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THE SUPRATIDAL ENVIRONMENT AND RECENT DOLOMITIZATION, BROAD SOUND, QUEENSLAND

by

P.J. Cook

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SUMMARY

Extensive supratidal mudflats occur on the landward side of thick mangrove swamps around the margins of Broad Sound, central Queensland coast. During inundation by spring or storm tides, abundant algal growth takes place on the mudflats but for the rest of the time the flats are sub-aerially exposed and subject to dessication. As a result, a thin veneer of evaporites covers the surface of the flats and large gypsum crystals form just below the surface. Interstitial pore waters are hypersaline, with salinities in excess of 12 percent being recorded. The Mg/Ca and K/Ca ratios become particularly high in these brines, attaining values of up to 9.9 and 2.2 respectively, primarily as a result of the removal of Ca from solution, in the form of gypsum. The supratidal muds are generally low in calcium carbonate but dolomitic concretions occur in the Charon Point area. These concretions are composed of low-magnesium calcites, and calcian dolomites with a compositional range of $Ca_{0.59} Mg_{0.41} CO_3$ to $Ca_{0.65} Mg_{0.35} CO_3$. Electron microprobe, X-ray diffraction, and whole rock analyses all suggest that the dolomites have formed by dolomitization of calcite. The dolomitization is associated with ferruginization, and possibly also phosphatization. Radiocarbon age determinations on associated wood and shell material, and on the concretions, indicate that the dolomitization has occurred within the past 2500 years.

INTRODUCTION

The Australian Bureau of Mineral Resources undertook a detailed sedimentological and geochemical study of Broad Sound on the central Queensland coast in 1970 and 1971, as part of a study of modern estuarine processes (Cook & Mayo, 1972). These investigations involved sampling of onshore and offshore sediments and oceanic, estuarine, and pore waters. Several depositional environments were delineated, characterized by their elevation above or below sea level, and by their sediments types. This paper discusses intertidal sediments and particularly the high intertidal (hereafter termed supratidal) zone and the Holocene diagenetic dolomitization which has occurred there.

Broad Sound is a large coastal embayment lying between latitudes 22°10'S and 22°40'S (Fig. 1); it has a sub-tropical, sub-humid climate. The average daily maxima at St Lawrence in the northwest of the study area range from 31°C in January to 23°C in July. The region has an average annual rainfall of about 100 cm with most rain falling in the period December to March. The average annual rate of evaporation at Rockhampton, 100 km south of Broad Sound is approximately 170 cm. Consequently, run-off from the rivers draining into Broad Sound (Fig. 1) is negligible for most of the year. During the drier months, salinities may become sufficiently high at the head of the Sound for it to be classed as an inverse estuary (Pritchard, 1967). There appears to be a total lack of vertical stratification of the estuarine water at all times, due to a combination of shallow water, vigorous wave activity, and a tidal range of up to 10 m. The large tidal range also produces extensive intertidal sediments.

Well sorted medium-grained quartz sands and calcareous sands predominate in the lower intertidal environment. A narrow belt of black intertidal muds generally no more than 100 m wide is landward of the sands; the mud is being derived mainly from the adjacent mangrove deposits. Tidal creeks meander through the mangrove swamps, their headwater commonly extending into the mudflats environment. The mudflats, which are up to 5 km wide, are flanked by coastal grasslands extending for up to 10 km inland. Drilling of the coastal plains (Burgis, 1972) and dating of chenier sequences (Cook & Polack, 1972a) showed that the coastal plain has extended seawards by depositional progradation over the past 5000 years. The spatial relationship of these environments, lying between low and high water springs, is shown schematically in Figure 2.

SUPRATIDAL MUDFLATS

Shinn et al. (1965) define the supratidal zone as follows: 'The supratidal zone lies above normal high tide but can be flooded by spring or storm tides. This zone is sub-aerially exposed for long periods between storms or excessively high spring tides'. This usage is followed in this publication.

Supratidal mudflats are well developed around the margins of Broad Sound as small patches surrounded by mangrove, or narrow supratidal channels extending up to 10 km into the Torilla Plains, but generally their form is that of featureless mudflats (Fig. 3A) up to 4 km wide. In places old beach ridges (cheniers) form topographic highs (Fig. 2) and support abundant vegetation, but the mudflats are bare of vegetation except for the occasional occurrence of halophytes. The supratidal muds are 1 to 2 m thick and rest on old mangrove deposits. They are grey-green at the surface and generally grey-brown in the sub-surface, although mottled red, brown, and orange muds are present in the sub-surface in places.

The mudflats slope gently seawards, but there are numerous shallow drainage channels and basins, where surface water may persist for some time. Because of the high rate of evaporation, much of the surface is salt-encrusted and mud-cracked, but during spring tides, when the flats are subject to marine inundation, there is abundant algal growth. Filamentous algal mats are important sediment binders in this environment and these impart a 'rubbery' texture to the grey-green surface sediments (Fig. 3B) and a rather characteristic vesicular texture due to the development of gas bubbles. Overall, however, there appears to be neither the variety of algal morphology nor the abundance of algae that is evident in the intertidal-supratidal environment of Shark Bay, Western Australia (Logan, 1961; Davies, 1970).

The supratidal sediments at Broad Sound are composed predominantly of silt and clay; the average texture of ten randomly selected samples was 2 percent sand and 98 percent silt plus clay. This contrasts with mangrove sediments which contain an average of 88 percent silt and clay, and intertidal sands which contain an average of only 9 percent silt and clay. The sand-silt-size fraction is invariably composed of poorly rounded and poorly sorted grains of quartz, feldspar, and shell fragments. The dominant clay minerals are illite, kaolinite, and montmorillonite. There is probably some conversion of montmorillonite into illite due to the hypersaline conditions prevalent on the supratidal mudflats (Gibson, 1972). The $CaCO_3$ content of the supratidal muds ranges from 37 percent to 0 percent with a mean of 4.3 percent. Thus these mudflats contrast markedly with the better known highly calcareous supratidal mudflats of the Bahamas (Deffeyes et al., 1965) or the sabhkas of the Persian Gulf (Illings et al., 1965; Kinsman, 1969a). The small amount of carbonate also contrasts with the other Broad Sound environments which have a mean $CaCO_3$ content ranging from 12 to 67 percent. Most of the carbonate is in the form of coarse biogenic material and only material fine enough to remain in suspension (predominantly quartz and clay minerals) is able to reach the supratidal environment and settle there.

The organic carbon content of the supratidal muds is low, ranging from 0.45 percent to 0.9 percent, and averaging 0.56 percent carbon (mangrove muds average 1.08 percent). Some of the organic carbon comes from leaves blown onto the mudflats and plant material washed from the mangrove environment by spring tides or storms, but mostly is probably derived from the incorporation of algal material in the sediment.

Fig 1 Distribution of intertidal and supratidal depositional environments, Broad Sound, Queensland.

