to 6 km (average of ~ 2.5 km) with a mean depth of about 4 m. Tides are semi-diurnal with spring tides of up to 2 m. Water temperatures range from 21°C in winter to 30°C in summer. Currents within the lagoon are complex, driven by winds, tides and waves (Hearn and Parker, 1988). Water residence time for the lagoon is usually < 24 h, as ocean water is pumped across the reef by wave-breaking.

The lagoon bottom is diverse, composed of carbonate sand with coral growth restricted to sparse bommies and thickets of staghorn coral; coral growth is poor in the inner part of the lagoon (May et al., 1989). The back-reef lagoon is intertidal to several hundred meters from shore and is frequently interspersed with coral outcroppings and unconsolidated sand. The shore is either sandy or rocky beach, interspersed with several smaller lagoons or embayments. Most of these areas are sanctuary zones within the Marine Park (May et al., 1989).

Mangrove Bay (21°58′S, 113°57′E), located on the upper west coast of North West Cape (Fig. 1), is one of the sanctuary zones within the lagoon. Mangrove Bay is a small (~ 70 ha) lagoon containing a well-developed mangrove forest composed mainly of the white mangrove, *Avicennia marina*. A single channel connects Mangrove Bay to the sea. The center of the lagoon is open and composed of relict, and some living, coral and fine sand composed of carbonates, siliciclastic material, and mangrove and algal debris. A rich and diverse epibenthic community composed mainly of red and green algae, hydrozoans and crabs, inhabits the lagoon floor. Mangrove Bay is a rich breeding ground and supports abundant populations of numerous species of birds (Johnstone, 1990). Some evidence indicates that this lagoon changes dramatically in response to tropical cyclones (Carter, 1903; Johnstone, 1990).

Two stations were established within the Ningaloo Reef lagoon complex (Fig. 1). The first station, MBL, was established in the open lagoon of Mangrove Bay. The second station, NR, was located within the intertidal back-reef lagoon of Ningaloo, ca. 0.5 km seaward of the single channel entrance to Mangrove Bay.

2.2. *Field sampling and sedimentological analyses*

At each station, triplicate, 20 cm deep sediment cores were taken each for (1) interstitial SO_4^{2-} and

H_2S, (2) dissolved metals (Ca, Mg, Sr, Mn and Fe), (3) total alkalinity, (4) dissolved inorganic and photo-oxidizable nutrients and Cl^-, (5) DOC, (6) solid-phase elements (TOC, Total N, P, Fe and S) and (7) sulfate reduction (using a different set of cores, see Section 2.4). Duplicate cores were taken at each site to 20 cm depth for pH and Eh measurements. All samples were collected randomly within a 5 m^2 plot at each site at low tide using stainless steel cores. Each core (7 cm i.d.) contained a recessed inner core tube made of PVC and subdivided into 2 cm rings. Other samples were taken at each site for benthic respiration ($CO_2 + O_2$), grain size, porosity and temperature, as detailed below.

Sta. MBL was sampled in November 1993 and October 1994. Sta. NR was sampled in October 1994. Triplicate cores were taken to 40 cm depth for porewater DOC and SO_4^{2-}, solid-phase elements (using a meter long stainless-steel corer) and sulfate reduction at Station MBL in October 1994. Duplicate water samples were taken at high tide within the lagoons of Mangrove Bay and Ningaloo Reef in

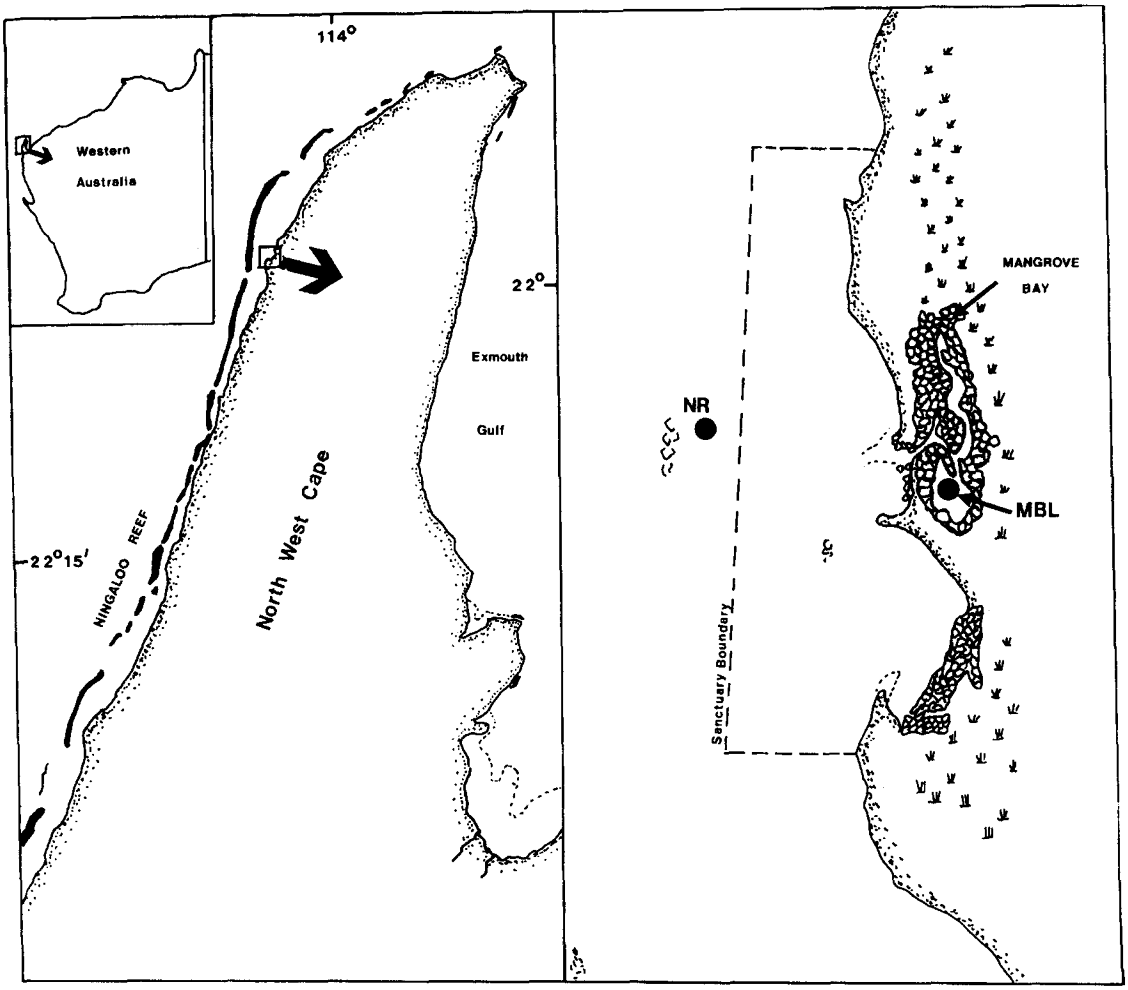

Fig. 1. Chart of the study area noting station locations in Mangrove Bay (*MBL*) and in the back-reef lagoon (*NR*) of Ningaloo Reef in relation to the Western Australian coast.

1993 and 1994 for nutrients and other elements using a sterile 50 ml syringe with a 0.45 μm cellulose acetate filter attachment (Sartorius® Minisart).

