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Modern and Holocene carbonate sedimentology of two saline volcanic maar lakes, southern Australia

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ABSTRACT

The Basin Lakes are two adjacent maar lakes located in the centre of the Western Volcanic Plains District of Victoria, Australia. Both lakes are saline and alkaline; West Basin Lake is meromictic whereas East Basin is a warm monomictic lake. The carbonate mineral suite of the modern offshore bottom sediments of these Basins consists mainly of dolomite and calcite, with smaller amounts of hydromagnesite and magnesite in West Basin and monohydrocalcite in East Basin. The dolomite, hydromagnesite, magnesite, and monohydrocalcite are endogenic in origin, being derived by primary inorganic precipitation within the water columns of the lakes or at the sediment–water interface. The calcite is biologically precipitated as ostracod valves.

In addition to the carbonates in the modern offshore (deep-water) sediments, the lakes also contain a girdle of nearshore carbonate hardgrounds. Both beachrock and microbialites (algal boundstones) are present. These modern lithified carbonate units exhibit a wide range of depositional and diagenetic fabrics, morphologies and compositions. In West Basin, the hardgrounds are composed mainly of dolomite, hydromagnesite, and magnesite, whereas dolomite and monohydrocalcite dominate the East Basin sediments. Aragonite, high-Mg calcite, kutnahorite, siderite, and protohydromagnesite also occur in these lithified carbonate units.

Stratigraphic variations in the carbonate mineralogy of the Holocene sediment record in the lakes were used to help decipher the palaeochemistry and palaeohydrology of the Basins. These changes, in conjunction with fluctuations in organic remains and fossil content, indicate a pattern of lake level histories similar to that deciphered from other maar lakes in western Victoria.

INTRODUCTION

Australia has more of its area in closed (endorheic) drainage than any other continent. Over 60% of mainland Australia has annual precipitation of less than 400 mm, with nearly one-third of the continent receiving less than 250 mm rainfall. Because of this predominance of arid to semi-arid climates and the abundance of closed drainage basins, Australia has a large number of saline lakes. As summarized by De Deckker (1982a, 1988), there is a considerable range of saline lake types, including large and small playas, volcanic crater basins, and coastal salt lakes.

Although endogenic and authigenic carbonate minerals are common components in the sediments of many modern salt lakes elsewhere (e.g. Müller, Irion & Förstner, 1972; Hardie, Smoot & Eugster, 1978; Dean & Fouch, 1983; Eugster & Kelts, 1987), there is a surprising paucity of carbonates in most of the Australian salt lakes. Exceptions to this are the well-studied coastal salinas of the Coorong and Spencer Gulf regions of South Australia (e.g. Von der Borch, 1976; De Deckker, Bauld & Burne, 1982; Warren, 1982, 1989; Rosen *et al.*, 1989), and the salt lakes of the volcanic plains region of western Victoria (e.g. Bowler, 1970, 1981; De Deckker & Last, 1988). This study focuses on the modern and Holocene carbonate sediments of two volcanic maar lakes in western Victoria, Australia: East Basin Lake and West Basin Lake. The objectives of the paper are to: (a) describe the occurrence and genesis of the carbonate components in the modern sediment of the two lakes, and (b) examine the fluctuations in carbonate mineralogy with depth in the Holocene sedimentary sequences found in these basins.

METHODS

Approximately 50 m of sediment core was collected from nine offshore sites in the two basins during October and November 1986. Coring was done using a Mackereth-style pneumatic corer (Mackereth, 1958). These long cores (up to 6 m in length) were supplemented by shorter (1 m) cores and samples collected from both offshore and nearshore locations using a modified Livingstone piston corer (Cushing & Wright, 1965) and by hand augering. Grab samples of the surficial sediment and shallow subsurface sediment (0·1–0·5 m depth) were collected from the shoreline and nearshore areas of the basins during the period 1986–1988. Soil samples were collected from the margins of the lake and from the steeply sloping walls of the crater basins. The water levels, brine chemistries, and various environmental data of the basins have been monitored since 1986. Water samples were collected from the lakes using a 1-l Kemmerer sampling bottle.

After extrusion, logging, and subsampling, the sediment cores were analysed for bulk mineralogy, clay mineralogy, and detailed carbonate mineralogy by X-ray diffraction (XRD). Mineral identification was aided by the use of an automated search–match computer program (Marquart, 1986). The percentages of the various minerals were estimated from the diffractograms using a method modified after Schultz (1964; see Last, 1980). Replicate analyses using this technique suggest that the precision of any individual mineral determination is about $\pm 8\%$. The core subsamples were also analysed for grain size and organic content. Grain size analysis was done using an automated X-ray particle size analyser (SEDIGRAPH); organic matter content was measured by calibrated loss on ignition. Non-stoichiometry of the dolomite and calcite was determined by measuring the displacement of the d_{104} X-ray peak (Goldsmith & Graf, 1958). The degree of ordering of the dolomite was quantified by evaluating the ratio of the intensity of the d_{015} ordering peak to the d_{110} non-ordering peak (Supko, Stoffers & Coplen, 1974). Because most of the nearshore and shoreline samples were lithified, or at least weakly cemented, standard petrographic thin-section examination was also undertaken in addition to the XRD analyses described above.

Standard analytical techniques were used to determine the chemistry of the water samples. Temperature, pH, Eh, and carbonate alkalinity were measured in the field; cation and anion concentrations were determined in the laboratory by atomic absorption, gravimetric, and turbidimetric methods. The molalities and activities of the chemical species in the brines and the saturation state of the waters with respect to a variety of mineral components were calculated using WATEQF (Rollins, 1989). Selected samples were also studied using scanning electron microscopy (SEM) and energy-dispersive analysis (EDAX).

SETTING

East Basin and West Basin lakes are located in the Western District Plains of Victoria, approximately 150 km west of Melbourne (Fig. 1). The Western Victorian Plains physiographic region is a large (40 000 km^2) area of Quaternary volcanics of mainly olivine tholeiite and alkali olivine basalt. There are a large number of small cones and eruption centres in the area, many of which contain lakes. The volcanics are mainly underlain by Tertiary and Mesozoic marine sediments. Thin, black, stony chernozem soils have developed on the basalt flows, while the soils developed from tuff and scoria are brown to red and coarse grained. Because the area is intensely cultivated and there is some concern about soil salination, a considerable effort has been placed recently on documenting the regional groundwater characteristics (Gill, 1987). Regionally the three main aquifers are: (a) the Quaternary basalt, tuff, and scoria, (b) the upper Tertiary limestone, and (c) the Upper Cretaceous–lower Tertiary quartzose sandstone (Land Conservation Council Victoria (LCCV), 1976). The groundwater salinity ranges from less than 500 mg l^{-1} to greater than 3000 mg l^{-1} total dissolved solids (TDS) (Lawrence, 1982) and is strongly Na–Cl dominated. Although the detailed groundwater flow and hydrochemistry in the immediate vicinity of the Basin Lakes is not yet known, the two lakes are, at present, considered to be hydrologically as well as topographically closed basins with little contact with the regional groundwater aquifers. De Deckker, Kershaw & Williams (1988) view the lakes as large palaeoclimatic rain gauges.