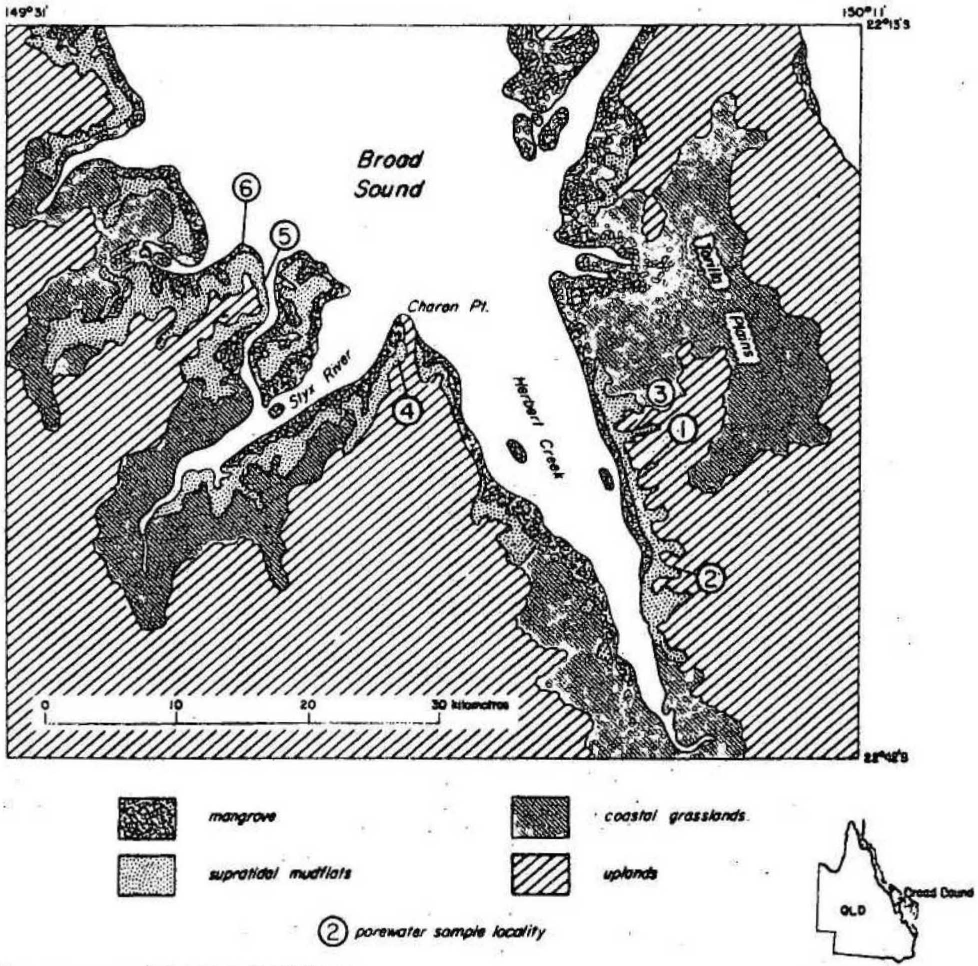

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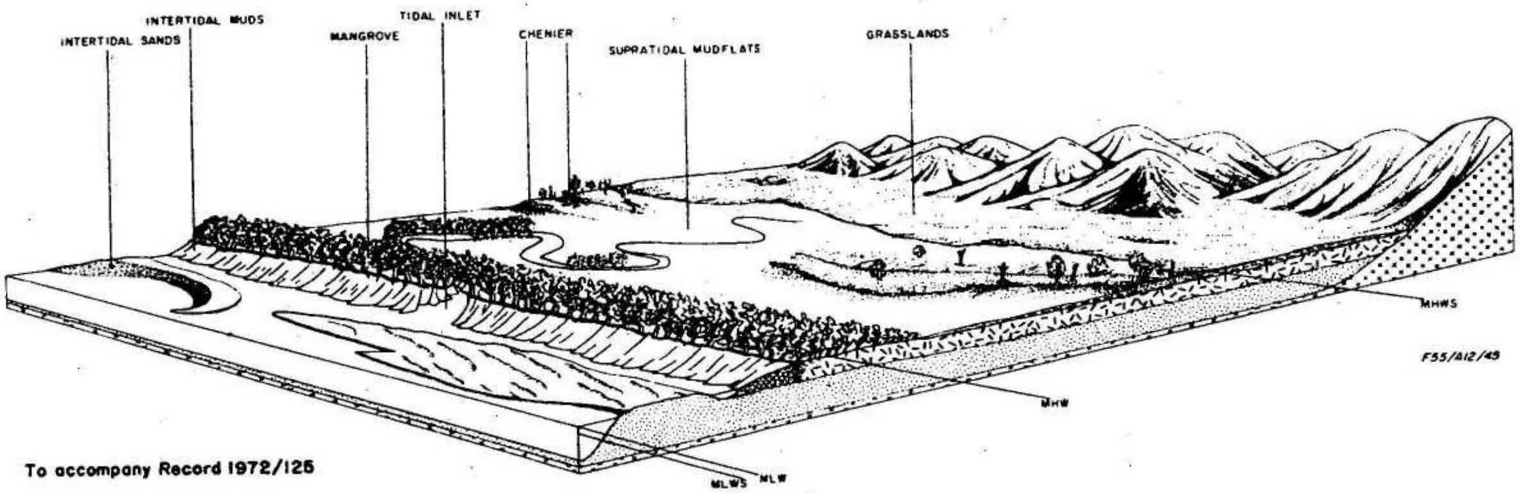
Fig 2 Schematic representation of depositional environments in the Charon Point area of Broad Sound.



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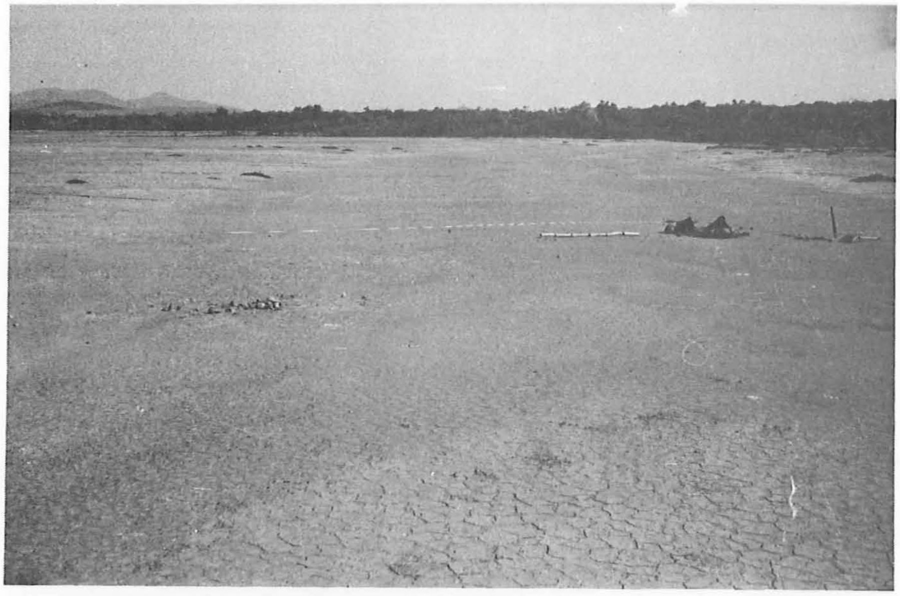

Fig. 3A. Supratidal mudflats in the Charon Point area; white pole is 2 m long.

(Film M1101, Neg. 4).