Sediment temperature was measured in situ by inserting a Model TPS temperature probe ~ 2–5 cm into the sediment. Redox potential and pH were measured at 2 cm intervals to 20 cm depth from duplicate cores (described above) modified with sampling ports on each 2 cm ring to allow insertion of a Model PRFO combination calomel reference-platinum electrode or a Model PBFC pH electrode. The electrodes were allowed to equilibrate for 10–15 min before readings were taken on a TPS LC80 mV–pH–temperature meter. The pH electrode was calibrated using pH 7.00, 8.00 and 9.00 standards. Porosity of triplicate 20 cm^3 samples was determined by difference in weight loss of wet sediment dried at 80°C for 16 h. Grain size analysis of duplicate bulk samples followed methods described in Folk (1974).

2.3. *Porewater and solid-phase element analyses*

For porewater, each core was sliced in a glove bag at 2 cm intervals under a N_2 atmosphere with each sediment patty kept intact and placed immediately into an acid-washed Petri dish. The covered dishes were removed from the glove bag, the intact sediment patties placed immediately into Teflon porewater extractor cassettes (Robbins and Gustinis, 1976) and extracted for 10–15 ml of interstitial water per sample. Each patty was squeezed under an applied N_2 pressure of 100 kPa, and the porewater passed through a 0.4 μm Nuclepore filter seated within the bottom of each cassette. Porewater was collected in N_2-filled, sterile polypropylene test tubes and frozen immediately. A preliminary test in November 1993 indicated no statistical ($P > 0.05$) difference in nutrient concentrations between this procedure and conducting the entire squeezing process within a glove bag, in agreement with an identical exercise for mangrove sediments (Alongi, 1996). Samples for DOC and dissolved metals were stored cooled (2–5°C) in sterile polypropylene test tubes. DOC was determined on the same samples by high-temperature catalytic oxidation on a Shimadzu TOC-5000 Analyzer (Hedges et al., 1993). Blanks ($n = 3$) using Milli-Q water were run for DOC at each site (Benner and Strom, 1993); blank values for DOC were never greater than the detection limit (0.05 $mg\,l^{-1}$). Average precision for DOC was 2%. Total dissolved Fe, Mn, Ca, Sr and Mg concentrations were measured on a Varian Liberty 220 ICP–AES. Analytical precision for Ca, Sr and Mg was within 5%; precision for Fe and Mn was ±1.7 and ±0.09 μM, respectively.

Excess Ca, Sr and Mg in the porewater relative to chloride concentration was estimated from overlying water ratios and porewater composition:

$$\text{excess}[M^{2+}]_{pw} = [M^{2+}]_{pw} - \left([Cl^-]_{pw}[M^{2+}]_{ow}/[Cl^-]_{ow}\right)$$

where $[M^{2+}]$ is the concentration of dissolved Ca, Sr or Mg, and [Cl] is the concentration of chloride, in pore water (pw) and overlying water (ow) (Walter and Burton, 1990). Ca, Sr and Mg in porewater were measured only in October 1994 to 20 cm sediment depth.

Saturation states for calcite and aragonite were calculated using the formula:

$$\Omega_{\text{cal or arg}} = [Ca^{2+}][CO_3^{2-}]/K_{\text{cal or arg}}$$

where the apparent solubility products for calcite (K_{cal}) and aragonite (K_{arg}) fit to temperature and salinity by Mucci (1983) were used (Millero, 1995). The carbonate concentration was calculated from the second apparent dissociation constant of carbonic acid at the appropriate temperature and salinity (Mehrbach et al., 1973; Millero, 1995). Carbonate alkalinity was estimated from total alkalinity by subtracting the contribution due to boric acid using the dissociation constant of boric acid at the appropriate temperature and salinity (Roy et al., 1993).

Porewater for sulfate and sulfide was collected directly in tubes containing 1 ml 20% zinc acetate fixative. Sulfide was measured spectrophotometrically from precipitated ZnS (Cline, 1969). Sulfate was determined gravimetrically by $BaSO_4$ precipitation and filtration. Average precision was 3% for sulfide and sulfate. Dissolved inorganic nutrients were determined by standard automated techniques (Ryle et al., 1981; Ryle and Wellington, 1982). DON and DOP concentrations were determined from a separate fraction of the same sample after overnight digestion in a LaJolla UV photo-oxidizer (Armstrong and Tibbitts, 1968) following the optimization procedures recommended by Hopkinson and Cifuentes (1993); Milli-Q water blanks for DON and DOP were never above detection limits (see Ryle et al., 1981). DON and DOP values were obtained by difference in concentrations between pre- and post-digested samples. Cl^- was measured on the same samples using a Radiometer CMT10 Chloride Titrator. Average precision was 1% for PO_4^{3-} and Cl^-, 1.5% for $NO_2^- + NO_3^-$ and NH_4^+, and 3% for silicates. Total alkalinity was measured on a separate set of samples using a Tacussel™ Processeur 2 automatic titrator. Samples were taken in October 1994 and alkalinity was measured within 2–4 h of porewater extraction. Precision for alkalinity measurements was 0.6%.

Solid-phase elements were determined from the same cakes squeezed for porewater. Sediments were placed into glass vials and frozen immediately. After drying and grinding, TOC was determined on a Beckman TOC Analyzer. Total C and N were measured on a Perkin Elmer 2400 CHNS/O Series II Analyzer. Total P, S and Fe were measured on a Varian Liberty 220 ICP–AES after aqua regia and $HClO_4$ digestion of sediments. Analytical precision was 5% for total N and 3% for the other elements. Elemental S and pyrite were measured on the same samples using the spectrophotometric methods of Troelsen and Jørgensen (1982) and Lord (1982), respectively. Precision was 5% for elemental S and 2% for pyrite.

2.4. Microbial respiration and sulfate reduction

CO_2 release and O_2 consumption across the sediment–air interface were measured in October 1994 using opaque glass bell jars placed into sediment cores taken at low tide using stainless steel liners from a boxcorer. Each liner was inserted into the sediment and removed as gently as possible. The bottom of each core was sealed using the rubber-padded plates normally used as seals on the boxcorer. These cores were then incubated in the shade in a large plastic bin filled with ambient seawater up to, but not over, the sediment surface. In each core, duplicate bell jars were gently inserted into the sediment. Each bell jar had a propeller-electric motor unit and sleeves to serve as sampling ports. Rates of gas exchange across the sediment–air interface were measured at ~30 min intervals for 3 h via the sampling ports by a GC–TCD using a portable MTI Analytical Instruments P200 gas chromatograph. Values were calibrated against mixed oxygen and carbon dioxide standards. Average precision was 0.3% for O_2 and 0.4% for CO_2. Two trials were conducted at each site on consecutive days.

Sulfate reduction was measured on replicate 2.7 cm diameter cores using the core injection technique (Fossing and Jørgensen, 1989). Injections of 2 μl carrier-free $^{35}SO_4^{2-}$ (70.4 kBq; Amersham Corp.) were made horizontally at 1 cm intervals through silicone-stoppered ports. The cores were incubated in shade for 6 h before being cut into 2 cm segments and transferred to 20% Zn acetate (1:1 vol) and frozen to terminate incubation and fix sulfides. The two-step distillation procedure of Fossing and Jørgensen (1989) was used to determine the fraction of reduced radiolabel in the acid-volatile sulfide (AVS = free sulfides, FeS) and chromium reducible sulfur (CRS = S^0, FeS_2) pools. Briefly, sediments were mixed and washed three times. A 2–3 g portion was transferred to a reaction flask with 20 ml 50% ethanol. After degassing for 10–15 min and acidification (8 ml 1 *N* HCl), AVS was liberated as H_2S at room temperature for 40 min using N_2 as carrier gas. The H_2S was trapped as ZnS in 10 ml 5% Zn acetate. CRS was determined from the remaining sediment slurry. A new Zn acetate trap was inserted and 16 ml 1 *M* Cr^{2+} in 0.5 *N* HCl was added before distillation was resumed by 45 min of boiling. ^{35}S radioactivity in both traps was determined on 5 ml subsamples on a Beckman scintillation counter. A control core was run at each station by cutting a core into segments, adding each slice to test tubes containing Zn acetate, mixing and then adding the radiolabel. Distillation of control cores revealed only background (~40 CPM) counts in the reduced S extracts.