The area experiences a warm subhumid climate, with an annual rainfall of about 700 mm (Lee, 1982)

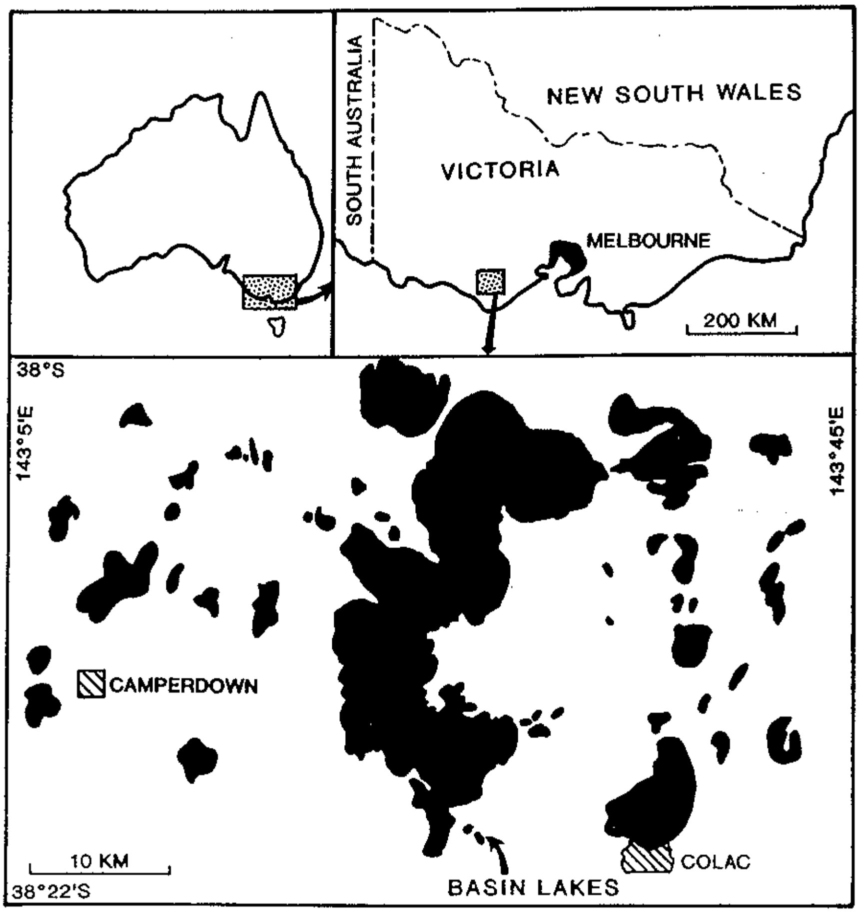

Fig. 1. Map showing the location of East and West Basin Lakes in southeastern Australia. Most of the many lakes in the region are saline. The largest lake, Lake Corangamite, is the largest permanent natural water body in Australia.

and mean annual temperature of 13°C (LCCV, 1976). Although evaporation rates are high (1200 mm yr^{-1}), the sheltered nature of the two maar basins, their conical shape, and the relatively high salinity of their brines would suggest that actual evaporative losses from the lakes are considerably less.

Because of the relatively young age of the volcanics and the low relief in the area, regional surface drainage is poorly developed and there are a large number of topographically closed basins. Although the limnology and hydrochemistry of many of the lakes occupying these closed basins have been well studied (see Williams, 1981, for summary), the sedimentological characteristics of the lakes are poorly documented.

The physical and chemical limnology of East Basin and West Basin lakes were originally reported by Timms (1972) and Timms & Brand (1973). In addition, Timms & Brand (1973) supplied data on modern zooplankton and benthos populations in the lakes. More recently, Hart & Davies (1981) investigated the trace metal content of East Basin Lake water.

The lakes are small, with surface areas of less than 1 km^2 and maximum depths of less than 15 m. The present-day water levels are approximately 40 m below the crest of the maar craters. Wave-cut scarps and ridges on the steep inner walls of the West Basin crater at about 2 and 4 m above the present water level indicate higher lake levels in the past. The bathymetric data presented by Timms & Brand (1973) show funnel-shaped morphologies for the basins, with average bottom slopes of about 3·6%. The catchment areas for the two basins are small: approximately 0·8 and 0·7 km^2 for East and West Basin, respectively. Neither lake has any permanent streams entering the basin nor is there any surface outflow. Timms & Brand (1973) indicate that between 1900 and 1960 East Basin

Lake was used as a disposal site for liquid wastes from a dairy located on the crest of the maar. Their data suggest that for the last decade of operation, this discharge would have been a major component of the hydrological budget of the lake. Diffuse groundwater discharge into the basins is evident in several areas along the shorelines. Although this inflow could not be quantified, it is most likely very shallow groundwater that originated from infiltration of rainfall into the porous scoriaceous sediment of the crater walls.

RESULTS

Water chemistry

The water of both East and West Basin lakes is saline, alkaline, and strongly dominated by Na^+ and Cl^-. The surface water of East Basin has a slightly higher pH than that of West Basin (9·2 vs. 9·0) and is less saline. The ionic ratios of the two brines are both $Na \gg Mg > K > Ca$ and $Cl \gg HCO_3 > SO_4$. At the time of sampling (1986–1988), West Basin was meromictic with a chemocline at 4 m depth separating the somewhat less saline water of the mixolimnion (76 p.p.t. TDS) from the more saline and dense monimolimnion (88 p.p.t. TDS). Timms (1972) reported considerably higher salinities for the two water masses in West Basin Lake (87 and 130 p.p.t.) and a much deeper chemocline (10 m). The East Basin water column showed little chemical variability and was still very similar in terms of total salinity to that reported by Timms & Brand (1973). They indicated that East Basin is a warm monomictic lake. The lower water masses in both lakes (below 3·5 m in West Basin and 8 m in East Basin) are anoxic, and Eh values of −200 to −400 mV have been recorded. Table 1 summarizes the present-day water chemistry of the two lakes. Of particular interest are the high Mg/Ca molar ratios (60–170), the relatively low sulphate concentrations (0·003–0·01 M), and the high carbonate alkalinities (20–35 mmol l^{-1}) of the brines.

Although both basins show a slight decrease in pH with depth in the lake, the water columns are everywhere thermodynamically strongly supersaturated with respect to calcite, aragonite, dolomite, magnesite, and hydromagnesite, but are several orders of magnitude undersaturated with respect to gypsum, halite, and other 'evaporites' (Table 1). The speciation and degree of saturation do not change significantly even if the higher concentration data reported by Timms (1972) are used in the calculations. Similarly, if West Basin were to mix completely, thermodynamic calculations using WATEQF indicate that the water column would still exhibit supersaturation with respect to the carbonates and undersaturation with respect to sulphates and evaporites.

Modern sediment

The modern sedimentary facies in the two basins are broadly similar. Both lakes contain a nearshore carbonate and coarse-grained clastic sequence which grades basinward into fine-grained, highly organic-rich, carbonate clays. One of the most conspicuous modern sedimentary features of the two lakes is that the nearshore and shoreline carbonate/coarse clastic sediment is lithified. This girdle of carbonate hardgrounds and crusts can form laterally continuous platforms extending several tens of metres into the basins. The sediments in these hardground areas display a complex array of fabrics, textures, and compositions. However, away from the shallow water, nearshore zones, there is little variation in composition or texture of the modern sediment.