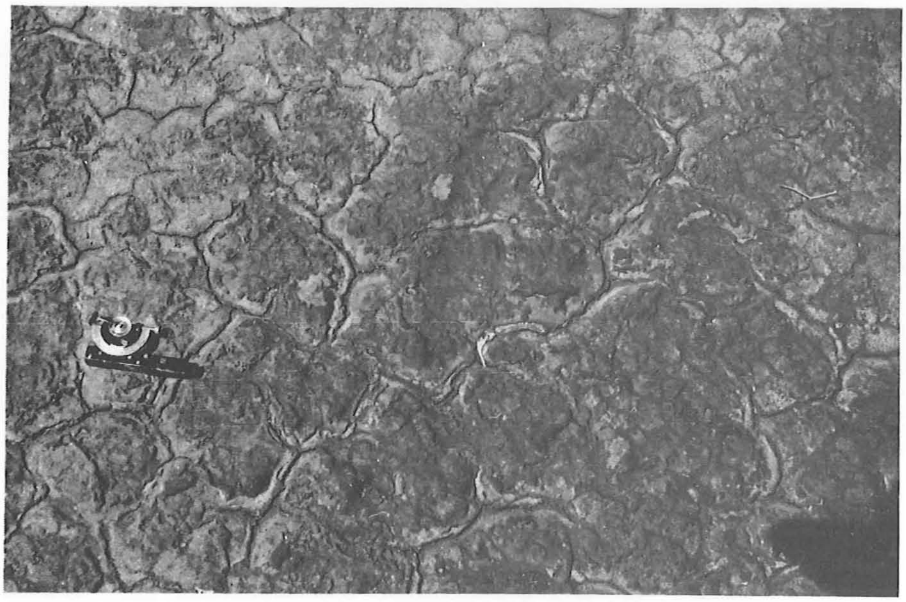

Fig. 3B. Supratidal muds with a sun-cracked surface covered by a thin veneer of filamentous algae. Clinometer is 12 cm long.

(Film M1101, Neg. 15).

Fig. 3C. Exposed dolomite concretions in supratidal muds; Charon Point area, Broad Sound. The pencil is 10 cm long.

(Film M1101, Neg. 9).

Fig. 3D. Dolomite concretions from the Charon Point area.

(Neg. GA.5774).

A thin veneer of evaporites covers the mudflats in many areas; gypsum is abundant, particularly in the sub-surface, where it occurs as flat discoid crystals up to 1 cm in diameter. Halite is present as an ephemeral surface encrustation which is rapidly removed either by wind action or solution. X-ray diffraction analysis showed that small amounts of bischoffite and bassinite are also present in the surface salts. Calcite, aragonite, or dolomite were not identified in the superficial evaporites.

X-ray diffraction analysis of the carbonate fraction of the sediments showed that aragonite, calcite, and high-magnesian calcite are present in approximately equal proportions. Using the Goldsmith & Graf (1958) relationship, the high-magnesian calcite ranges from about $Ca_{87}Mg_{13}CO_3$ to $Ca_{83}Mg_{17}CO_3$, the upper limit being somewhat higher in the supratidal sediments than in the intertidal sediments. The carbonate fraction appears to be overwhelmingly of biogenic origin. Trace amounts of calcian dolomite were detected in a number of muds but it could not be isolated in order to ascertain whether it was forming in situ or was of detrital origin. Some dolomitic concretions, were, however, found in the Charon Point area (Locality 4, Fig. 1). These occur close to the contact between the supratidal muds and the underlying mangrove deposits. They will be discussed in more detail later.

Total sediment analysis was undertaken on six randomly selected samples from various depositional environment. The mean values are given in Table 1. The abundance of quartz, feldspar, and clay minerals in the supratidal muds is reflected in the high SiO_2, Al_2O_3, K_2O, and H_2O concentrations. The abundance of Fe_2O_3 is probably due to the proximity of the environment to lateritized uplands. The low concentration of CaO and CO_2 is to be expected in view of the paucity of calcite and aragonite in the environment. The environment is, however, noticeably more magnesium-rich than any other, particularly if the MgO/CaO ratio is considered (Table 1). The location of the MgO is uncertain; it is unlikely that any magnesium chlorides were present in the sediments analysed, as all were washed with distilled water before analysis. Some of it is likely to be present as interlayer cations in the clay minerals; the remainder is probably associated with carbonates, particularly magnesian calcites, and to a lesser extent, dolomites.

COMPOSITION OF INTERSTITIAL WATERS

In June-July 1971, interstitial pore waters were extracted from intertidal and supratidal sediments (including the buried mangrove deposits which underlie the supratidal muds) at several localities in the Broad Sound area (Fig. 1). A modified Baroid filter press was employed for the extraction, using nitrogen at a pressure of 9 kg/cm^2 (130 p.s.i.). Salinity was measured conductometrically. Eh and pH were measured on the extracted pore waters in the field, and in situ, by placing the glass electrodes directly into the mud or sand; there were found to be marked differences in the results obtained by the two methods. Values obtained in situ were up to 2 pH units lower than those obtained on the pore waters, the results of the 'suspension' or Pallmann effect (Bates, 1964), caused by abnormal junction potentials in colloidal systems. Similarly, Eh values obtained by the two methods varied widely, with the in situ value being as much as 200 mV less than the result obtained on the pore waters. Consequently, any attempt to evaluate the Eh and pH data must be viewed in the light of the uncertainty of which value is closest to the true value. All other analyses on the pore waters were undertaken by C.W. Claxton in the Laboratories of the Bureau of Mineral Resources or by the Australian Mineral Development Laboratories. Mg, Ca, and K were determined by atomic absorption spectroscopy (Table 2). P_2O_5, Cu, Zn, Fe, Ni, Pb, and Mn were also determined, but are not considered here. Although this paper is primarily concerned with the supratidal pore waters environment, other environments will also be briefly considered.

Salinity, Eh, and pH

Seawater in Broad Sound has a salinity of 35.5 to 36.5 parts per thousand, a pH of 7.9 to 8.0, and an Eh of about +210 mV. Surface waters deviate markedly from these values only in the narrow tidal creeks where run-off from the adjacent mangrove environment can result in an increase in salinity to as high as 45 parts per thousand, and a decrease in pH to as low as 6.5. In addition, the ephemeral surface waters of the supratidal zone rapidly attain high salinities as a result of evaporation, and during periods of algal growth the pH will rise as high as 9 due to extraction of CO_2 from the seawater by algal photosynthesis.

The composition of the pore waters (Table 2) is in part a function of the frequency of tidal inundations; consequently, the interstitial waters of the intertidal sediments are somewhat similar in salinity to normal seawater, although surprisingly there does appear to be some dilution of seawater, perhaps by fresh or brackish groundwaters. However, a satisfactory explanation for this dilution awaits further work.

The supratidal pore fluids (including those of the buried mangrove deposits which directly underlie the mudflats) generally have salinities of about 3 times that of normal seawater. pH and Eh conditions are varied (Fig. 4) and in part are dependant on how soon after a marine inundation the determinations were made; algal growth can induce a pH as high as 8.5 in the interstitial waters, but the value can also drop as low as 6.7, possibly due to the release of CO_2 and the formation of organic acids in the sediments. It is evident both from Table 2 and Figure 4 that physico-chemical conditions in the supratidal environment and the buried mangrove deposits are rather different to those prevailing in any of the intertidal environments.