Statistical tests are noted in the Results and were calculated as described in Sokal and Rohlf (1969).

3. Results

3.1. Sediment characteristics

Sediments at Sta. NR were composed of fine, mainly carbonate (73% $CaCO_3$) sand with low water

Table 1
Mean sedimentological characteristics of the Ningaloo Reef lagoon and Mangrove Bay stations

Characteristics	Stations		
	NR	MBL (1993)	MBL (1994)
Percent sand (by DW)	93.0	70.1	61.2
Percent silt (by DW)	0.5	19.5	23.4
Percent clay (by DW)	6.5	10.4	15.4
Percent $CaCO_3$ [a]	73	43	41
Mean grain size (μm)	225	67	63
Water content (%)	14	17	19
Sediment temperature (°C)	22	22	27
Classification	fine sand	very fine sand	very fine sand

Values are means of replicate samples to 20 cm depth for Stas. NR and MBL (1993) and to 40 cm depth for Sta. MBL (1994).
[a] (total carbon) − (total organic carbon) × 8.33.

content (Table 1). The sediments in Mangrove Bay lagoon were classified as very fine sand with lesser amounts (41–43% $CaCO_3$) of carbonate; water content was low (Table 1). Mean grain size at Sta. MBL was not significantly (*t*-test; $P > 0.05$) different between years (Table 1). At both stations, mean pH (Table 2) was ≥ 7.5 and increased with increasing sediment depth (data not shown). pH differences between years at Sta. MBL were not significant, but pH was significantly ($P < 0.05$) higher at Sta. NR. Redox potential was positive at Sta. NR (Table 2), with only a marginal change with increasing sediment depth. At Sta. MBL, redox potential was negative with values ranging from −252 to −79 mV over the depth profile (data not shown).

3.2. Porewater solutes

Free sulfide concentrations (Table 2) were significantly ($P < 0.05$) greater at Sta. MBL in 1993 than in 1994 and compared with Sta. NR. Differences between Sta. NR and MBL in 1994 were not significant ($P > 0.05$). There were no significant trends with sediment depth at either station (runs test; $P > 0.05$).

Cl^- and SO_4^{2-} concentrations (Table 2) varied more among replicates than between stations and between years at Sta. MBL; there were no clear increasing or decreasing trends (runs test; $P > 0.05$) for either solute with sediment depth. Porewater Cl^- concentrations were greater than in the overlying water (Table 3) at Sta. NR and at Sta. MBL in 1994. Differences in SO_4^{2-} concentrations between porewater and overlying water at both sites were not significant ($P > 0.05$).

Ca^{2+} concentrations (Fig. 2, top left) declined significantly with depth below the top 0–2 cm sediment layer at both stations, but differences between sites were significant only at the surface and at the 6–8 cm layer. Interstitial Ca^{2+} was in excess at both stations only in the 0–2 cm depth layer and at 10–12 cm depth at Sta. NR (Fig. 2, top right). Porewater

Table 2
Mean (and range) of redox potential, pH and porewater elements at the Ningaloo Reef lagoon and Mangrove Bay stations

Parameter	Stations		
	NR	MBL (1993)	MBL (1994)
Eh (mV)	+193 (+154 to +221)	NA	−194 (−252 to −79)
pH	7.9 (7.8–8.3)	7.5 (7.4–7.5)	7.5 (7.3–7.8)
Cl^- (m*M*)	607 (566–637)	587 (561–606)	677 (639–733)
SO_4^{2-} (m*M*)	27 (24–29)	30 (26–32)	30 (26–34)
H_2S	8 (0–25)	44 (24–69)	7 (1–15)
NH_4^+	28 (3–41)	233 (129–284)	156 (44–205)
$NO_2^- + NO_3^-$	0.18 (0.0–1.6)	0.05 (0.05–0.10)	0.03 (0.0–0.09)
$Si(OH)_4^+$	51 (24–81)	134 (109–159)	157 (62–294)
PO_4^{3-}	1.9 (0.8–5.3)	11.8 (6.3–30.9)	7.6 (1.2–15.6)
DOC	600 (420–1260)	530 (380–760)	570 (300–2500)
$Fe^{2+,3+}$	–	9.7 (3.7–25.4)	8.0 (1.9–26.3)

Values are means (and ranges) of replicate samples to 20 cm depth at Stas. NR and MBL (1993 and 1994), and to 40 cm depth for DOC at Sta. MBL (1994). Solute concentrations are μ*M*, except where noted.
– = below detection limit.

Ca^{2+} was in deficit (i.e., "excess" Ca was < 0) throughout the rest of the cores at both stations with greater deficiency at most depths at Sta. MBL. The calculated saturation state for calcite was > 1 at most sediment depths at both sites, but the calculated saturation state for aragonite was ≤ 1 at most depths at both stations (Fig. 2, bottom). Interstitial Mg^{2+} (Fig. 3, top left) and Sr^{2+} (Fig. 3, top right) concentrations were maximal at the sediment surface (0–2 cm layer) and declined significantly ($P < 0.05$) with sediment depth; the decrease in Mg^{2+} was more apparent at Sta. NR than at Sta. MBL. Porewater Mg was in deficit (Fig. 3, bottom left) below the upper 4–6 cm at both stations, except between 10–14 cm depth at Sta. NR. Porewater at both stations was deficient in Sr (Fig. 3, bottom right).

Total alkalinity (Fig. 4) was significantly ($P < 0.05$) greater at Sta. MBL than at Sta. NR. Alkalinity increased with sediment depth at Sta. MBL (Fig. 4). No significant trend was observed at Sta. NR (runs test; $P > 0.05$).

Dissolved inorganic nutrients were dominated by NH_4^+ and $Si(OH)_4^+$, followed by lesser concentrations of PO_4^{3-} and $NO_2^- + NO_3^-$ (Table 2). Variations among replicate cores were greater than variations between stations and sediment depths (2-way ANOVA's). On average, except for $NO_2^- + NO_3^-$, nutrient concentrations were greater at Sta. MBL