Offshore sediments

The modern (upper 20 mm) offshore bottom sediment of both East and West Basin lakes is mainly clayey silt and silty clay (mean grain size ranges from 6·2 to 8·1 ϕ) composed of generally subequal proportions of organic matter (35–45%) and inorganic material (55–65%). The sediment is soft and gelatinous with very high (90–97%) moisture contents. West Basin sediment is black coloured (1·5 Y 3/3, Munsell), while that of East Basin is greenish black (10 Y 3/2).

The inorganic fraction of the modern offshore sediment in each basin is roughly similar: mainly carbonate minerals, clay minerals, feldspars and quartz. Inorganic amorphous iron oxides and silica are also usually present but these were not quantified. Dolomite is the dominant carbonate mineral, comprising about 18 and 35% of the total mineral fraction in West and East Basin, respectively. About half of the dolomite in East Basin sediment is a poorly ordered and calcium-rich species—'protodolomite'—with an average of 10 mol% excess Ca. The remaining dolomite in East Basin and all of the dolomite in West Basin sediment is poorly ordered but close to stoichiometric composition. Examination of the dolomite by SEM shows no differences in morphology, size, or fabric of the two types: the $CaMg(CO_3)_2$ appears to be uniformly anhedral, very fine grained (less than

Table 1. The water chemistry of East and West Basin Lakes.

	East Basin	West Basin	
		Mixolimnion	Monimolimnion
Ionic concentration (mmol l^{-1})*			
Ca^{2+}	0·8 (0·7–0·9)	0·5 (0·4–0·5)	0·5 (0·4–0·5)
Mg^{2+}	49·4 (38·2–53·1)	53·7 (49·3–58·2)	60·7 (60·1–62·1)
Na^{+}	708·1 (691·6–703·3)	1119·3 (1104·8–1148·3)	1261·4 (1148·3–1374·5)
K^{+}	14·9 (13·8–15·6)	18·8 (18·4–19·2)	19·7 (18·9–19·7)
Cl^{-}	825·3 (761·6–843·4)	1274·1 (1241·1–1311·7)	1509·2 (1424·6–1607·9)
HCO_3^{-}	32·8 (29·8–36·4)	20·1 (20·1–20·2)	23·4 (22·4–26·1)
SO_4^{2-}	4·5 (3·3–6·0)	14·1 (13·9–14·3)	16·1 (15·3–16·3)
TDS (p.p.t.)	49·0 (48–51)	75·5 (75–76)	88·3 (85–92)
pH	9·15 (8·9–9·25)	9·0 (8·95–9·15)	8·9 (8·35–8·95)
Mg/Ca ratio	74 (59–81)	139 (128–149)	157 (139–170)
Mineral saturations [log(IAP/Ksp)]†			
Calcite	1·3 (1·1–1·3)	0·9 (0·8–0·9)	0·6 (0·5–0·7)
Aragonite	1·0 (0·9–1·2)	0·6 (0·5–0·6)	0·5 (0·4–0·6)
Dolomite	4·3 (4·1–4·6)	3·8 (3·8–3·9)	3·6 (3·2–3·7)
Magnesite	2·7 (2·6–2·9)	2·6 (2·6–2·7)	2·6 (2·5–2·6)
Hydromagnesite	4·1 (2·7–4·7)	8·6 (8·5–8·8)	7·6 (7·5–7·8)
Gypsum	−2·6 (−2·6 to −2·7)	−2·3 (−2·3 to −2·4)	−2·3 (−2·2 to −2·4)
Halite	−2·1 (−2·1 to −2·2)	−1·6 (−1·5 to −1·7)	−1·5 (−1·5 to −1·6)
Nesquehonite	−0·2 (−0·1 to −0·4)	−0·4 (−0·3 to −0·4)	−0·5 (−0·4 to −0·7)
Mirabilite	−2·5 (−2·4 to −2·6)	−1·6 (−1·5 to −1·7)	−1·4 (−1·4 to −1·5)

*Mean with range in parentheses.

†A positive value indicates oversaturation, a negative value indicates undersaturation with respect to the particular mineral.

5 μm), and homogeneously disseminated throughout the sediment. There is no evidence of replacement fabrics nor does the dolomite appear to be associated specifically with other carbonate phases. Calcite and small amounts of hydromagnesite [$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$], and magnesite ($MgCO_3$) are also present in West Basin, while East Basin sediment also contains calcite and monohydrocalcite ($CaCO_3 \cdot H_2O$). All of the calcite in the modern offshore sediment of both basins is low-Mg calcite.

Shoreline/nearshore sediments

The modern sediments in the nearshore and shoreline areas of the Basin Lakes range from unconsolidated sand and gravel to well-indurated limestone and dolostone. The degree of lithification, the siliciclastic-to-carbonate ratio, and the specific mineralogical composition of these shoreline sediments are highly variable in the basins.

In general, the unconsolidated shoreline/nearshore material is relatively coarse grained (medium–coarse sand to sandy gravel; mean grain size ranges from 2·4 to − 1·1 ϕ) and dominated by quartz, feldspar, olivine, pyroxene, amphibole, and volcanic rock fragments. However, both basins also contain isolated shoreline areas of unconsolidated coarse clastic sediment rich in carbonate fragments. In addition to this dominantly coarse-grained material, small areas of the nearshore zones in both basins have finer grained (clayey silt to silty sand) sediment. This finer grained material is soft with high moisture contents and is often associated with rooted vegetation. In East Basin, several of these muddy shoreline sections are juxtaposed to areas of obvious (but diffuse) groundwater discharge. Spatially, about one-third of the West Basin shoreline and 40% of East Basin is characterized by this unconsolidated, coarse–fine siliciclastic and/or carbonate clastic material in which little or no lithification has occurred.

As shown in Fig. 2, large areas of the perimeters of both basins are made up of sediments which are at least partially indurated. Although these sediments exhibit a considerable range of fabrics, morphologies, and compositions, they all show evidence of relatively recent carbonate mineral precipitation and sedimentation. Radio-carbon dating of these strandline carbonates confirms an essentially modern genesis (^{14}C ages of 150–1430 yr BP), as does the fact that bottles,