Mg, Ca, and K

Although environments with more saline pore waters also have higher interstitial cation concentrations, the cations do not show the same degree of concentration with increasing salinity. Thus, interstitial waters from the supratidal muds show a mean concentration factor for Ca of about x 2.3 compared with normal seawater, whereas Mg and K show mean concentration factors of x 4.7 and x 4.2 respectively; the Mg/Ca and K/Ca ratios increase as the salinity increases (Fig. 5). If Mg and Ca retained a constant relationship with increasing salinity then all points in Figure 5

Fig 4 Range of Eh and pH values (measured on extracted pore waters) for various depositional environments at Broad Sound

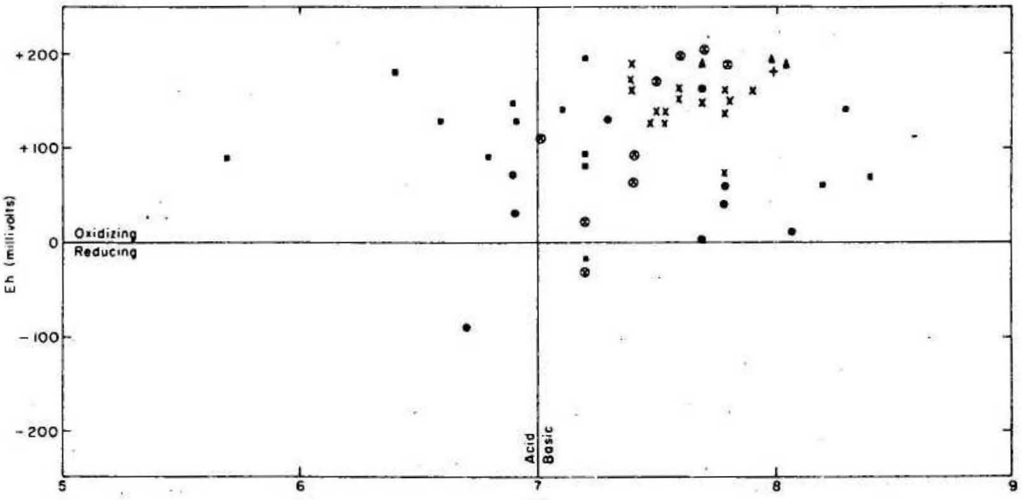

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Fig 5 Graph to show the increase in the magnesium content of various pore waters with increasing salinity.

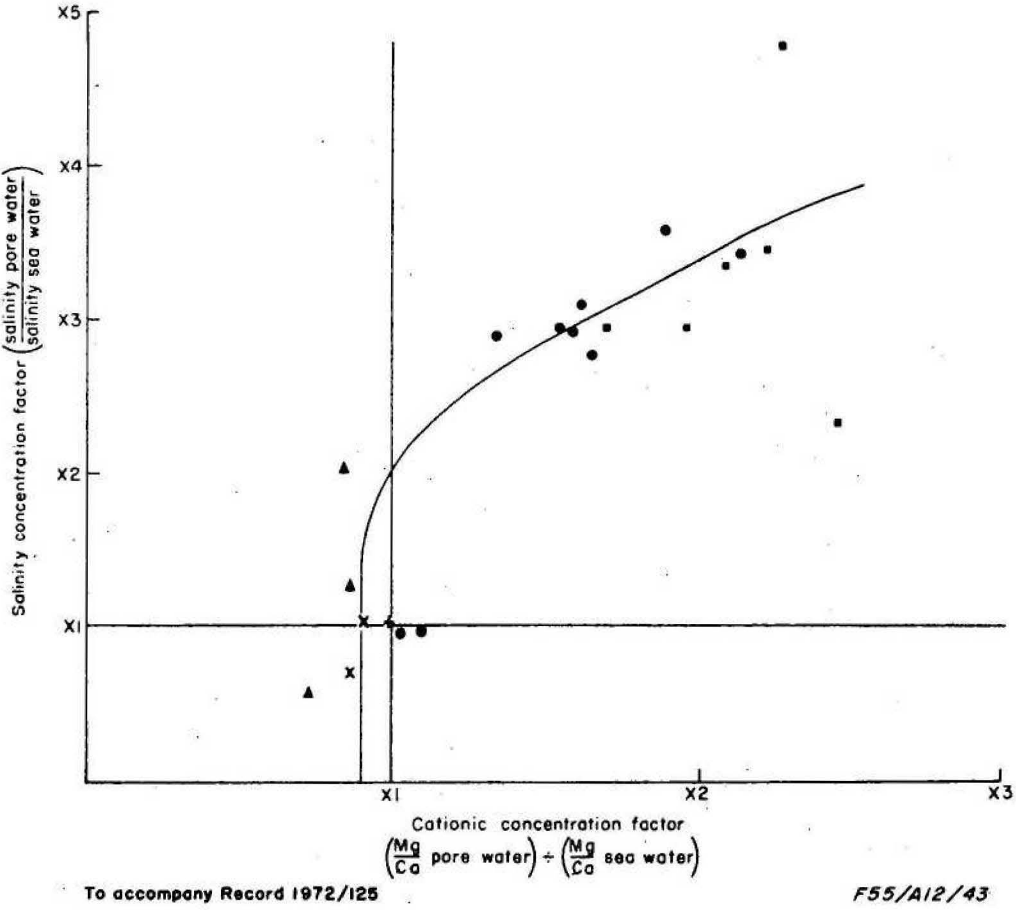

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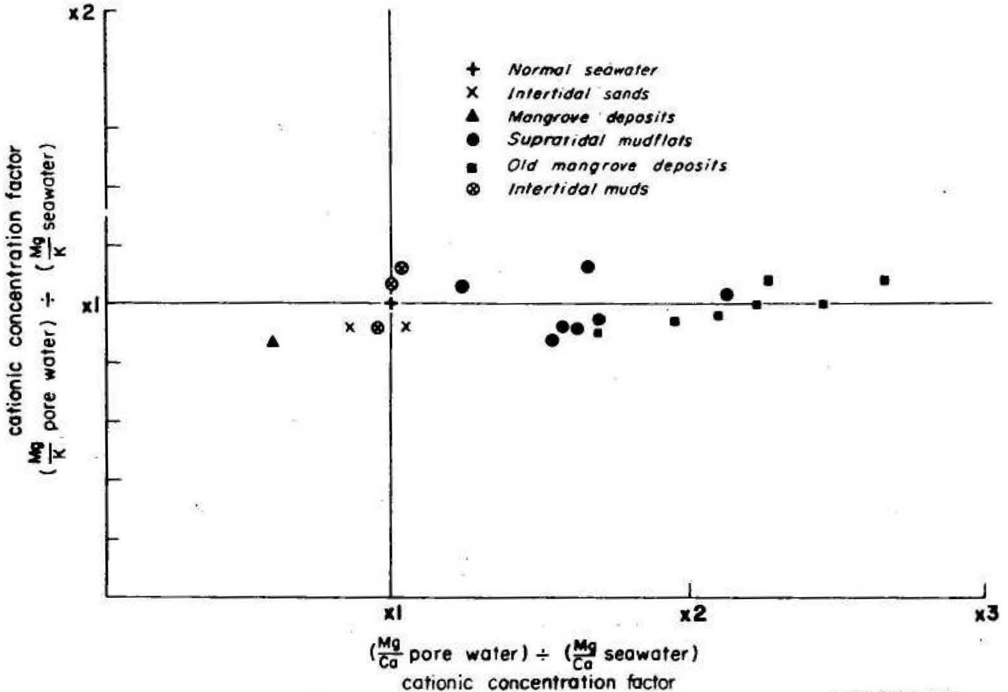
Fig 6 Graph to show the wide range of values for the Mg/Ca ratio compared with the constant Mg/K ratio for various pore water



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would plot along the line representing the cationic concentration factor of x 1. This appears to be the case up to a salinity of twice that of normal seawater but at greater concentrations, the curve deviates markedly from the x 1 factor line. Increasing Mg/Ca with salinity is a phenomenon which has been described from experimental work (Wiedemann, 1969) and supratidal environments, particularly those of the Caribbean and Persian Gulf areas (e.g. Illing & Wells, 1964). It would be reasonable to assume that the increased Mg/Ca ratio results from preferential removal of Ca from the system, perhaps to a limited extent as calcite, but mainly as gypsum as postulated by Kinsman (1969) for the Sabkhas. The abundance of gypsum in the supratidal muds of Broad Sound undoubtedly supports this suggestion. The possibility should, however, be considered of whether additional Mg is being added to the system by some outside source such as magnesium-rich groundwaters or from magnesium-rich sediment (we have already noted from Table 1 that the supratidal muds have a high MgO content compared with other Broad Sound sediments). This alternative hypothesis of a source of additional Mg is tested by a modified plot of Mg/K against Mg/Ca (Fig. 6). It is apparent from this graph that the Mg/K cationic concentration factor remains at x 1 whereas the cationic concentration factor for Mg/Ca ranges from about x1 to x 3. If groundwaters were responsible for bringing in additional cations they would have to carry Mg and K in the same proportion that they are present in seawater. This is unlikely and therefore it can reasonably be assumed that the high Mg and K concentrations in the interstitial supratidal waters are primarily the result of evaporation of seawater and the attendant withdrawal of Ca in the form of gypsum and that there is little or no contribution from the groundwaters. It is probable that this Mg- and K-rich brine is in part responsible for the higher MgO and K_2O content of supratidal sediments compared with other sediments (Table 1).