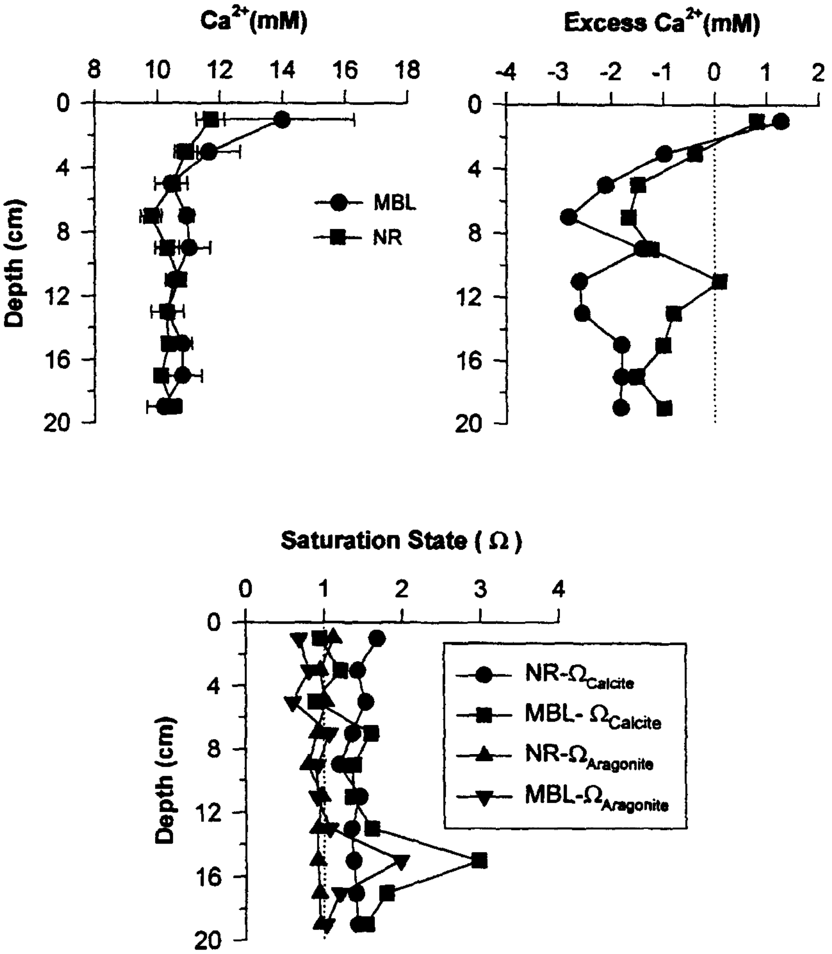

Fig. 2. Vertical profiles of interstitial Ca^{2+} (*top left*), excess Ca^{2+} (*top right*) and calculated saturation states of calcite and aragonite (*bottom*) for Stas. MBL and NR (October 1994). Saturation values > 1 indicate supersaturation; values < 1 indicate undersaturation. Ca concentrations and Ca/Cl ratios in overlying waters are in Table 3. *Bars* depict ± 1 SE.

than at Sta. NR. Water-column nutrient concentrations were lower than in porewater at both stations for all species except $NO_2^- + NO_3^-$ (Table 3).

Mean DOC concentrations (Table 2) ranged from 530 to 600 μM; differences between sites were significant only over the 0–8 cm horizon. DON and DOP concentrations were extremely variable among cores, sites and with sediment depth (i.e., no clear trends). DON concentrations at Sta. NR were 0.7 ± 2.5 μ*M* with no detectable DOP. At Sta. MBL, DON concentrations in 1993 averaged 438 ± 386 μ*M*, but DON was undetectable in 1994. DOP concentrations at Sta. MBL averaged 14 ± 12 μ*M* in 1993 and 7 ± 4 μ*M* in 1994. Porewater concentrations of DOC were greater at both sites than in overlying water (Table 3). Porewater DON and DOP levels were equivalent or less than in the overlying tidal water (Table 3) at Sta. NR but highly variable at Sta. MBL.

Interstitial Fe concentrations (Table 2) at Sta. MBL were greater than in the overlying water column (Table 3). Fe concentrations in porewater at Sta. NR were at or below detection limits. The Fe concentrations measured in 1994 exhibited a decline

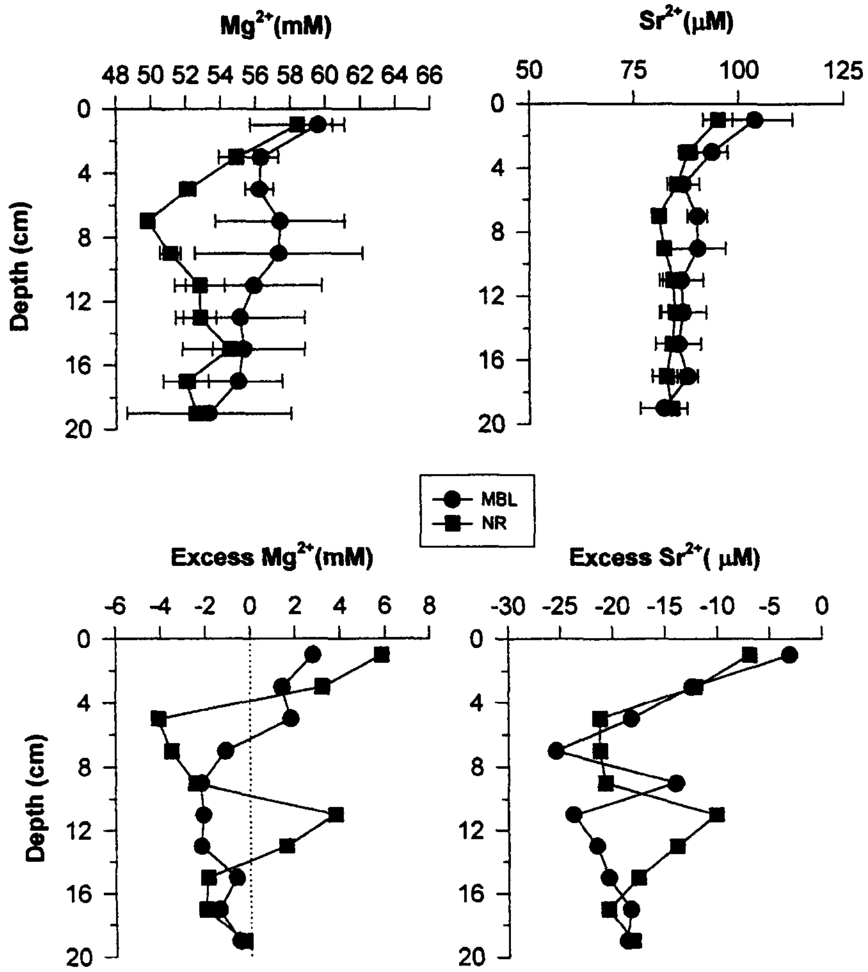

Fig. 3. Vertical profiles of interstitial Mg^{2+} (*top left*) and Sr^{2+} (*top right*) and excess Mg^{2+} (*bottom left*) and excess Sr^{2+} (*bottom right*) at Stas. *MBL* and *NR* (October 1994). Mg and Sr concentrations and Mg/Cl and Sr/Cl ratios in overlying water are in Table 3. *Bars* depict ±1 SE.

