Magnesian Calcite at Macquarie Rivulet Delta, Lake Illawarra, New South Wales

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ABSTRACT. A thin, indurated carbonate layer comprising calcium and magnesium in varying proportions, is developed in the near subsurface of a barren, salt-encrusted zone and adjacent algal mat-covered flat at Macquarie Rivulet delta, Lake Illawarra. The presence of this layer appears anomalous since not only is the climate of the area humid with an annual rainfall in excess of 1100 mm, but furthermore, the associated sediments contain abundant decomposing organic matter and are essentially devoid of shell fragments and other detrital carbonate grains. In an attempt to understand the geochemical conditions that have given rise to precipitation of the carbonate layer, analyses have been made of the groundwaters and algal mats in addition to the associated sediments. It is concluded that although the mechanism of formation of the carbonate layer is incompletely understood, the algal mats may have exercised a controlling influence.

INTRODUCTION

The Macquarie Rivulet delta, which protrudes out from the southwestern shore of Lake Illawarra, a coastal lagoon located approximately 80 km south of Sydney (Fig. 1), has an areal extent of about 1 km². The subaerial plain of the delta is mostly covered by grassland with scattered Casuarina sp. on the levees and ridges but, as the lake margin is approached, the rush Juncus kraesi (J. maritimus) generally becomes abundant and not infrequently the grassland gives way rather abruptly, to an algal flat with the glasswort Salicornia quinquiflora. Moreover, near the southeastern extent of the subaerial plain (Fig. 2), the grassland is separated from the algal flat by a barren, mud-cracked and salt-encrusted zone that varies in width up to 25 m. Although essentially devoid of shell fragments and other detrital carbonate grains, this zone and the adjacent algal flat contain in the near subsurface, a thin, persistent, indurated carbonate layer that comprises appreciable amounts of magnesium in addition to calcium. Since decomposing organic matter is prevalent in the deltaic sediments and the rainfall of the area exceeds 1100 mm annually, much of which penetrates the surface, it would be expected that in such an environment precipitation of carbonates would be inhibited by downward percolating waters charged with carbon dioxide. The primary objective of this investigation, therefore, has been an elucidation of the geochemical parameters that have given rise to the development of the carbonate layer.

THE MACQUARIE RIVULET DELTA

The Macquarie Rivulet, which is the largest stream draining into Lake Illawarra, rises in the highlands of the southern Sydney Basin where the rainfall is 1500 mm, and flows in an easterly direction. The upper reaches drain Tertiary basalt and shales of the Triassic Wianamatta Group before descending the escarpment of the Hawkesbury Sandstone to the more easily erodible strata of the Narrabeen Group and the underlying Late Permian Illawarra Coal Measures. Because of the rapid runoff over this section, a large mass of alluvial and colluvial debris has accumulated at the base of the escarpment. In its lower course the stream traverses lavas and volcanic sandstones of the Middle Permian Gerringong Volcanics or soil and alluvium derived from these rocks. Young (1976) believed that the alluvial and colluvial accumulations on the hillsides at the base of the escarpment supplied the bulk of the detritus for construction of the delta but, judging from the prevalence of feldspar in the deltaic sediments, it would appear that the Gerringong Volcanics have also been a major contributor.

The delta, which is of the bird's foot type, projects about 1.5 km out from the shorelines of adjacent Koono and Hayward's Bays (Fig. 2). Most of its growth has been over the past hundred years (Young, 1976) and is undoubtedly attributable to accelerated erosion resulting from the clearing of the natural vegetation to make way for urban and agricultural development. Prior to the floods of 1974 and 1975, discharge into the lake was principally through the northern distributary but the
eastern channel, which is located on the site of an earlier crevasse, was considerably widened by these floods and now forms the main outlet. As Young (1976) noted, the delta is mostly constructed of the coarse fraction of the stream-borne debris whereas much of the clay and silt has been carried well beyond the mouths of the distributaries. Some of this fine detritus is being swept into Koona Bay, particularly during periods of high lake-water level, by waves generated by easterly and northeasterly winds. As a result, the shoreline of Koona Bay, including the southern margin of the delta, is prograding rapidly (Jones et al., 1976).