DOLOMITIZATION IN THE SUPRATIDAL ZONE

Bulk X-ray diffraction of the sediments indicates that the high-magnesian calcite is more magnesian-rich in the supratidal environment than in intertidal sediments but free dolomite was in general detected in no more than trace amounts. However, dolomitic concretions occur in supratidal muds of the Charon Point area (Locality 4, Fig. 1). Because the mode of occurrence of the dolomite is rather different to other previously described Recent dolomites in that the dolomite occurs in predominantly non-calcareous muds, these concretions will be discussed in some detail.

Petrology of the dolomite concretions

The dolomite concretions are found 10 to 20 cm below the surface of the mudflats but are exposed in a shallow drainage channel (Fig. 3C). They are varied in shape and size although most are elongate (Fig. 3D). Some are platey, a few are spherical or subspherical, and several have a characteristic cylindrical form. They range in length from 1 to 20 cm and in width from 0.5 to 10 cm.

Thin sections show that the concretions consist predominantly of a calcareous micritic groundmass showing irregular dark and light patches; poorly developed dark and light concentric banding may also be present. No dolomite rhombs are apparent in any of the concretions. Polished, etched, and broken surfaces were examined by scanning electron microscopy; these showed that the groundmass is composed of poorly developed subround granules but again no dolomite rhombs were apparent.

Angular detrital silt-size grains of quartz and feldspar are sparsely scattered throughout the concretions. The micrite adjacent to these grains tends to be slightly coarser and there appears to be some rim replacement of the grains by micrite. This is supported by electron microscopy, which showed that many of the faces of the quartz grains have sharp, re-entrant, triangular holes etched in them, due possibly to marginal replacement of the quartz. Staining by brown organic material and/or iron oxides is present in places. Vugs are common throughout the concretions and are generally lined by gypsum crystals. Fragments of gastropods were also observed in two concretions.

Two electron probe traverses were undertaken across a concretion. Although the results are not quantitative and values are expressed only in counts per second, it is nevertheless evident from Figure 7 that both magnesium and calcium increase towards the margin. The Mg/Ca ratio is not constant, and increases markedly at the margin. Electron probe analysis also indicated that the darker micritic areas have higher Mg/Ca ratios than the lighter-coloured areas.

Mineralogy

X-ray diffraction analysis shows that the concretions are composed predominantly of dolomite and calcite in the proportion (based on their relative peak areas) of 0.30 to 1.66. Minor quantities of quartz, feldspar, halite, and gypsum are also present. Some typical X-ray diffraction patterns for these concretions (Fig. 8) show that the 211 peak for dolomite ranges from a low diffuse peak (Fig. 8, analysis 4) to a sharp well defined peak (Fig. 8, analysis 8). In some patterns such as that shown in analysis 3 (Fig. 8) more than one 211 peak is evident, suggesting dolomites of varying molar proportions may be present in the same concretion. Material from the outer and inner portions of the concretion represented by analysis 3 was subsequently X-rayed. This showed (analyses 1 and 2, Table 3) that the more magnesium-rich phase ($Ca_{0.59}Mg_{0.41}CO_3$) is located in the outer part of the concretion whereas the inner part is made up predominantly of $Ca_{0.63}Mg_{0.37}CO_3$. No ordered dolomite peaks (100, 221, 111) were evident in any of the diffraction patterns. It is clear from Figure 9 that all 211 peaks of Broad Sound dolomite are located at a lower 2θ value than the Coorong dolomite (Fig. 8, analysis 11). They range from 30.47°2 (2.934 Å) to 30.70°2 (2.912 Å) which corresponds to a compositional range of $Ca_{0.65}Mg_{0.35}CO_3$ to $Ca_{0.59}Mg_{0.41}CO_3$ (Goldsmith & Graf, 1958).

The calcite in the dolomite concretions is low-magnesian calcite, with a narrow compositional range of $Ca_{0.93}Mg_{0.07}$ to $Ca_{0.92}Mg_{0.08}$. No high-magnesian calcite was detected from the X-ray diffraction charts. This was somewhat unexpected, as high-magnesian calcite (ranging from $Ca_{90}Mg_{10}$ to $Ca_{82}Mg_{18}$) is common in all other Broad Sound sediments. Aragonite was also absent from the concretions.

Fig 7 Electron microprobe traverse across a dolomite concretion showing the sympathetic behaviour of Mg and Ca in the concetion, and the marked increase in the Mg/Ca ratio at the margin.

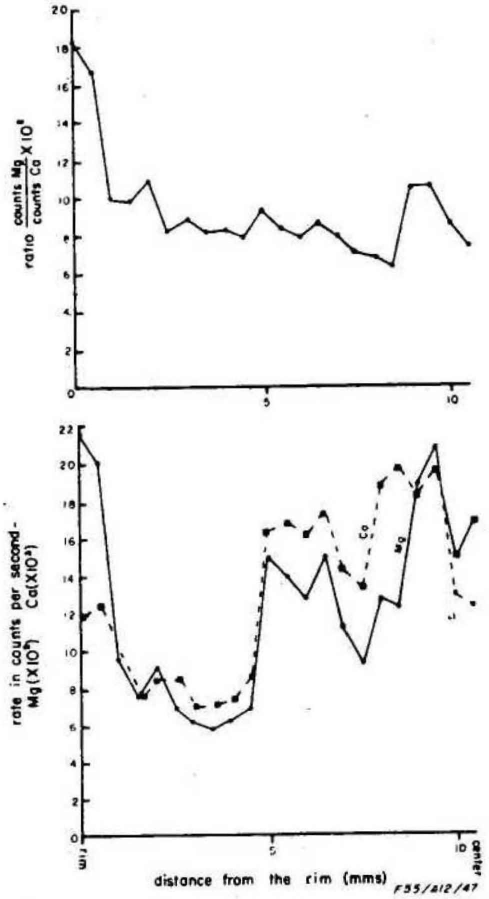

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Fig 8 X-ray diffraction patterns of some Broad Sound dolomites, together with a pattern of Coorong (lagoonal) dolomite for comparison purposes.