Table 3
Mean (± 1 SE) nutrient and other element concentrations (μ*M*, except where noted) in duplicate, overlying water samples taken at high tide in Ningaloo Reef lagoon and Mangrove Bay

Species/element	Station		
	NR	MBL (1993)	MBL (1994)
DOC	290 ± 8	290 ± 0	350 ± 4
DON	17.4 ± 1.3	26.3 ± 6.6	13.7 ± 2.1
DOP	–	0.24 ± 0.21	0.09 ± 0.02
NH_4^+	1.3 ± 0.2	5.3 ± 0.4	1.9 ± 0.2
$NO_2^- + NO_3^-$	0.41 ± 0.17	0.05 ± 0.01	0.13 ± 0.08
$Si(OH)_4^+$	10.4 ± 1.6	8.5 ± 4.5	3.1 ± 0.4
PO_4^{3-}	0.14 ± 0.02	0.26 ± 0.01	0.02 ± 0.0
$Fe^{2+,3+}$	–	NA	0.9 ± 0.01
Ca^{2+} (m*M*)	10 ± 1	NA	11 ± 1
Mg^{2+} (m*M*)	46 ± 1	NA	48 ± 1
Sr^{2+}	89 ± 2	NA	96 ± 2
Cl^- (m*M*)	536 ± 6	584 ± 4	586 ± 4
SO_4^{2-} (m*M*)	28 ± 2	30 ± 1	30 ± 1
$Ca^{2+}/Cl^- (\times 10^{-3})$	19	NA	19
$Mg^{2+}/Cl^- (\times 10^{-3})$	86	NA	82
$Sr^{2+}/Cl^- (\times 10^{-4})$	1.7	NA	1.6
$SO_4^{2-}/Cl^- (\times 10^{-3})$	5.2	5.1	5.2

– = below detection limit.

with increasing sediment depth at Sta. MBL (data not shown). Dissolved Mn concentrations were at or below detection limits in all samples from both stations.

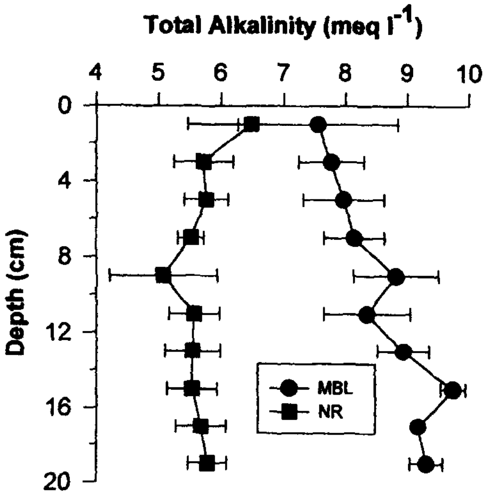

Fig. 4. Vertical profiles of total alkalinity (meq l^{-1}) at Stas. *MBL* and *NR* (October 1994). *Bars* depict ± 1 SE.

3.3. Solid-phase elements

TOC (Fig. 5, top) and TN (Fig. 5, bottom) concentrations declined significantly ($P < 0.05$) with sediment depth at both stations. Concentrations of TOC and TN were significantly less at Sta. NR than at Sta. MBL; values at Sta. MBL in 1993 were, at most sediment depths, less than concentrations in 1994. TP concentrations did not vary with sediment depth, averaging 0.040% at Sta. NR, 0.082% at Sta. MBL (1993) and 0.045% by sediment DW at Sta.

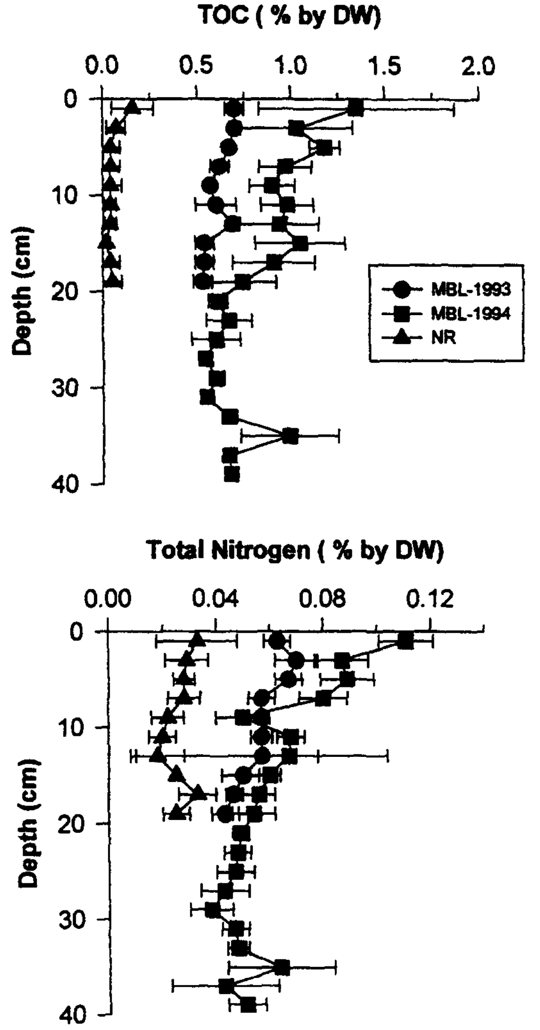

Fig. 5. Vertical profiles of total organic carbon (*top*) and total nitrogen (*bottom*) at Stas. *MBL* and *NR*. Depth interval is 40 cm at Sta. *MBL* (1994). *Bars* depict ± 1 SE.

MBL in 1994. TP concentrations at Sta. MBL in 1993 were significantly higher than at Sta. NR and at Sta. MBL in 1994.

Total S concentrations (Fig. 6, top) at Sta. MBL (both years) were significantly greater than those at Sta. NR. Total S concentrations increased significantly ($P < 0.05$) at both stations, particularly below 20 cm depth at Sta. MBL (1994). C:S ratios (Fig. 6, bottom) were less at Sta. NR than at Sta. MBL (both years). The C:S ratio decreased with increasing sediment depth at both stations (runs test; $P < 0.05$).

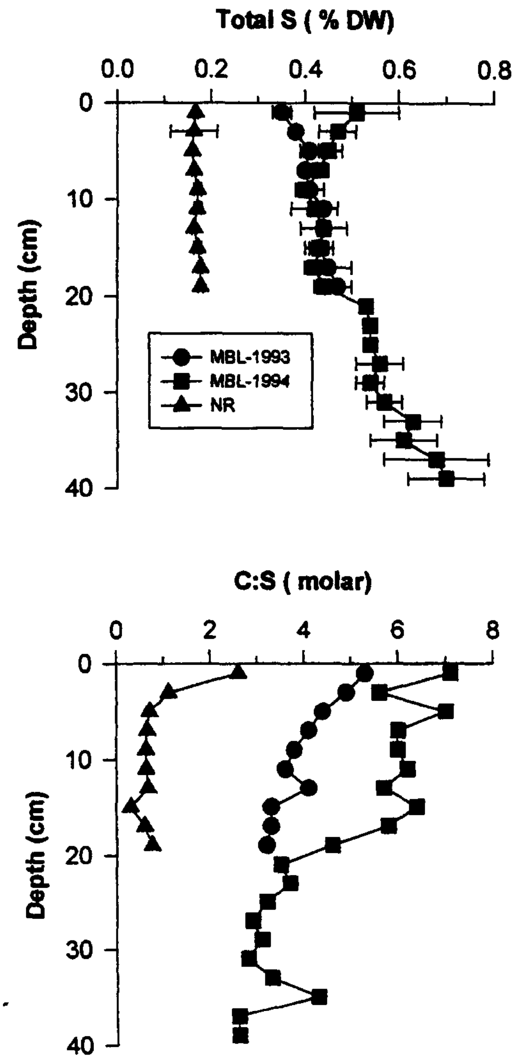

Fig. 6. Vertical profiles of total sulfur (*top*) and the mean C:S ratio (*bottom*) at Stas. *MBL* and *NR*. Note that depth interval is 40 cm at Sta. *MBL* (1994). *Bars* depict ± 1 SE.