Brown (1968) has drawn attention to the influence of longshore currents on the growth of the delta. As the levees were extended out into the lake, curved spits developed on the downcurrent side and these eventually grew to enclose lagoons. Ultimately the lagoons were filled with fine grained detritus leaving shallow depressions separated by low ridges over much of the subaerial delta.

The small lagoon located on the southeastern flank of the delta (Fig. 2) represents an intermediate stage in the development of one of these depressions. At times of high lake levels this lagoon is filled with marine water but, during protracted arid spells, it may dry out completely leaving a thin residual crust of gypsum and halite. However, there does not appear to be a build up of these salts on the floor of the lagoon and apparently the crust is destroyed during the ensuing period of inundation.

Although Lake Illawarra is virtually non-tidal, fluctuations in water level of the order of half a metre, brought about by the intermittent opening and closing of the lake entrance and variations in stream discharge into the lake, are apparently of sufficient frequency to maintain a saltmarsh environment along part of the foreshore including the southern margin of the delta. In this environment the glasswort Salicornia gmelinii flora tends to flourish and blue-green algae have built almost continuous mats. (Fig. 4). The uppermost layer of these mats comprises Lyngbya sp. and Nostocaceae sp. and appears relatively free of sediment and particulate matter whereas the underlying layer, consisting of Trichodesmium sp. and Trichodesmium sp., contains appreciable amounts of solid sediment adsorbed on the algal filaments (S. Lupton - pers. comm.). The carbonate layer is generally located within a few centimetres of the base of the algal mats.

The succeeding barren, salt encrusted zone contains mud cracks and stromatolites in addition to the layer of magnesium-calcium carbonate in the sub-surface, features that have been recorded from a range of supratidal zones including those of humid areas (Shinn et al., 1965) as well as the extremely arid sabkhas (Illing et al., 1965; Kinsman, 1969). It is slightly more elevated than the algal flat and apparently encroachment by lake water does not reach this zone or is too infrequent to support algal growth. Nevertheless, the presence of stromatolites in the surface mud immediately above the carbonate layer attests to the former development of algal mats and presumably in the recent past the lake level stood somewhat higher. Wind blown spray would seem the most likely source for the accumulation of salt and apparently replenishment by this means is adequate to offset loss through solution by meteoric water and also, to inhibit the spread of grass across the zone.

CHEMICAL AND MINERALOGICAL DATA

In an attempt to gain an understanding of the geochemical conditions that have given rise to precipitation of the carbonate layer, a series of auger holes extending from near the lake edge to the margin of the grassland, were put down (Fig. 3). Representative samples of the sediments were obtained
for determination of the mineral composition and pH measurements of the groundwater in each of the holes were made in situ using a portable meter. Samples of the groundwater were also collected for determination of the calcium, magnesium, sodium and chlorine contents and similar analyses were made of the lake water for comparison. In addition, samples of the carbonate layer, the algal mats and the glasswort were initially washed in distilled water to remove adhering salt and sediment and subsequently, analysed for their calcium and magnesium contents.

Water analyses

As shown in Table 1, the pH value of the lake water is 8.3 but the groundwaters in the auger holes tend to be more acidic due to the concentration of bicarbonate ions arising from the decay of organic matter. The lowest reading was for hole A where organic matter is most abundant, whereas the remaining holes yielded values about or slightly above neutrality. The curve for the variation in pH values across the algal flat and salt-encrusted zone (Fig. 5) appears characteristic of coastal sections generally, including the sabkhas of the Persian Gulf (Illing et al., 1965).

The chlorinity expressed in parts per thousand, decreases from 18.5 at the lake edge to 13.2 in hole A but from there it increases gradually to a maximum of 22.3 in hole E, which is located near the outer margin of the salt-encrusted zone. Although the trend of the curve shown in Fig. 5 bears a resemblance to that furnished by Illing et al., (1965) for the Faishakh Sabkha, the values are appreciably lower and undoubtedly reflect the greater humidity of the Macquarie Rivulet delta.