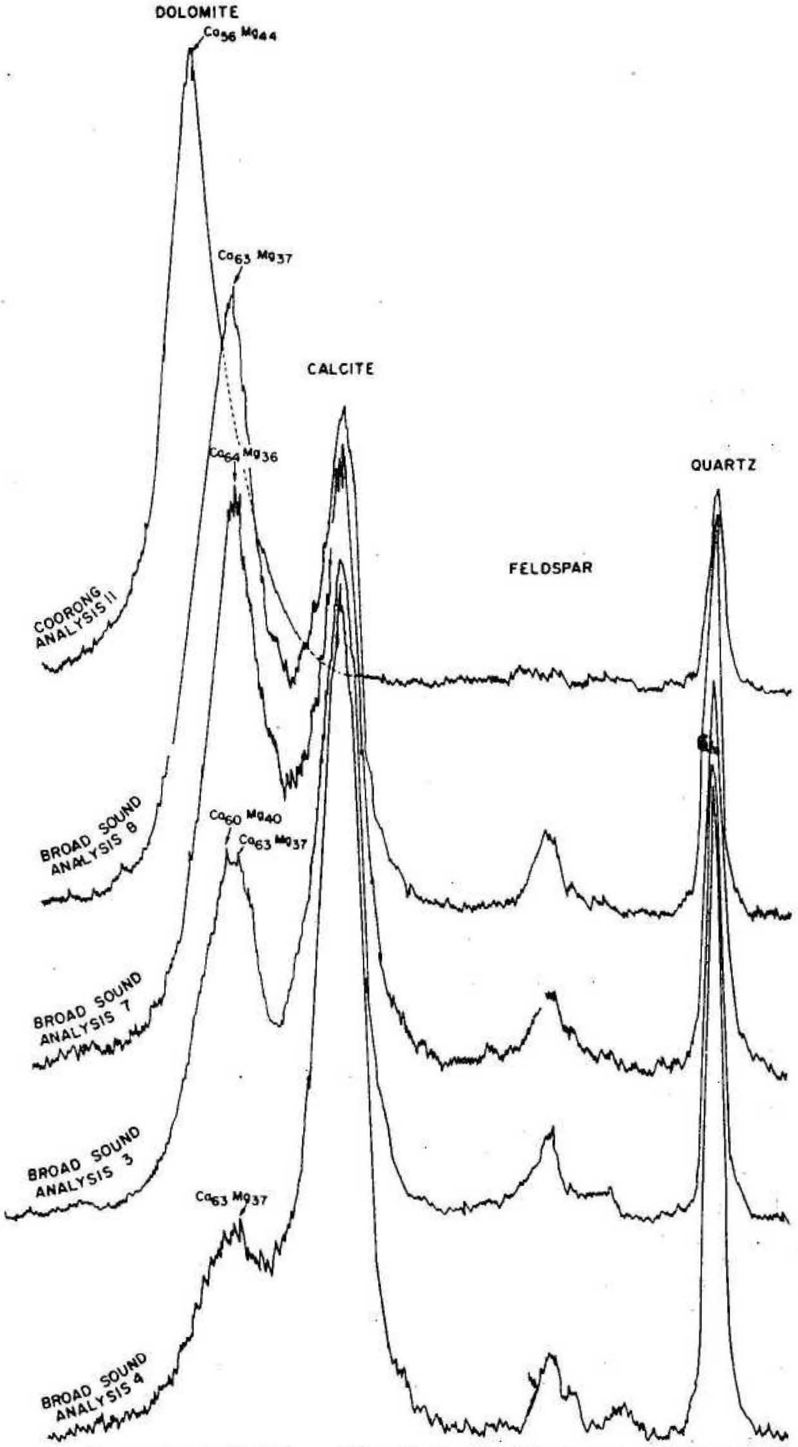

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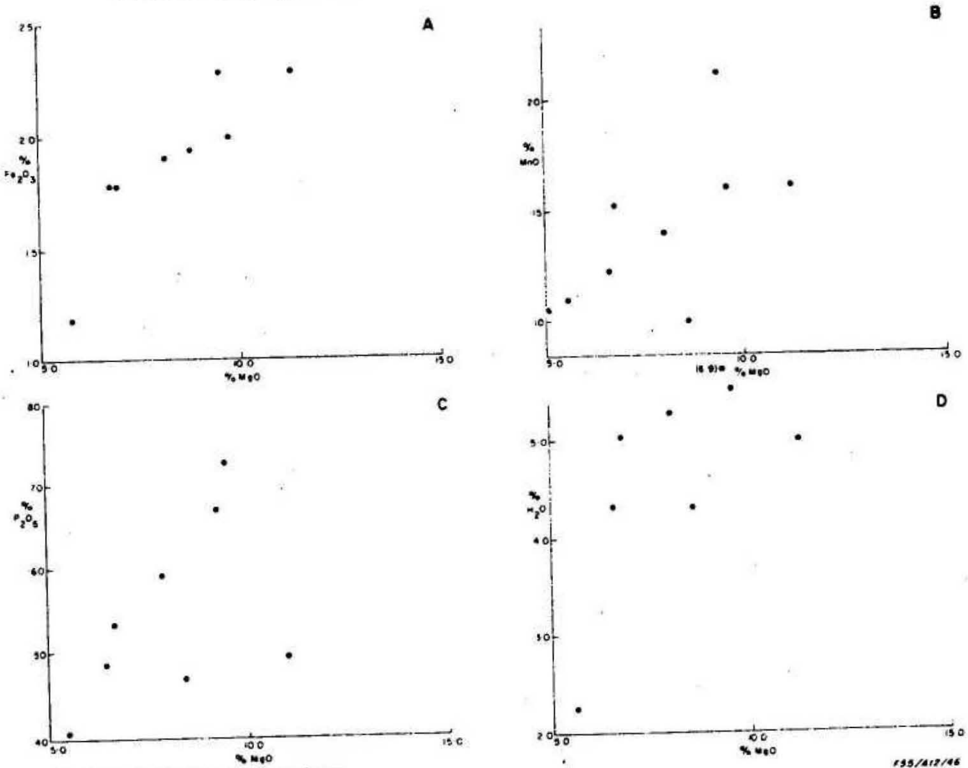
Fig 9 Plots to show the correlation of MgO content in Broad Sound dolomites, with (A) F_2O_3 content (B) MnO content (C) P_2O_5 content (D) H_2O content.



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Geochemistry

Mineralogical and chemical analyses of several dolomite concretions from the Charon Point area are given in Table 3 (analyses 1 - 8). For comparison, analyses of other carbonates are also supplied including a typical marine carbonate (non-dolomitic) nodule dredged from the northern end of Broad Sound (analysis 9), a pedogenic nodule from the Broad Sound area (analysis 10) and a sample of Recent dolomite from the saline lagoons of the Coorong region of South Australia (analysis 11). All analyses were carried out at the Australian Mineral Development Laboratories under the supervision of A.B. Timms: oxides SiO_2 to TiO_2 were determined by direct reading optical spectrography; Cl and SO_4^2 were determined by classical wet chemical methods. CO_2 was determined by weight loss on ignition less H_2O, Sr by X-ray fluorescence and Cu, Pb, Zn, Co, and Ni by atomic absorption spectroscopy.

It is evident that the degree of dolomitization in the concretions is highly variable, with the MgO/CaO ratio ranging from .19 to .37. The earlier findings that the outer margin is the most dolomitic part of a nodule are confirmed, with the outer part of the nodule (analysis 1) containing 9.5% MgO whereas the inner portion of the same nodule (analysis 2) contains only 8.0% MgO.