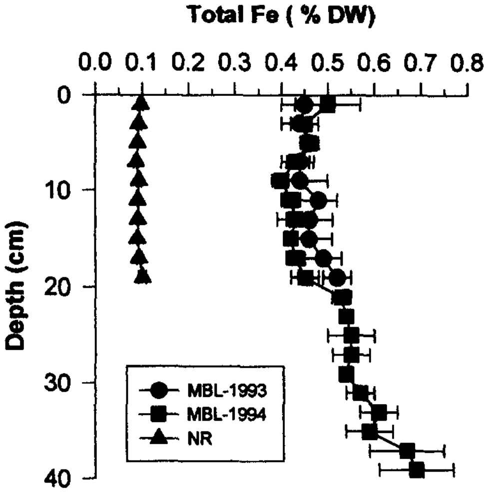

Fig. 7. Vertical profiles of total solid-phase iron at Stas. *MBL* and *NR*. Note that depth interval is 40 cm at Sta. *MBL* (1994). *Bars* depict ± 1 SE.

Pyrite concentrations ranged from 0.04 to 0.10% sediment DW at Sta. NR; on average, pyrite accounted for 21 and 35% of the total S and Fe pools, respectively. At Sta. MBL, pyrite concentrations were significantly greater than at Sta. NR, ranging from 0.2 to 0.3% sediment DW in 1993 increasing significantly with sediment depth; in 1994, pyrite concentrations were within a similar range (0.19–0.50%) and increased with sediment depth. At Sta. MBL, pyrite accounted for a greater proportion (mean = 35% in 1993 and 34% in 1994) of the TS pool than at Sta. NR. Pyrite accounted for 28% (1993) and 30% (1994) of the total Fe pool at Sta. MBL. Elemental S concentrations were low at both stations. At Sta. NR, S^0 concentrations averaged 17 $\mu g\, g^{-1}$ sediment DW and accounted for only 0.01% of the total S pool. Similarly, at Sta. MBL, S^0 concentrations averaged 30 and 52 $\mu g\, g^{-1}$ sediment DW in 1993 and 1994, respectively, accounting for ~ 0.01% of the TS pool in both years.

Total Fe concentrations (Fig. 7) were significantly ($P < 0.05$) less at Sta. NR than at Sta. MBL (both years). Fe concentrations increased marginally with sediment depth at Sta. NR, but did increase significantly ($P < 0.05$) at Sta. MBL, particularly below 20 cm depth; differences between years were not significant ($P > 0.05$).

Table 4
Mean (±1 SE) rates of oxygen consumption, carbon dioxide release, total sulfate reduction (mmol m^{-2} day^{-1} S) and mean percentage of labeled reduced S recovered as acid-volatile sulfide (% AVS) at the Ningaloo Reef lagoon and Mangrove Bay stations

	Station		
	NR	MBL (1993)	MBL (1994)
O_2			
Trial 1	2.8 ± 0.2	NA	9.0 ± 0.3
Trial 2	1.5 ± 0.1	NA	12.1 ± 2.2
CO_2			
Trial 1	2.3 ± 3.8	NA	10.0 ± 2.5
Trial 2	4.6 ± 1.7	NA	8.9 ± 1.4
RQ			
Trial 1	0.8	NA	1.1
Trial 2	3.1	NA	0.7
ΣSRR	1.0 ± 0.1 [a]	25.3 ± 2.8 [a]	6.1 ± 2.5 [b](5.4) [a]
% AVS	38	64	64

RQ is the respiratory quotient ($= CO_2/O_2$).
[a] To 20 cm depth.
[b] To 40 cm depth.

3.4. Microbial activity

Rates of oxygen consumption varied significantly ($P < 0.05$) between trials and among sites, with faster rates at Sta. MBL than at Sta. NR (Table 4). Rates of CO_2 release were not significantly different between trials, but were faster at Sta. MBL than at Sta. NR (Table 4). The respiratory quotient (RQ = CO_2/O_2) varied between trials, particularly at Sta. NR (Table 4).

Rates of sulfate reduction were significantly (2-way ANOVA; $P < 0.05$) different between sites and with sediment depth (Fig. 8a, b). Sulfate reduction rates were also significantly different at Sta. MBL between 1993 (Fig. 8b, top) and 1994 (Fig. 8b,

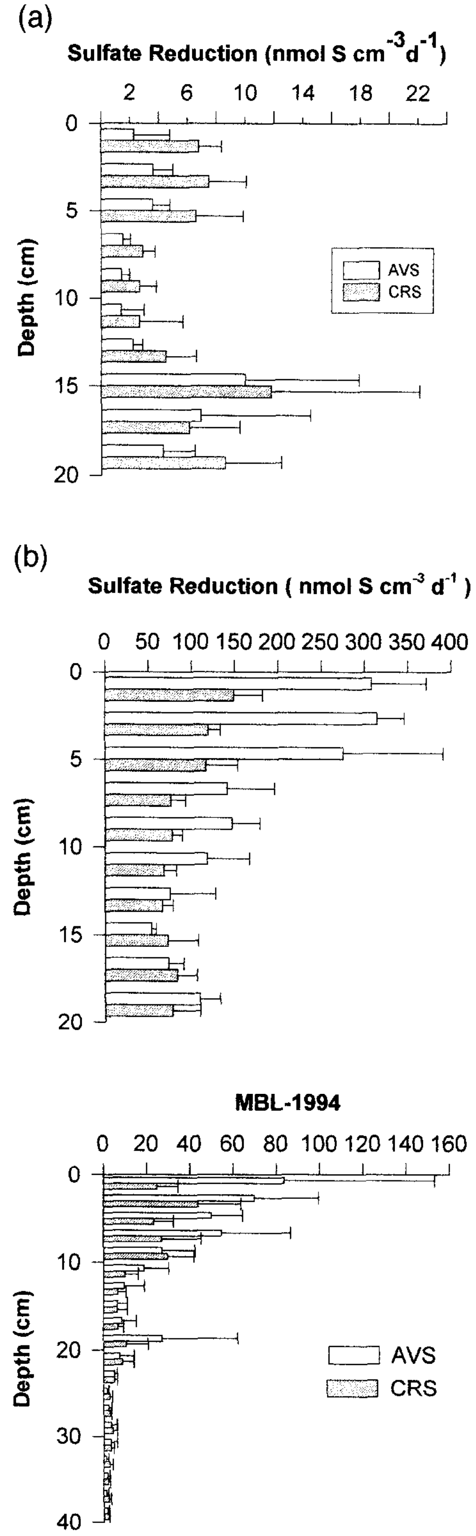

Fig. 8. a. Vertical profiles of mean rates of sulfate reduction and the proportion of reduced ^{35}S recovered in the acid-volatile sulfide (*AVS*) and chromium-reducible sulfur (*CRS*) pools at Sta. NR (October 1994). *Bars* depict +1 SE.
b. Vertical profiles of mean rates of sulfate reduction and the proportion of reduced ^{35}S recovered in the *AVS* and *CRS* pools at Sta. MBL in 1993 (*top*) and at Sta. MBL in 1994 (*bottom*). Note change in rate scale; depth interval is 40 cm for 1994 data. *Bars* depict +1 SE.

bottom), with faster rates in 1993 (Table 4). At Sta. NR, 38% of the radiolabel was incorporated into the AVS fraction, whereas a greater percentage (64%) of the ^{35}S was incorporated into the AVS fraction at Sta. MBL (Table 4). Rates of sulfate reduction at Sta. NR. (Fig. 8a) were slower than at Sta. MBL with no clear trend (runs test; $P > 0.05$) with sediment depth for both the AVS and CRS fractions. At Sta. MBL (Fig. 8b), the proportion of radiolabel incorporated into the AVS fraction declined, and the proportion into the CRS fraction increased with depth, although total rates declined. Rates of reduction at Sta. MBL were slow, but measurable, in sediments deeper than 20 cm (Fig. 8b, bottom).