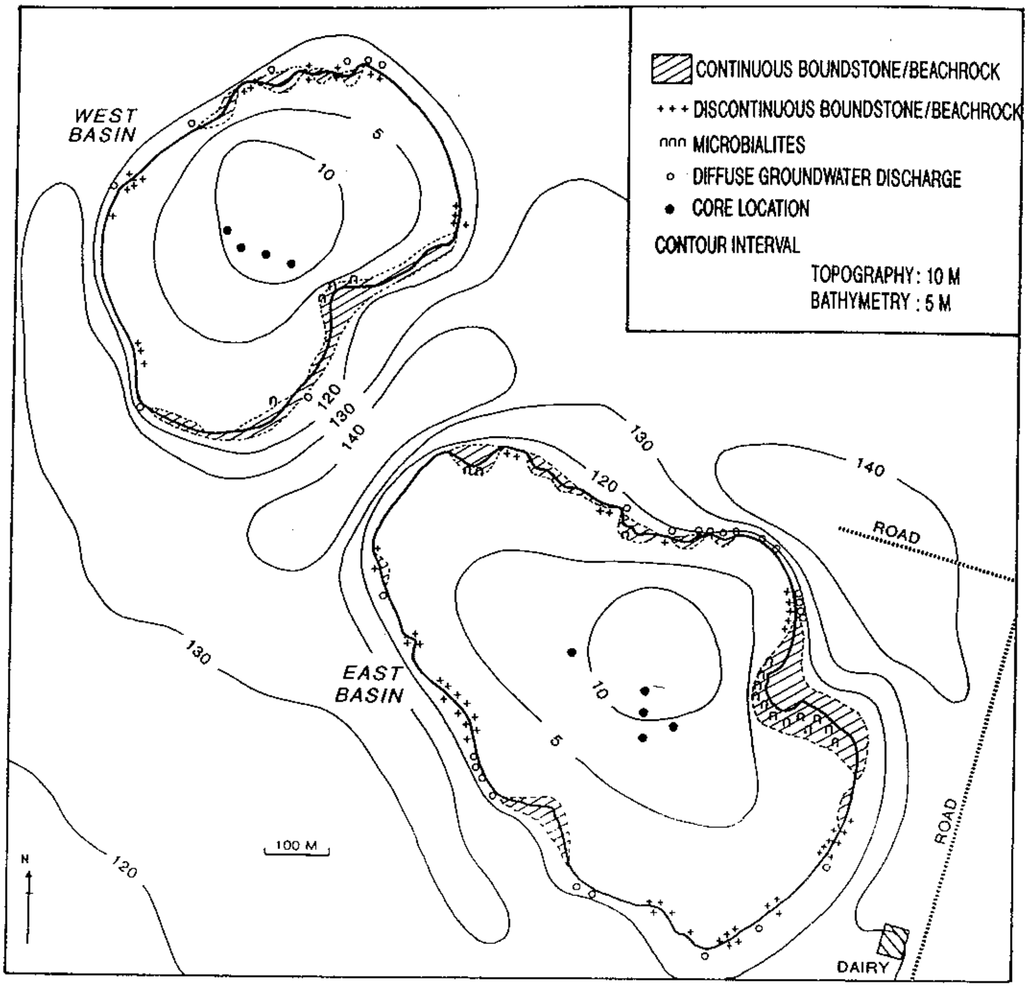

Fig. 2. Map showing the bathymetry of East and West Basin Lakes, the general topography of the area, and the distribution and nature of the shoreline and nearshore sediments in the two lakes.

cans, and other obvious anthropogenic debris are included in the hardgrounds and crusts.

The thickness of the lithified carbonate units varies from about 50 mm to greater than 1·5 m. In places, the hardgrounds can extend basinward into water depths of 2–3 m, but normally the lithified material grades into unconsolidated, poorly sorted, gravelly sandy silts and silty clays in less than 2 m water depth. In East Basin Lake, the lithified crusts form several broad, coalescing platforms which can extend nearly 50 m from the shoreline. These lithified platforms most likely formed subaqueously as a result of mixing of lake water with shallow groundwater. During periods of seasonally low water levels, these platforms are exposed showing that the near-horizontal hard-ground pavements are brecciated and disrupted by cross-cutting cracks and joints. The resulting carbonate fragments range from small polygonal clasts and plates 50–200 mm in diameter (Fig. 3) to large slabs several metres in diameter. Some of the plates and slabs are tilted and upturned, but classic tepee structures, such as those common in the crusts of sea-margin saline lakes in South Australia (e.g. Muir, Lock & Von der Borch, 1980; Warren, 1982; Ferguson, Burne & Chambers, 1982), are rare.

The non-siliciclastic material making up the carbonate fringes in West Basin is composed of mainly dolomite, hydromagnesite, and magnesite, whereas in East Basin dolomite and monohydrocalcite predominate. In detail, however, the composition of individual

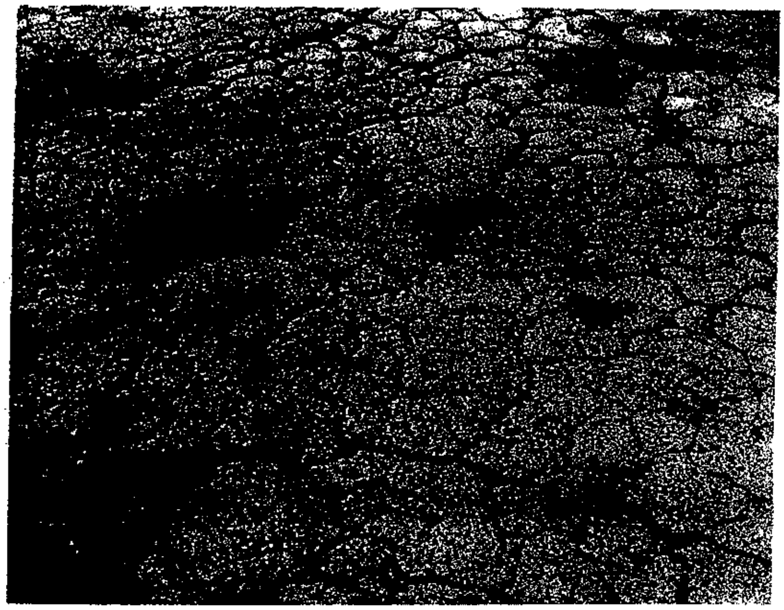

Fig. 3. Typical boundstone pavement exposed along the eastern shoreline in East Basin Lake (geological hammer for scale).

samples can be much more complex. Kutnahorite [$CaMn(CO_3)_2$], siderite ($FeCO_3$), protohydromagnesite ($MgCO_3 \cdot 2H_2O$), and aragonite have all been identified as major carbonate mineral components in some of the crusts in West Basin Lake; the hardgrounds in East Basin also contain hydromagnesite and aragonite. While few generalizations can be made regarding the specific carbonate mineralogy of the crusts and hardgrounds in the two basins, subaqueous samples (i.e. those collected below present-day water levels) have the most complex carbonate mineral assemblages, whereas the samples collected from subaerially exposed locations along the shorelines usually have only one or two carbonates present as a result of subaerial diagenetic processes altering the metastable assemblage upon exposure.

Two different types of carbonate hardgrounds can be easily recognized in the modern shoreline sediments of the basins on the basis of morphology and geographical occurrence: (a) beachrock, and (b) algal boundstone. These basic types are summarized below. The detailed petrography and composition of the sediments will be presented elsewhere.

Beachrock. Although the term beachrock is normally used in reference to clastic marine intertidal sediments that have been cemented by aragonite or high-Mg calcite (Friedman & Sanders, 1978), much of the indurated sediment in the lake-margin areas of the basins exhibits gross petrographical and morphological features similar to classic marine beachrocks.

The particles comprising the beachrock are similar to that of nearby unconsolidated sediment: mainly coarse-grained volcanic rock fragments, quartz, and feldspars, although gravel and cobble-sized carbonate (dolomite) clasts and smaller bioclastic carbonate (calcite and aragonite) shell debris can also be found cemented into discrete units (Fig. 4). Several sites in West Basin Lake contain beachrock composed mainly of pisoliths, while East Basin also has ooid grainstones. Re-cementation of previously lithified and fragmented crusts to form intraclast breccias is a common occurrence in both basins.