Computer plots with an XY output together with summary statistics were obtained for all possible variables. Some examples of these are illustrated in Figure 9. In many cases the relationships were completely random. Oxides which are tied to detrital minerals tend to vary sympathetically and Al_2O_3, for instance, correlates positively with TiO_2. An inverse relationship holds between the detrital oxides such as TiO_2 and the 'carbonate oxides' such as MgO. As a consequence of the replacement of calcite by dolomite, CaO varies inversely with MgO. A positive correlation (at a 99% confidence level) is evident between MgO and total iron expressed as Fe_2O_3 (Fig. 9A). Both MnO (Fig. 9B) and total H_2O (Fig. 9D) have a positive correlation with MgO but the confidence level is only 90%. P_2O_5 may correlate positively with MgO, (Fig. 9C) but the confidence level is low (80%); this is primarily the result of the marked deviation shown by two samples (analyses 7 and 8, Table 3); the remainder of the points fall on a regression line showing a positive correlation of MgO and P_2O_5 with a confidence level of greater than 95%. Consequently, it appears that dolomitization and ferruginization, and possibly also manganization and phosphatization, may be related processes in the Broad Sound supratidal environment. The reason for the MgO-H_2O correlation is uncertain; a hydrated carbonate phase may be present, but it is possible that the H_2O is accompanying the Fe_2O_3 rather than the MgO.

It is evident from Table 3 that no real similarities exist between the Broad Sound dolomites (analyses 1 - 8) and any of the other carbonates (analyses 9 - 11). Both the marine and the pedogenic nodules from Broad Sound are low in magnesium and no dolomite is evident from their X-ray diffraction patterns. The Coorong dolomites are equally dissimilar, but for the opposite reason - the abundance of magnesium. The variation in strontium content in the various types of carbonates (Table 3) is marked. The pedogenic and the marine nodules contain only .035 percent and .040 percent strontium respectively; the supratidal dolomite nodules on the other hand have a strontium content ranging from .060 percent to .080 percent and the strontium content of the Coorong dolomite is as high as .74 percent. The strontium level may be in part controlled by a depositional factor such as the water temperature (Dodd, 1965; Hallam & Price, 1968), but the diagenetic history of the carbonate is likely to be of far greater importance (Kinsman, 1969b; Davies, 1972). Consequently, the fact that the Broad Sound dolomites are probably secondary, whereas the Coorong dolomites may be primary (von der Borch, 1965) is likely to have influenced the strontium concentration. In addition, much of the strontium in the Coorong material is present not in the carbonate lattice, but as the separate mineral phase celestite (Alderman & Skinner, 1957; Skinner, 1963). Copper, lead, and zinc are rather more abundant in the supratidal dolomites from Broad Sound than in any of the other carbonates given in Table 3, but the data are insufficient to show whether the base metal enrichment is related in any way to the dolomitization or to weathering, or both.

Age of dolomite concretions

The concretions occur 10 to 20 cm below the surface of the supratidal mudflats. Approximately 300 m seaward from the concretion locality, the muds interfinger with shells derived from the flanks of a chenier, which has been dated as 4520 + 125 years B.P. (Cook & Polach, 1972a). In addition, a sample of wood (ANU-908) from the buried mangrove deposits underlying the supratidal mudflats, at a locality about 250 m from the concretion locality, gave an age of 2980 + 95 years B.P. Thus deposits associated with the concretions are undoubtedly of Holocene age. An age of 2500 + 200 years B.P. was also obtained on a composite sample (ANU-1037) made up of a number of carbonates fragments from various dolomite concretions (Cook and Polach, 1972b). There can be little doubt that the concretions formed approximately 2500 years ago and that they have probably been dolomitized at sometime within the past 2500 years under conditions closely similar to those prevailing in the present-day supratidal environment. It is possible that dolomitization is continuing at the present time.

DISCUSSION AND SUMMARY

As a consequence of the high tidal range and the warm climate, hypersaline conditions prevail in the extensive supratidal mudflats of the Broad Sound area. The sediments are generally low in $CaCO_3$, with quartz, feldspar, and clays being the dominant minerals. Despite this, the composition of the interstitial waters is similar to the interstitial waters of the sabkhas of the Persian Gulf (Kinsman, 1969a), Andros Island (Shinn, Ginsburg, & Lloyd, 1965) and Bonaire (Deffreyes, Lucia, & Weyl, 1965). As a consequence of the high Mg/Ca ratio in the Broad Sound interstitial waters, conditions are ideal for dolomitization of $CaCO_3$ but the mudflats are in general poorly calcareous. The only volumetrically important dolomites so far discovered are the concretionary dolomites of the Charon Point area.

The mineralogy of the dolomites is somewhat unusual as application of the Goldsmith & Graf (1958) relationship shows that they range in composition from $Ca_{0.59}Mg_{0.41}CO_3$ to $Ca_{0.65}Mg_{0.35}CO_3$, a range not commonly encountered in the calcite - dolomite series. Schroeder et al. (1969) state that 'No natural calcium-magnesium-carbonates with compositions between $Ca_{0.68}Mg_{0.32}CO_3$ and $Ca_{0.57}Mg_{0.43}CO_3$ have been reported'. The Broad Sound concretions are composed of dolomite and calcite, and minor quartz, clay minerals, gypsum and feldspar; consequently, chemical analyses can neither confirm nor deny the dolomite compositional range. It is possible that the Broad Sound dolomites have undergone lattice substitution, by for instance Fe, Mn, or Sr, to produce a non-ideal d spacing-composition relationship (i.e. the Goldsmith & Graf curve does not hold for these dolomites) or alternatively there is no gap in the calcite - dolomite series. No ordering peaks are evident but despite this, the 211 peak is sharp and well defined in most of the concretions. Consequently the term 'protodolomite' is not applicable. The Broad Sound dolomites should be regarded as magnesium-deficient or calcian dolomites.

The positive correlation that is evident between MgO and Fe_2O_3, and to a lesser extent between MgO and P_2O_5 and MnO, suggests that the processes of ferruginization, and perhaps also manganization and phosphatization, may be closely related to dolomitization at Broad Sound. In addition, concentrations of copper, lead, and zinc in the dolomitic concretions are higher than those normally found in Broad Sound sediments, lending support to the suggestion by Sonnenfeld (1962) that 'dolomitization and metallization seem to be related'.

It appears probable, from the more magnesium-rich nature of the outer margin, that the concretions were originally predominantly calcitic and have been progressively dolomitized, presumably by magnesium-rich pore waters. What is rather more uncertain is how the original concretions formed. Some are sub-spherical nodules which give no indication of their origin; a number are cylindrical (Fig. 3D) and appear to have formed around wood or root material; the abundance of small organic inclusions in the concretions supports this. Also, many of the elongate concretions have external ornamentation similar in appearance to that of wood fragments. Wood and root material is comparatively sparse in the supratidal muds although it occasionally floats into the zone during spring tides. The concretions are exposed in a shallow drainage channel, but a detrital origin is incompatible with the unabraded nature of the concretions, their distribution, and their size (the current velocities likely to be encountered in these supratidal channels would be incapable of moving concretions up to 15 cm in diameter). Coastal grasslands may have covered the supratidal mudflats and been recently eroded (in the past 1000-2000 years), as soil remnants are present in places, surrounded by supratidal mudflats. Therefore, the concretions could perhaps be of pedogenic origin. In morphology and petrology they are, however, different from nodules located in the present-day soil profile. Sparry calcite is, for instance, abundant in pedogenic nodules from the Broad Sound area but absent from the supratidal concretions.

The most likely way in which the concretions have formed is believed to be as a calcitic precipitate around mangrove roots and stems but no concretion has as yet been found with woody material in the core.