In general, the Mg/Ca ratios for the samples of groundwater obtained from the auger holes do not deviate greatly from that of the lake water. Nevertheless, there is a tendency toward a higher concentration of magnesium relative to calcium in
Detrital mineral composition

From petrographic and X-ray diffraction analyses of the sediments obtained from various levels above the water-table in the auger holes, it is apparent that quartz is the dominant detrital mineral, not only of the silts and sands but also of the muddy surface layer. Feldspar, which in some samples amounts to nearly 20% of the total mineral content of the sediment, is almost invariably associated with the quartz occurring as discrete grains and less frequently as a constituent of rock fragments. Disordered kaolinite is by far the most abundant of the clay minerals being frequently present to the exclusion of other members of the group. Nevertheless, minor amounts of mixed layer clay minerals and highly degraded illite were detected in some samples. The predominance of kaolinite over the other clay minerals undoubtedly reflects the influence of the high rainfall on the decomposition of the source rocks. However, possibly there has been preferential concentration of the mineral as a result of differential flocculation by the marine water.

Similar analyses made of washed samples of the algal mats revealed that quartz and feldspar are the only crystalline phases present.

Authigenic minerals

Halite and magnesian calcite were the only non-detrital minerals detected in the sediments intersected in the auger holes. Gypsum was found associated with halite on the floor of the dried out lagoon during one of the visits to the area but this mineral appears absent from the subsurface samples, a point that seems pertinent to discussion of the origin of the magnesian calcite.

Halite, which varies in content up to 10% of the total constituents, was encountered in about half the number of samples of sediment examined from the auger holes. Its distribution within the sedimentary succession however, appears somewhat random.

Magnesian calcite is mainly confined to the persistent layer located from 2 cm to 8 cm below the surface of both the algal flat and salt-encrusted zone. In this layer, which has a thickness of only a few centimetres, it is fine grained to micritic and infills desiccation fractures as well as the interstices between siltsize quartz and feldspar grains. It has also been found lower in the sequence as a cement in small fragments and nodules that probably represent remnants of an earlier formed layer.

As shown in Table 2, the composition of the magnesian calcite is quite variable with some samples tending to approach the Mg/Na mole ratio of dolomite, and this is borne out by the X-ray diffraction data. The 10.4 spacing, which is the only reflection observed on the X-ray chart, is generally very broad and lies between 2.90 Å and 2.99 Å (cf. the 10.4 spacing for dolomite at 2.886 Å and for calcite at 3.035 Å — Graf, 1961). Nevertheless, for some samples two or more maxima are evident within this range (Fig. 6) and where the mineral is richer in the CaCO₃ molecule, the peak appears less diffuse and is located closer to the 10.4 spacing of calcite. Heating the mineral at 250°C for 90 hours failed to produce detectable change to either the form or position of the reflectance.

The differential thermal curve (Fig. 7) for a sample of the carbonate layer has a sharp endothermic peak at 860°C, which is approximately midway between the two endothermic peaks registered by dolomite. The broad exothermic peak between 200°C and 600°C is attributed to oxidation of organic matter and that commencing a little before 900°C is probably due to reaction of the carbonate mineral with quartz and possibly also kaolinite.

ORIGIN OF THE MAGNESIAN CALCITE

From the chemical, X-ray and differential thermal data it is apparent that the carbonate mineral encountered in the sediments of the algal flat and the salt-encrusted zone is a highly disordered, solid solution of calcite and dolomite and that the composition is within the range assigned to high magnesian calcite (Friedman, 1964). It differs from dolomite not only in composition and lack of ordering but also, by the fact that it is a metastable phase and in time will invert through depletion of magnesium ions, to low magnesian calcite (Chave, 1952). Considering the high rainfall of the delta this inversion should proceed rapidly and hence, the mineral is of very recent origin and is probably still forming in the algal flat sediments.