The degree of cementation varies from poorly consolidated, friable sands that can be easily crushed by hand to very hard, completely cemented rock. Texturally, the sediment includes mainly grainstones, packstones, and wackestones, with only minor occurrences of mudstone.

The lithified units often display a basinward dip approximately equal to the slope of the adjacent unconsolidated foreshore sediments. In West Basin, which contains the thickest sequence of indurated material, the dipping beds are emphasized by vertical variations in the degree of cementation and, hence, the resistance of the section to wave erosion. Bedding

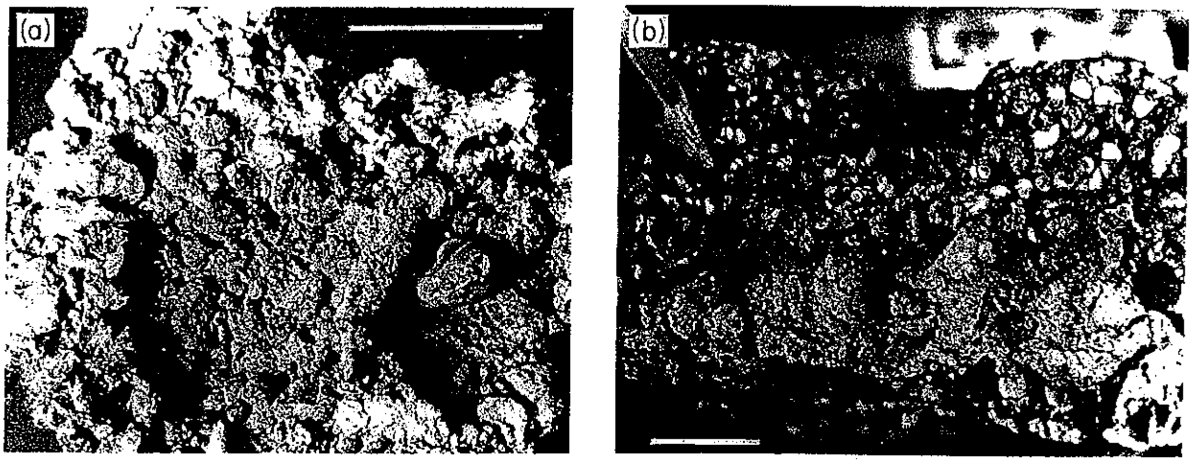

Fig. 4. Modern beachrock from East Basin Lake. (a) This sample is composed mainly of coarse-grained volcanic rock fragments cemented by dolomite; scale bar = 50 mm. (b) This sample is composed mainly of bioclastic debris (gastropod shells) in the upper part and sandy siliciclastic material in the lower part, all cemented by dolomite; scale bar = 20 mm.

planes commonly contain preserved mudcracks and rip-up clasts.

The total carbonate content of these lithified units varies greatly, from less than 20% to nearly 95%. The cements are mainly dolomite with minor magnesite, hydromagnesite, kutnahorite, and siderite in West Basin, and dolomite and monohydrocalcite in East Basin. The dolomite in both basins is anhedral, very fine grained, and slightly Ca-rich (50–54 mol% $CaCO_3$). There is no evidence of replacement fabrics or recrystallization; dolomite is commonly found cementing aragonitic *Coxiella* (gastropod) shells and calcitic ostracod valves. Although, in general, cementation has produced a dense, non-porous rock, some of the lithified sediment shows a very porous texture, with large fenestral to cavernous voids up to several centimetres in size. Multiple phases of carbonate mineral precipitation are evident in the roofs and floors of these cavities.

Algal boundstone. The term algal boundstone [illegible]

[illegible] activity. Algal boundstone here is synonomous with 'microbial lithoherm' and 'microbialite' as defined by Burne & Moore (1987). Mounds, domes, and ridges [illegible]

[illegible]

along the northern edge of East Basin Lake. Here the algal boundstone buildups give the floor of the lake an undulating, hummocky morphology, with relief as much as 0·75 m over short distances. Similar structures occur on the east side of West Basin Lake, but these have not yet been investigated.

The mounds and domes in both basins are well lithified throughout and, because of the normally poor visibility of the water, can only be investigated by laborious hammering and prying of the structures from the floor of the lake. None are subaerially exposed. The algal boundstones range in size from small (10–20 mm diameter), thin, delicate tufa pinnacles to larger, more robust, oval to circular mounds. Typical examples excavated from East Basin are rounded, ovoid, non-lobate heads 0·5–0·75 m in diameter and 0·2–0·4 m high (Fig. 5a). Whether these larger mounds represent coalescing of smaller algal structures into one large feature, or whether they are [illegible] algal heads is not known.

Similar to modern non-marine algal [illegible]

[illegible] exhibited by the algal boundstones in the Basin lakes are quite variable. Non-laminated, clotted textures are most common (i.e. the thrombolitic structures of [illegible]

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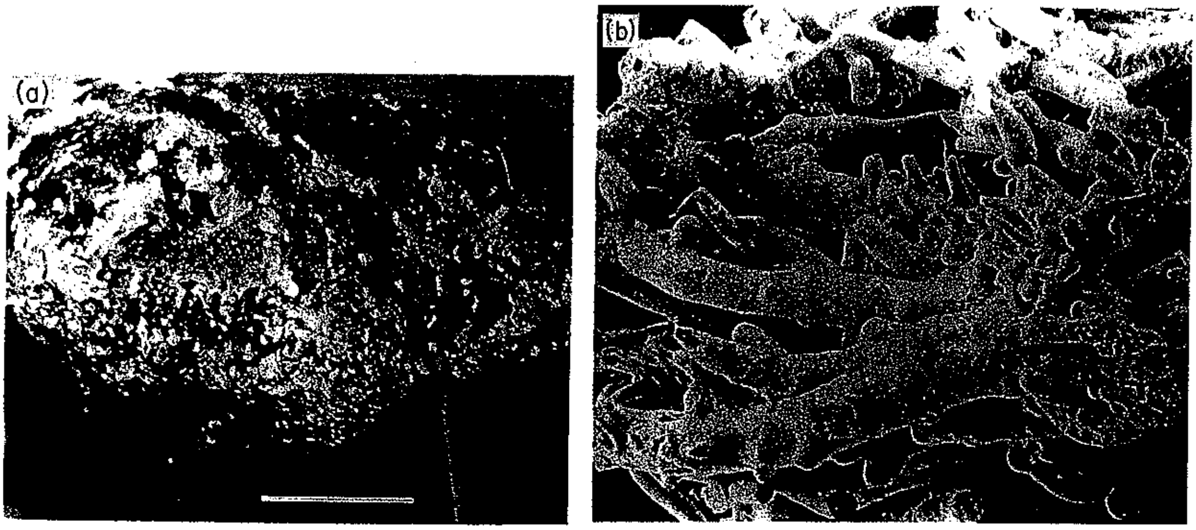

Fig. 5. (a) Modern algal boundstone (microbialite) collected from approximately 1 m water depth in East Basin Lake; scale bar = 80 mm. (b) Scanning electron photomicrograph of the surface of modern algal boundstone from East Basin Lake (width of micrograph = 3 mm).

up to several centimetres thick. This algae is firmly attached to the substrate. Beneath this is a thin (5–10 mm), white carbonate layer composed of micritic monohydrocalcite in East Basin samples and hydromagnesite in West Basin. The surface of this carbonate layer is not smooth but has considerable relief with small (10–20 mm deep) pits and cavities. This surface carbonate is friable to weakly cemented relative to the underlying internal sediment and easily flakes off upon collection. It consists mainly of algal filament moulds and casts with minor amounts of organic and inorganic debris (Fig. 5b). The internal sediment of the algal boundstone generally exhibits an indistinctly pelloidal to well-defined clotted/grumous texture. It is composed mainly of micritic dolomite with minor amounts of monohydrocalcite or hydromagnesite and siliciclastic material.