4. Discussion

4.1. Organic matter oxidation

The rates of O_2 and CO_2 flux and sulfate reduction, and the interstitial and solid-phase element chemistry, show that early diagenesis is greater within the lagoonal sands of Mangrove Bay than in the more carbonate-rich deposits of Ningaloo Reef lagoon. The faster rates of diagenetic activity in Mangrove Bay reflect the fact that this area has restricted water circulation; a rich benthic community with a unique mixture of macroalgae, relict and living corals, and mangroves; a rich community of birds and other wildlife; and a geomorphology conducive to retaining nutrients. It is therefore likely that both the rate of supply and retention of organic matter is high in Mangrove Bay sediments compared to the more exposed and disturbed sands of Ningaloo Reef lagoon. Indeed, the back-lagoon of Ningaloo Reef is subject to considerable wave and tidal action; hydrodynamic data show that the lagoon has water residence times of less than 24 h, as a result of ocean water pumping across the reef by wave action. These wave-driven currents are modified by tides (Hearn and Parker, 1988). These differences between sites are reflected in the redox potentials which show that sediments were more reducing in Mangrove Bay than in Ningaloo Reef lagoon.

The rates of sulfate reduction in Mangrove Bay lagoon were rapid for very fine sand, equivalent to rates measured in temperate muds (Canfield, 1993; Tyson, 1995), tropical seagrass beds (Hines, 1991) and mangroves (Kristensen et al., 1991). Unlike other tropical habitats, most ($\sim$ 64%) of the reduced ^{35}S was incorporated into the AVS fraction with the proportion of radiolabel incorporated into the CRS fraction increasing with sediment depth. These sediments contained iron sulfides, and rates of sulfate reduction correlated inversely with redox status ($r^2 = -0.58$; $P < 0.01$). These conditions are more typical of those found in organic-rich sediments of temperate coastal areas (Martens et al., 1992; Canfield, 1993) than those in most sediments of tropical, shallow-water habitats (Kristensen et al., 1991; Alongi, 1995). The much faster rates of sulfate reduction in 1993 than in 1994 in Mangrove Bay were likely due to differences in the rate or quality of nutrient input, and disturbance, rather than temperature. Rates of nutrient supply to these sediments are not known. Bioturbation was not quantified, but visual observations indicated that numbers of crabs and epibenthos, including macroalgae, were lower in 1994 than in 1993. Bioturbation is known to stimulate sulfate reduction (Berner and Westrich, 1985).

The rates of sulfate reduction measured in the Ningaloo lagoon sediments were slow compared to those measured in Mangrove Bay. However, the rates and the percentage (mean = 38%) of radiolabel recovered in the acid-volatile sulfide fraction are at the upper range of values measured in other reef carbonates (Skyring, 1985; Nedwell and Blackburn, 1987). Slow rates of anaerobic activity in reef sediments have been attributed to slow rates of nutrient input, extreme bioturbation, and the dominance of aerobic metabolism (Skyring, 1987). It is likely that physical disturbance plays an important role in regulating organic matter oxidation in the Ningaloo deposits, considering the influence of a wave-dominated hydrography, and the seasonal occurrence of cyclones.

Physical disturbance is a significant factor given earlier observations (Carter, 1903; Johnstone, 1990) that these habitats are severely affected by cyclones. A cyclone did impact the area between the 1993 and 1994 visits. Unconsolidated sediments in Mangrove Bay lagoon are also shallow, lying atop relict coral. Preliminary coring in both lagoons in 1993 indicated that the average sediment depth was 20–30 cm with the deepest deposits being 40–50 cm. It is likely that the surface (< 20 cm) sediments periodically shift as a result of extreme climatological and hydrodynamic conditions. Severe physical disturbances are known to inhibit anaerobic activity and stimulate aerobic decomposition by resuspending and reoxidizing deposits to ~ 20 cm depth (Alongi, 1995). Periodic disturbances may also partially explain the high core-to-core variations observed for most porewater constituents.

The O_2 and CO_2 fluxes agreed well with the site differences in rates of sulfate reduction, even though the gas exchange rates were highly variable between trials. Rates of gas exchange were probably affected by patchiness in microbial respiration, the short dark-acclimation period, exposure to air for 3 h, disturbance due to coring and transport of the box-core samples, and incubation in the field. Incubation times were short, but no attempt was made to control temperature other than replenishing the seawater in the incubation bins every hour. Similar variations in O_2 and CO_2 results between trials using this method have been noted by Kristensen et al. (1991) in mangroves.

Nevertheless, averaging gas flux measurements and assuming 2 moles of C oxidized for each mole of S reduced (Tyson, 1995), sulfate reduction accounts for all (mean = 129%) of the organic carbon mineralized in the Mangrove Bay deposits, and 57% of total C oxidation in the lagoon sands of Ningaloo Reef. The very high proportion (> 100%) of carbon oxidation accounted for by sulfate reduction in Mangrove Bay may reflect variations in the gas exchange measurements, but also limitations in the tracer method for sulfate reduction (Fossing and Jørgensen, 1989). Other studies have reported similar discrepancies that have been attributed to such factors as isotope exchange reactions and reoxidation of radiolabeled sulfides (King et al., 1985; Mackin and Swider, 1989; Kristensen et al., 1991). Sulfide reoxidation is plausible considering that the porewater sulfate profiles showed no depletion with sediment depth at both locations.

Despite these problems, it is clear that sulfate reduction dominates, and accounts for all or nearly all, organic carbon oxidation in Mangrove Bay. Methanogenesis was not measured, but may be minor considering that the deepest deposits (40 cm) in the lagoon still showed measurable sulfate reduction (Fig. 8b, bottom). The respiratory quotient (CO_2/O_2) averaged ~ 1 (Table 4), but rates of oxygen consumption reflect not only aerobic respiration, but also oxidation of reduced products of anaerobic carbon mineralization (e.g., H_2S). In Ningaloo Reef lagoon, other pathways of carbon oxidation must account for the balance of C mineralization. The porewater $NO_2^- + NO_3^-$ concentrations (Table 2) and profiles suggest that denitrification occurred. It is known that oxic respiration and nitrification–denitrification reactions are major pathways in reef sediments (D'Elia and Wiebe, 1990; Capone et al., 1992) and that sulfate reduction accounts for a lesser or an equivalent (to Sta. NR) proportion of total organic matter oxidation (Skyring, 1985; Nedwell and Blackburn, 1987).

The concentrations, depth profiles and stoichiometry of solid-phase constituents generally reflected the rates of organic matter oxidation. Concentrations of TOC and TN decreased with sediment depth reflecting the well-known, sequential oxidation of metabolizable organic matter leaving proportionately more refractory organic material with increasing sediment depth. These profiles may also reflect temporal changes in the rate and quality of organic matter sedimentation, or algal enrichment of the sediment surface. The profiles of the total S (Fig. 6) and Fe pools (Fig. 7) indicate that the rates of sulfate reduction were sufficiently high to result in significant burial of iron sulfides, particularly below 20 cm depth at Sta. MBL. The decline in the C:S ratios with increasing sediment depth (Fig. 6) suggest selective oxidation of labile organic matter and burial of S and Fe as iron sulfides at both sites.