The mechanism whereby Ca²⁺ and Mg²⁺ have been and apparently are being concentrated in the pore water to the point of precipitation however, seems far from clear and indeed, is linked to the "dolomite problem" (Krauskopf, 1967), one of the
remaining unsolved mysteries in sedimentary geochemistry. Although dolomite and high magnesian calcite have been observed forming in a range of environments including the arid sabkhas of the Persian Gulf (Illing et al., 1965; Butler, 1969), the semi arid Coorong of South Australia (Alderman & Skinner, 1957; Skinner, 1963) and the intertidal and supratidal zones of the humid Bahamas (Shinn et al., 1965), Bermuda (Friedman, 1964) and Bonaire (Deffeyes et al., 1965), they have not been synthesised at ambient temperatures when left in contact with the precipitating solutions (Glover & Sippel, 1967). Consequently, there has been much speculation on the origin of these minerals.

In the more arid areas of dolomite and high magnesian calcite development, gypsum is frequently present and this association has led to the concept that these minerals form through evaporative processes. As evaporation of the pore waters intensifies, gypsum precipitates and the brines, correspondingly enriched in magnesium relative to calcium, permeate and react with detrital aragonite and calcite fragments converting them to either high magnesian calcite or dolomite (Adams & Rhodes, 1960; Illing et al., 1965; Shinn et al., 1965). But, to invoke this mechanism for the formation of the high magnesian calcite at Macquarie Rivulet delta would introduce difficulties since neither gypsum nor carbonate detritus including shell fragments, has been encountered within the sedimentary sequence.

The aspects that seem most pertinent to discussion of the origin of the carbonate layer at Macquarie Rivulet delta are the association of the layer with algal mats or remnants of such mats, and the prevalence of CO₂ in the underlying sediments. Perhaps to these should be added the fact that CO₂ constitutes the principal, if not the sole, source of carbon for the blue-green algae (Smith, 1973). Since normal sea water is at least saturated and possibly supersaturated, with respect to CaCO₃ (Krauskopf, 1967), precipitation should ensue if the concentration of Ca²⁺ were increased or, alternatively, the partial pressure of CO₂ above the water table were reduced. The concentration of Ca²⁺ in the groundwater associated with the carbonate layer tends to be a little greater than that of sea water but precipitation is inhibited by the release of CO₂ from the decaying organic matter. Nevertheless, it is possible that at times of active mat growth, assimilation and hence, reduction in the partial pressure of carbon dioxide, or even the direct uptake of bicarbonate ions, by the algae is sufficient to promote local precipitation of carbonates.

![Fig. 6. Part of the X-ray diffraction trace of a sample of the magnesian calcite. M-C = magnesian calcite; F = feldspar; Q = quartz and K = kaolinite.](image1)

![Fig. 7. Differential thermal curve for a sample of the magnesian calcite layer.](image2)
Alternatively, since the algal mats contain both Ca$^+$ and Mg$^+$ (Table 2), the high magnesium calcite may have been derived directly from the mats. Pertinent in this respect, Gebelein and Hoffman (quoted by Golubic, 1973) found that sheaths of blue-green algae are capable of accumulating Mg$^+$ in concentrations up to 5 times that of sea water while Monty (1967), from a study of magnesium calcites at Andros Island in the Bahamas, concluded that the mineral is mostly precipitated within blue-green algal mats. These views also accord with those expressed earlier by Chave (1952) that solid solutions of calcite and dolomite can arise only through deposition from organisms and that "inorganically precipitated calcites almost invariably show less than 2 per cent MgCO$_3$". The principal difficulty with this concept in accounting for the origin of the magnesium calcite at Macquarie Rivulet delta, however seems to be the distance separating the carbonate layer from the algal mats for if the layer were derived from the algae, a more intimate association would be expected.

Nevertheless, irrespective of the actual mechanism of formation of the high magnesium calcite at Macquarie Rivulet delta, it is apparent that neither an arid climate nor the presence of calcite and aragonite detritus was an essential prerequisite.

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