Wright et al. (1972) have described calcareous concretions around mangrove rootlets from the Ord River region of Western Australia which may be comparable to those of Broad Sound. An ancient analog may be the so-called 'coal balls' or 'peat dolomites' which commonly incorporate plant stems and are believed to be a product of the metabolism of the plants they enclose (Sonnenfeld, 1962). There is no immediately apparent chemical mechanism for the precipitation of calcite (or dolomite) around mangrove roots although Kitano & Hood (1965) have shown that organic matter has a marked effect on the crystallization of $CaCO_3$. Sonnenfeld (1962, p. 126) makes the important point of that 'recent dolomites appear restricted to areas of plant growth and plant decay'. Rotting woody material will produce CO_2 and humic acids, thus lowering the pH of the surrounding water to produce the slightly acid condition which prevails in the buried mangrove deposits (Table 2), but the net effect of all this would be to dissolve rather than precipitate $CaCO_3$. If, as commonly is the case, the rotting woody material projects from the mangrove deposits into the overlying more alkaline supratidal deposits then a 'channel' of acid carbonate-rich waters will project into the more alkaline supratidal muds, and calcite would perhaps be precipitated at the contact of the acid and alkaline waters. Bacterial activity around the plant material may also have been equally important in producing conditions suitable for the precipitation of carbonate. Whatever the method by which the calcite was originally precipitated, the increasing Mg/Ca ratio towards the margin of the concretions strongly supports a secondary origin for the dolomite by the progressive inward replacement of Ca^{++} by Mg^{++}. It is uncertain whether the dolomitization occurred almost immediately after, or many years (perhaps hundreds of years) after, precipitation of the calcite. Dolomitization may be continuing at the present day as the modern pore waters undoubtedly constitute a rich source of magnesium. There can, however, be little doubt that dolomitization has taken place within the past 2500 years, an age comparable with that obtained for most other 'modern' dolomites.

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TABLE 1 : MEAN SEDIMENT COMPOSITIONS TAKEN FROM SIX ANALYSES OF NEARSHORE ENVIRONMENTS, BROAD SOUND

	SUPRATIDAL MUDS	MANGROVE MUDS	INTERTIDAL SANDS
SiO_2	63.0	54.4	54.5
Al_2O_3	13.9	10.8	4.0
Total Fe (as Fe_2O_3)	5.6	3.1	1.3
CaO	0.96	10.3	18.4
MgO	2.76	1.85	1.50
Na_2O	0.93	1.39	1.08
K_2O	1.76	1.44	0.55
MnO	0.12	0.06	0.10
P_2O_5	0.13	0.13	0.10
TiO_2	0.91	0.80	0.33
Cr_2O_3	0.10	0.10	0.10
V_2O_5	0.05	0.05	0.05
CO_2	0.31	7.66	15.21
H_2O^{-2}	2.83	1.97	0.42
H_2O^+	6.18	3.69	1.76
	99.49	97.59	99.25
MgO/CaO	2.88	0.18	0.08

TABLE 2 : SOME CHEMICAL CHARACTERISTICS OF INTERSTITIAL WATERS FROM BROAD SOUND DEPOSITIONAL ENVIRONMENTS

PARAMETER	ENVIRONMENT					
	Intertidal sand	Intertidal mud	Mangrove mud	Supratidal mud	Buried mangrove mud	Broad Sound seawater
Eh - in situ (mV)						
(lower	+130	-150	-120	-20	-360	
range(upper	+210	+200	+270	+290	+220	
mean	+160	+40	+140	+170	+80	
pH - in situ						
(lower	7.2	6.9	6.6	6.5	3.5	
range(upper	7.9	7.3	7.3	7.8	6.1	
mean	7.6	7.1	6.8	7.0	4.9	
Eh - pore waters (mV)						
(lower	+130	-20	+60	-90	-120	+190
range(upper	+190	+210	+210	+160	+180	+250
mean	+150	+110	+140	+40	+70	+210
pH-pore waters						
(lower	7.4	7.0	7.1	6.7	5.7	7.9
range(upper	7.9	7.8	8.3	8.5	7.2	8.0
mean	7.6	7.5	7.8	7.6	6.7	7.9
Salinity (p.p.m.)						
(lower	24800	28900	34300	96300	69800	34600
range(upper	35500	37900	70300	128600	123000	36600
mean	30000	32600	45800	110700	103100	35800
Mg(p.p.m.)						
(lower	1080	1140	2130	5260	5360	1300
range(upper	1410	1620	2520	7000	7160	1400
mean	1250	1450	2350	6220	6240	1340
Ca(p.p.m.)						
(lower	300	350	310	800	500	410
range(upper	420	435	1110	1290	860	450
mean	360	395	610	970	731	430
K (p.p.m.)						
(lower	280	320	455	1320	1380	400
range(upper	365	420	660	1840	1640	460
mean	320	370	570	1510	1540	430

TABLE 3 : CHEMICAL AND MINERALOGICAL COMPOSITION OF DOLOMITIC CONCRETIONS FROM BROAD SOUND AND SOME OTHER CARBONATE CONCRETIONS.

	1	2	3	4	5	6	7	8	9	10	11
SiO_2	14.5	14.8	13.3	14.0	13.9	14.4	11.2	14.5	8.4	7.9	6.8
Al_2O_3	5.15	5.3	4.1	4.4	4.9	4.95	4.1	3.8	2.3	2.4	0.11
Fe_2O_3	2.3	1.9	2.0	1.2	1.8	1.8	1.95	2.3	6.1	0.95	0.53
CaO	32.0	32.0	32.5	30.0	35.0	35.0	35.0	30.0	43.0	48.0	6.5
MgO	9.5	8.0	9.7	5.65	6.8	6.6	8.6	11.2	2.0	1.5	19.5
Na_2O	0.39	0.54	0.96	2.4	0.25	0.32	0.18	0.39	0.15	0.2	0.16
K_2O	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MnO	0.21	0.14	0.16	0.11	0.15	0.12	0.10	0.16	0.49	0.03	0.03
P_2O_5	0.68	0.60	0.73	0.41	0.54	0.49	0.48	0.50	0.21	0.08	0.12
TiO_2	0.28	0.22	0.19	0.26	0.26	0.28	0.23	0.21	0.13	0.14	0.03
CO_2	28.6	31.4	30.6	28.3	30.8	30.7	32.8	31.0	33.1	34.5	39.2
H_2O	6.90	5.35	5.60	8.20	5.15	4.40	4.40	5.10	3.40	2.30	5.25
SO_4	-	-	0.56	-	0.43	-	0.43	0.47	0.29	-	0.46
Sr	0.06	0.08	0.065	-	0.065	0.065	0.070	0.065	0.04	.035	0.74
Cl	-	0.07	0.15	-	0.09	0.06	0.04	0.04	0.11	.01	.07
Cu	.0025	.0015	.0010	-	.0010	.0010	.0010	.0015	.0010	.0010	.0015
Pb	.0020	.0015	.0005	-	.0005	.0025	.0005	.0005	.0005	.0005	.0005
Zn	.0110	.0045	.0020	-	.0040	.0070	.0020	.0055	.0015	.0020	.0015
Co	.0010	.0010	.0010	-	.0010	.0010	.0020	.0010	.0020	.0020	.0010
Ni	.0015	.0015	.0015	-	.0015	.0015	.0010	.0015	.0020	.0010	.0005
Ratio Peak areas											
calcite/ dolomite	54:46	53:47	64:36	71:29	71:29	67:33	46:54	38:62	100:0	100:0	0:100
Composition of calcite											
Ca-Mg	93-7	92-8	92-8	93-7	93-7	93-7	92-8	93-7	89-11	97-3	84-16 to 77-23
Composition of dolomite											
Ca-Mg	59-41	63-37	60-40	63-37	65-35	63-37	64-36	63-37	-	-	56-41

Analyses:

1 - outer part of dolomite concretion, Broad Sound

2 - inner part of same dolomite concretion

3 to 8 - dolomite concretions, Broad Sound

9 - marine calcareous nodule Broad Sound

10 - pedogenic nodule, Broad Sound area

11 - Coorong dolomite (sample supplied by C.J. Downes)