Stratigraphic changes in carbonate parameters

The offshore Holocene stratigraphic records recovered from the two Basin Lakes each consist of approximately 5–6 m of mainly fine-grained, organic-rich, laminated silty clay and clayey silt. Similar to the modern sediments in the lakes, the pre-modern deposits are composed of varying amounts of carbonate minerals, organic matter, and siliciclastics. However, the stratigraphic character differs between the two lakes in spite of their close proximity, similar overall morphologies, and identical origin. Last & De Deckker (1987a,b) subdivided the recovered sections into a series of lithostratigraphic units. West Basin Lake shows a change from a firm, relatively coarse-grained, dolomitic mud with low moisture content and abundant fecal pellets (Unit 1 in Fig. 6) at the base of the section upward into a finely laminated, aragonitic, silty clay (Unit 2) which, in turn, is overlain by a 3-m-thick unit composed of indistinctly bedded dolomite-rich clay that also contains magnesite (Unit 3). The dolomite content in this unit increases upward and shows a gradation from Mg-rich at the base to Ca-rich at the top. Finally, at the top of the section, the sediment consists of very finely laminated and rhythmically bedded silty clay (Unit 4). The sequence from East Basin is, overall, less distinctly laminated than that of West Basin. Three lithostratigraphic units are distinguished: a thick basal unit of black, non-bedded, pyritic clay with low total carbonate content (Unit 1) grades upward into a rhythmically colour-banded, dolomite-rich clay which contains magnesite (Unit 2), and finally, at the top of the section, a generally non-bedded, very organic-rich calcareous and dolomitic mud (Unit 3).

Except for the lowermost dolomitic clayey silt unit in West Basin, the total carbonate content in the Basins' sediments shows a general increase upward in

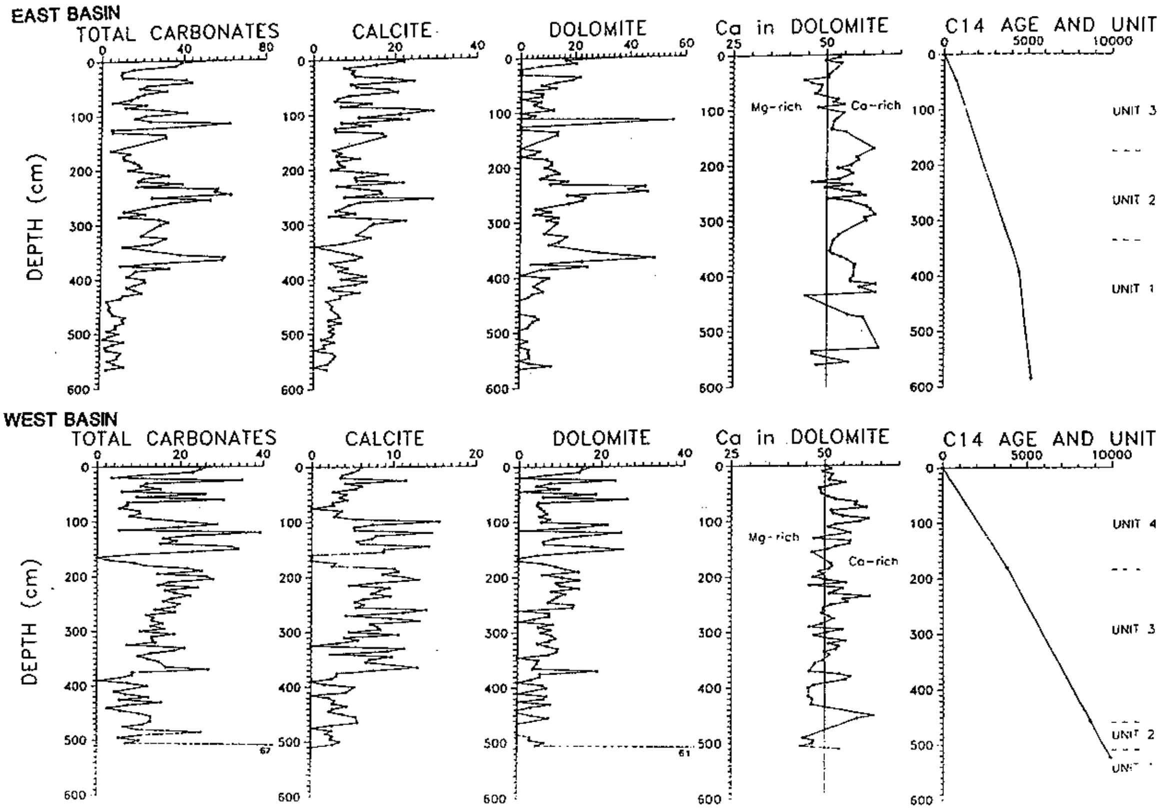

Fig. 6. Stratigraphic changes in carbonate mineralogy in representative cores of East and West Basin offshore sediment. Unit definition and radio-carbon dates are discussed in Last & De Deckker (1987a,b).

the sections, ranging from less than 10% to nearly 40% of the total inorganic fraction in West Basin cores and from about 5% to greater than 60% in East Basin. Because thin laminae composed almost entirely of carbonate minerals exist in each basin, the actual maximum percentage of carbonates approaches 100%. In each lake dolomite is the dominant carbonate mineral, comprising an average of about 15% in West Basin and 20% in East Basin. The next most abundant carbonate is calcite averaging about 8% in East Basin and 12% in West Basin sediment. Smaller amounts of magnesite and hydromagnesite occur in each section. The uppermost 1 m of sediment in East Basin also contains small amounts (less than 10%) of monohydrocalcite. As mentioned above, laminae composed of nearly pure aragonite are present in the lower part of the section in West Basin Lake. Siderite, kutnahorite, and protohydromagnesite, which are present in the modern surficial sediment, are not present in the pre-modern deposits. Stratigraphic changes in the carbonate mineral parameters from each basin are illustrated in Fig. 6. The time scale shown is based on radiocarbon dates presented in Last & De Deckker (1987a).