The solid-phase C:N ratios at Sta. NR (mean = 5:1) and at Sta. MBL [means = (3–18):1] reflect the high-quality organic matter present at both stations. Patches of seagrass, macroalgae, and cyanobacterial and microalgal mats are present in both lagoons. Moreover, low C:P ratios [Sta. NR 3:1; Sta. MBL (19–35):1] indicate high levels of P relative to C. These elevated P concentrations probably reflect P bound to the Ca fraction due to precipitation of carbonate minerals such as calcium phosphate (McGlathery et al., 1994), or guano from birds in the sanctuary. The mean solid-phase C:N:P ratios are low compared to stoichiometry in mangrove sediments (Alongi, 1996) and compare well with C:N:P ratios in marine plankton (Redfield et al., 1963), coral mucus (Coles and Strathmann, 1973), and benthic macroalgae and seagrasses (Atkinson and Smith, 1983).

Our data imply that early diagenesis may not be in steady-state in these deposits, considering (1) the lack of a clear zonational sequence of solutes with sediment depth, (2) the lack of agreement between vertical profiles of dissolved and solid-phase elements, (3) the lack of significant correlations between dissolved metals and DOC, (4) imbalance between the estimated amounts of DIC generated by sulfate reduction and the calculated deficiencies in dissolved Ca, Mg and Sr, and (5) high core-to-core variation in conservative element concentrations and rates of microbial activity, including respiration. Alternating patterns of exposure, oxidation, burial and reduction related to changes in sediment mobility/stability can maintain diagenetic disequilibrium. Non-steady state diagenesis has been suggested by Aller et al. (1986), Mackin et al. (1988), Alongi (1995) and Alongi et al. (1996) to explain similar discrepancies in the composition and behavior of porewater solutes, and the stoichiometry of solid-phase elements, in physically disturbed sediments of the Fly and Amazon rivers.

Physical disturbance fostering non-steady state diagenesis may not entirely explain the inconsistency of some solid-phase element gradients being preserved (e.g., TOC, Fe), but concentrations of most porewater solutes being homogenous, with depth. Either sediment disturbances are limited in depth (to 20 cm?) or other factors, such as extensive bioirrigation, tidal advection, temporal changes in the quality and rate of sedimentation, or surface enrichment by benthic biota, may affect solid-phase and porewater elements separately. Sediment disturbances, either biotic- or climate-induced, are likely to be limited with sediment depth as few, if any, macrobiota were observed below the upper 10–20 cm, and only a very severe storm would resuspend the entire unconsolidated sediment column. As noted earlier, the concentrations of TOC and TN decreased, and total S and Fe concentrations increased, with sediment depth but these gradients are sharpest below 20 cm, particularly for S and Fe, suggesting that the deposits deeper than ~ 20 cm are relatively undisturbed. As it is likely that some porewater gradients would re-establish fairly quickly after a disturbance, frequent advection and replenishment of porewater pumped by tides may explain the scarcity of porewater concentration gradients. For example, sulfate depletion would be expected at Sta. MBL given the rapid rates of microbial decomposition, even after a disturbance. A significant proportion of H_2S is presumably oxidized completely to sulfate in sediments (Thode-Andersen and Jørgensen, 1989) and may explain the lack of a sulfate deficit, but the re-oxidation mechanism(s) are not well understood. In any case, the inconsistencies between solid-phase and dissolved elements are novel compared to other shallow-water marine deposits, and may reflect non-steady state conditions.

4.2. Carbonate dissolution / precipitation

The rates of organic matter oxidation greatly affected the precipitation/dissolution kinetics of carbonate at these sites. Normally in carbonate-rich sediments, carbonates undergo dissolution due to production of carbonic acid generated by aerobic respiration and by sulfate reduction (Morse et al., 1985; Walter and Burton, 1990; Walter et al., 1993). As carbonate sediments are normally Fe-poor (≤ 200 ppm), iron sulfide precipitation is limited, leading to accumulation of H_2S and porewater pH at slightly < 7, causing carbonate mineral dissolution. In Fe-rich clastic sediments, carbonate dissolution occurs mainly in surface sediment layers due to carbonic acid generation from aerobic metabolism and Fe-sulfide oxidation, but in deeper layers, Fe sulfide precipitation increases pH and causes carbonate supersaturation (Ben-Yaakov, 1973; Gardner, 1973; Walter et al., 1993).

In the mixed terrigenous-carbonate sediments at both stations, the dissolved Ca, Mg and Sr profiles and calculations of their "excess" concentrations relative to Cl^- (Fig. 2 and Fig. 3) indicate that these deposits are depleted in these elements below the upper few centimetres (at least to 20 cm), indicating either precipitation of a carbonate mineral or that the system is not at steady-state. Interstitial pH was high, within the range of 7.3–8.3, and increased with increasing sediment depth, as expected under conditions of carbonate precipitation. The saturation states for calcite indicate supersaturation at most sediment depths at both sites, but the aragonite saturation values were nearly all ≤ 1 indicating undersaturated to equilibrium conditions.

The rates of DIC generated by the observed rates of sulfate reduction are not in balance with the amounts of Ca, Mg and Sr calculated to precipitate in these sediments. However, the relationship between sulfate reduction and carbonate mineral kinetics is complex and non-linear (Ben-Yaakov, 1973; Gardner, 1973; Morse and Mackenzie, 1990; Walter and Burton, 1990). In Fe-poor sediments, Walter and Burton (1990) found a good positive correlation between sulfate reduction and "excess" Ca. However, in iron-bearing sediments, sulfide precipitation increases pH and leads to aragonite supersaturation, independent of the degree of sulfate reduction. Thus, the impact of pH is greater than that of alkalinity on carbonate mineral equilibria (Ben-Yaakov, 1973; Gardner, 1973). As shown by Morse and Mackenzie (1990), aragonite saturation state as a function of rate of sulfate reduction is non-linear (fig. 6.11, p. 269); aragonite supersaturation occurs at both comparatively slow and rapid rates of sulfate reduction. A similar scenario may be occurring in the Ningaloo deposits. We have no information on the composition of carbonate minerals in these sediments; calcium phosphate may be precipitating rather than calcium carbonate as suggested by Berner (1966) to explain a similar mass balance discrepancy in intertidal carbonate-bearing deposits in Bermuda and Florida.

Despite these uncertainties, our preliminary results suggest that these mixed clastic-carbonate sands are more diagenetically similar to siliciclastic sediments than to carbonate sediments, at least with regard to net carbonate dissolution/precipitation behavior. The most likely cause is that these sediments are Fe-rich (900–6800 ppm; Fig. 7) compared to other marine carbonate-rich sediments (Lyons et al., 1980; Entsch et al., 1983; Matson, 1989; Walter and Burton, 1990) where solid-phase Fe concentrations are normally very low (50–200 ppm). The high Fe concentrations at Ningaloo are not surprising given that the region has the world's largest iron and nickel ore deposits (Marston and Kay, 1980; Walker, 1984). Our use of aqua regia and $HClO_4$ to extract solid-phase Fe from these sediments roughly equates to the method used by Canfield (1989) for determination of reactive Fe in marine sediments. Therefore, we presume that our total solid-phase Fe data represent reactive Fe. It appears that these concentrations of reactive iron, coupled with the rates of sulfate reduction measured, were sufficent to result in the production and, in Mangrove Bay lagoon, accumulation of iron sulfides. This process increased pH to levels promoting net carbonate precipitation from below the upper 2–6 cm to at least 20 cm sediment depth.

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