All of the dolomite that occurs in the offshore Holocene sediments of the Basins is non-stoichiometric and poorly ordered. Dolomite compositions in West Basin range from slightly Mg-rich $[Ca_{0.92}Mg_{1.08}(CO_3)_2]$ to Ca-rich $[Ca_{1.24}Mg_{0.76}(CO_3)_2]$. East Basin dolomite shows a similar range in compositions. The ordering is uniformly poor, with *R* values ranging from 0·03 to 0·5 (this ratio for well-crystallized, stoichiometric dolomite is generally between 0·8 and 0·9; Lumsden, 1988). The dolomite occurs mainly in two forms: (i) as micrometre-sized crystallites and amorphous aggregates of anhedral grains finely disseminated throughout the clay and organic-rich muds, and (ii) as very thin beds and millimetre-scale laminae composed of relatively pure carbonate material (Fig. 7). The greatest concentration of dolomite laminae occurs in the youngest lithostratigraphic units in the Basins. In these uppermost units, the brown to buff coloured dolomite-rich beds show

Fig. 7. Photomicrograph of a section of sediment core from West Basin Lake showing dolomite laminae (light) alternating with organic clays (dark). The sample is from Unit 4, 1·1 m below the sediment–water interface. Scale bar = 1 mm.

regular, rhythmic alteration with green, red, and black organic-rich, non-carbonate clays. Although most of the dolomitic laminae in the offshore sediments of the Basins are soft and non-cemented, the East Basin section also contains several thin but indurated dolomitic laminae (hardgrounds). The dolomite in these thin hardgrounds is indistinguishable from that of the non-indurated laminae.

Nearly all the calcite in the offshore Holocene sediment of both basins is low-Mg calcite. In the East Basin section, the amount of calcite shows a gradual increase in abundance upward from less than 5% at the base to an average of about 16% in the upper 3 m. A similar upward increase in calcite is present in West Basin cores, except values return to low levels in the upper 1 m of sediment. A small amount of high-Mg calcite (less than 5%) occurs in the lower stratigraphic unit in East Basin and in Units 2 and 3 in the West Basin section. The magnesium content of this calcite ranges from 14 to 20 mol% $MgCO_3$, but does not show any distinct stratigraphic trend.

DISCUSSION

Lacustrine carbonates often pose an interesting but somewhat difficult problem for sedimentologists attempting to interpret the origin of the minerals and to deduce the history of a stratigraphic sequence. As shown in numerous studies of modern and Quaternary lake deposits, the carbonate fraction of lacustrine sediments frequently represents a complex mixture of detrital material brought into the basin from the surrounding watershed and endogenic plus authigenic precipitates originating within either the water column or the sediment column itself. The proportion of allogenic versus endogenic versus authigenic carbonates in a lake or stratigraphic sequence depends on many factors, chief among which are drainage basin bedrock lithology, lake water and porewater chemistry, and the amount and type of organic productivity. Unfortunately, distinguishing these various genetic types is very difficult.

Of the three main genetic types of carbonates, the least important in East and West Basin lakes is detrital carbonate. Although other volcanic maars in the region have been reported to contain relatively large proportions of detrital carbonate grains (Bowler, 1970; Melbourne College of Advanced Education, 1984), presumably derived from Tertiary limestone bedrock, we found no evidence of this type of carbonate in the Basins' sediment. Similarly, soils in the small watersheds are devoid of carbonate minerals. However, 'detrital' (locally reworked) carbonates in the form of bioclastic debris can be an important component of the modern beachrock sediment in the Basins.

Both low-Mg calcite and aragonite originate from biogenically precipitated carbonate shell material. The calcite is derived from ostracods, especially the planktonic species of *Diacypris*, which can occur in large quantities in the water. As pointed out by De Deckker (1982b), the occurrence of extremely large numbers of ostracods (20–40 ml of ostracods collected in 1 l of water) is a common phenomenon in these and other lakes of the region with salinities between about 45 and 77 p.p.t.

Most of the carbonate phases in the modern offshore sediment of the two basins is interpreted to be endogenic in origin, being derived from inorganic precipitation within the water columns of the lakes. The role of primary organic productivity in triggering this inorganic carbonate precipitation may be important, but this cannot be quantitatively evaluated until photosynthetic rates are known for the two lakes.

The high Mg/Ca ratio of the water is responsible for the generation of dolomite and hydromagnesite as opposed to the more commonly occurring calcite or aragonite in many other lacustrine environments. This dolomite–magnesite mineral assemblage agrees well with that predicted from observational data in other lake systems as well as theoretical and experimental data (e.g. Usdowski, 1968; Braitsch, 1971; Müller *et al.*, 1972; Möller & Kubanek, 1976). Whether these Mg-bearing carbonates are the result of inorganic precipitation within the water columns (i.e. true endogenic precipitates) or originate as authigenic components at the sediment–water interface is not yet known. The presence of iron sulphides in the pre-modern sediments of the Basins suggests that microbial reduction of sulphate dissolved in porewaters may be instrumental in generating H_2S (or HS^-) and HCO_3^- according to: $2FeOOH + CH_2O + 3SO_4^{2-} \rightarrow 6HCO_3^- + FeS + FeS_2 + 4H_2O$. This increased alkalinity, in turn, would be conducive to authigenic precipitation of carbonate minerals in the pore space. Alternatively, methanogenic bacteria active at the sediment–water interface or in the anaerobic porewater can reduce carbon dioxide to create methane ($CO_2 + 8H \rightarrow CH_4 + 2H_2O$; Wetzel, 1975), thereby increasing the pH and enhancing carbonate mineral precipitation. Talbot & Kelts (1986) demonstrated that this CO_2 reduction/methanogenesis was responsible for early carbonate mineral diagenesis and calcite/dolomite precipitation at or very near the sediment–water interface in Lake Bosumtwi, Ghana, during parts of the Holocene and late Pleistocene. Sediment trap experiments are currently being undertaken in the Basin Lakes in order to determine the specific site of carbonate mineral generation in the offshore areas.

The genesis of the carbonate minerals making up the limestones and dolostones in the nearshore zones of the lakes is considerably more complex. The pore-filling morphology of the dolomitic cements of the boundstones and beachrock suggests precipitation from pore solutions. Similarly, the travertine-like coatings and crusts of dolomite, kutnahorite, magnesite, hydromagnesite, protohydromagnesite, siderite, and monohydrocalcite are most probably formed by primary precipitation from pore- or lake water. Once formed, however, these shoreline carbonates are subjected to rapid and extensive diagenesis that ranges from large- and small-scale physical deformation, breakage to dissolution and neomorphism. The fact that the internal sediments of the microbialites in both basins are entirely dolomite whereas the outermost, active (living) surfaces are composed of non-dolomitic carbonates suggests a diagenetic sequence from a primary, hydrated magnesium (or calcium) carbonate to a secondary, metastable calcium–magnesium carbonate. In West Basin sediments, the specific sequence is: hydromagnesite + protohydromagnesite → magnesite → dolomite; in East Basin this sequence appears to be: monohydrocalcite + hydromagnesite → magnesite → dolomite.

The question as to why monohydrocalcite is present in East Basin but absent in West Basin sediments remains largely unanswered. Although thermodynamic data suggest that this hydrated calcium carbonate should be a common precipitate from waters with high Mg/Ca ratios (Hull & Turnbull, 1973), it has only rarely been identified in natural environments (see summaries in Stoffers & Fischbeck, 1974; Taylor, 1975). This is presumably due to the mineral's instability in NaCl-rich solutions, which favour the rapid transformation of monohydrocalcite to aragonite (Marschner, 1969; Sonnenfeld, 1984). However, because both Basin lakes are dominated by Na–Cl brines, other mechanisms appear to be controlling $CaCO_3 \cdot H_2O$ precipitation. In each previously reported occurrence of lacustrine monohydrocalcite, the precipitating waters have been characterized by *moderate* Mg/Ca ratios and salinities. With an average Mg/Ca ratio of about 70 and salinity of 45 p.p.t. in the upper few metres, East Basin water more closely matches these previously reported conditions than does that of West Basin (Mg/Ca = 140; TDS = 76 p.p.t.).

Given the modern carbonate sedimentology described above, several comments are in order regarding the variation in carbonates in the Holocene stratigraphic sequences in the Basins as illustrated in Fig. 6. The fact that the type, abundance, and composition of the carbonate minerals change significantly with depth in the sedimentary fill in the basins indicates that limnological conditions have fluctuated considerably over the last 10 000 years. These variations in carbonate mineralogy, along with stratigraphic changes in other mineralogical, physical, and biological parameters, can be related to fluctuations in hydrology, water chemistry, organic productivity, watershed characteristics, and climate. The details of these interpretations are presented elsewhere (De Deckker *et al.*, 1987, 1988; Last & De Deckker, 1987a).

The abundance of carbonate minerals and the presence of laminae composed almost entirely of endogenic precipitates in the upper half of the East Basin section and in the entire West Basin section implies that the Basins maintained alkaline conditions at the sediment–water interface throughout much of their Holocene history. At the same time, however, the general increase in the amount of carbonates upward in cores from both basins indicates that the lakes experienced highest clastic sedimentation rates during early to mid-Holocene, after which decreased rates of supply of detrital material, probably due to formation of drainage basin soils and stabilization of the crater slopes, resulted in a higher proportion of chemical precipitates.

The oldest sediment recovered from the lakes, the basal, coarse-grained, dolomite-rich, clayey silt (Unit 1) from West Basin, was probably deposited in a relatively shallow-water, highly evaporitic lake, although there is nothing in the sediment to indicate complete drying and desiccation. The brine had a very high Mg/Ca ratio and carbonate precipitation was probably very rapid as suggested by the incorporation of excess magnesium into the dolomite lattice (see also Rosen *et al.*, 1989). The abundance of carbonate fecal pellets (probably produced by a brine shrimp such as *Parartimia*) and the absence of ostracods provides further evidence of a shallow-water, high-salinity lake environment. By about 9000 yr BP, a slightly improving climate gave rise to less evaporitic conditions and deeper water levels in West Basin. The relatively fine-grained sediment deposited in the offshore part of the basin at this time is characterized by irregularly spaced inorganic aragonite laminae alternating with organic clays that contain high-Mg calcite. The change from Mg-rich dolomite to aragonite (and high-Mg calcite) indicates a dramatic decrease in Mg/Ca ratios in the lake. This decrease was probably the result of a change in the hydrological budget of the lake: an increase in the amount (or proportion) of surface runoff would contribute more *low*-Mg/Ca water to the lake relative to the earlier dominance of groundwater influx (high-Mg/Ca water).

After 3000–4000 years of relatively humid climatic conditions, positive hydrological budgets, and high water levels, increased aridity in the region between about 5000 and 3000 yr BP initiated lower water levels and a return to more saline conditions in the lakes. In East Basin, this change is marked by an increase in total carbonate content due mainly to a dramatic increase in dolomite in the sediment at about 4500 yr BP. In the West Basin section, a similar increase in carbonate mineral content is present in the sediments deposited during the mid-Holocene. Although the dominance of Mg-dolomite and the presence of magnesite indicate a return to highly evaporitic conditions, rapid crystallization of the carbonate material, and very high Mg/Ca ratios in West Basin Lake, a gradual change to somewhat lower Mg/Ca ratios and probably less evaporitic conditions is indicated by the disappearance of magnesite and the shift toward Ca-enriched dolomite by about 2000 yr BP.

The most recent 2000-yr period of carbonate sedimentation in the two basins has not been significantly different from that of today. Both basins show a slight decrease in the amount of carbonates preserved in the younger sediment relative to that of the mid-Holocene. The dolomite in both basins shows an overall trend toward less calcium enrichment (i.e. more magnesium incorporation) upward in the most recent sediment suggesting increasing Mg/Ca ratios in the brines during the past 2000 yr. The dolomite–magnesite (+hydromagnesite) assemblage in West Basin points again toward elevated Mg/Ca ratios and probably higher salinities, whereas in East Basin the dolomite–monohydrocalcite assemblage may be consistent with more moderate ratios and salinities. This trend is reversed in the post-700 yr BP sediment in East Basin, indicating a decrease in the Mg/Ca ratio in this lake over the past several centuries. At about 1400 yr BP, conditions became suitable for the development of beachrock and boundstones in the near-shore areas of the basins, and shallow-water, shoreline carbonate sedimentation/cementation began. At present, the precise conditions responsible for initiation of these shoreline carbonate boundstone units are unknown.

SUMMARY AND CONCLUSIONS

Althouth the hydrochemistry and limnology of the saline lakes in the Western Plains District of Victoria, Australia, have been well studied for some time, there has been very little geolimnological work done on most of the basins. The lakes of this region are important from a sedimentological perspective because they offer an unusual opportunity to examine, in detail, the genesis and diagenesis of a wide variety of chemical precipitates. Our investigations of the carbonate sediments in two of these lakes have shown the following.

(1) A considerable range of endogenic and authigenic carbonates occur in these two small, adjacent volcanic maars. Because of the high Mg/Ca ratios in the brines of these lakes, the modern precipitates

are dominantly magnesium carbonates, consisting mainly of dolomite, magnesite, and hydromagnesite. Smaller amounts of kutnahorite, siderite, monohydrocalcite, aragonite, and protohydromagnesite also occur in the modern sediments of one basin or the other depending on the availability of source ions (i.e. Mn, Fe) on a local basis and on the specific Mg/Ca ratio of the precipitating brine.

(2) The carbonates in the modern offshore (deep-water) areas of the basins are most likely the result of inorganic precipitation within the overlying water column or within pore solutions at the sediment–water interface. High levels of organic productivity may be instrumental in creating supersaturated conditions with respect to the carbonates; alternatively, sulphate reduction and/or methanogenesis are equally viable processes. In either case, the carbonates in the offshore surficial sediments are interpreted to be 'primary' in origin. There is no evidence to suggest an early secondary (i.e. replacement) origin for the carbonates.

(3) The well-indurated carbonate hardgrounds in the margin areas of the basins are considerably more complex in terms of origin, with both primary precipitation of carbonates as cements and crusts and early diagenesis of these primary components operating to create a very active environment. The sedimentation and diagenesis of these shoreline carbonate boundstones began relatively recently in the history of the Basins and is continuing today.

(4) The record of Holocene carbonate sedimentation in the two Basins shows that dramatic fluctuations in Mg/Ca ratio, salinity, and water level have occurred in the lakes.

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