# CHAPTER FOUR

## REGIONAL ASPECTS OF DOLOMITE FORMATION

### INTRODUCTION

Recent dolomite is known from numerous locations, virtually from all over the world. Recent dolomite has been recognized in the marine as well as the non-marine environment. Special consideration should be given to the question in how far any of the dolomite, reported to be "Recent", really is of Holocene age. There is a marked tendency among geologists to accept only radiocarbon age readings as evidence. Since isotope techniques did not become available until the late fifties of the 20th century, most of the discoveries of Recent dolomite were made after that time. Because before 1950 only geological evidence could be used to determine the stratigraphic position of a certain occurrence of dolomite, one might tend to disregard the earlier work. But there can be no doubt concerning older descriptions of authigenic dolomite, in which geologists have interpreted stratigraphic relations in the field prior to 1950.[1]

It is almost certain, that not all of the occurrences of dolomite mentioned in this chapter will be found to consist entirely of Holocene deposits, when using detailed isotope studies. However it would be an unnecessary denial of much of the geologists' experience in field work, to exclude all those occurrences of dolomite, that have not yet been dated with the aid of radioactive isotopes.

The following listing of dolomite occurrences is not claimed to be complete, not even at its time of preparation. It should give the reader an impression of the worldwide distribution of Recent dolomites. At the same time the listing has the purpose of providing possible clues to solve the dolomite problem, even though the local paragenesis may seem quite complicated.

### AFGHANISTAN

Dolomite of Holocene age (radiocarbon measurements of 7300 ± 310 and 6725 ± 600 years) has been found by Förstner (1973) in the Dasht-i-Nawar seasonal lake, Afghanistan. The playa-lake situated south of Kabul shows distinct seasonal changes in for example size (between 7.5 and 52 km$^2$) in water depth (from 0.3 to 1.0 m) and especially in water chemistry. Considerable seasonal changes in the concentrations of $HCO_3^-$, $CO_3^{2-}$, $SO_4^{2-}$, $Mg^{2+}$, $Ca^{2+}$ and $Na^+$ were measured. The Mg/Ca ratio of the lake water showed an annual fluctuation from 5 to 100. Although the Dasht-i-Nawar does not support any plant growth, plant remains are being washed into the basin from agricultural areas bordering the salt lake.

AUSTRALIA


The description of dolomite occurring in Recent carbonate sediments in the southeast of South Australia by Sir Douglas Mawson (1929), formed the first of a long series of publications on this regional occurrence. The southeast of South Australia contains ranges of consolidated sand dunes with a NNW trend parallel to the present coastline (Alderman & Skinner, 1957). "The inter-dune areas are always more or less inundated with water in the winter months, which period is the rainy season ... Elsewhere, soon after the dry season commences, the swamp water sinks down ... or is evaporated": Mawson (1929, p.614). One of the largest dune ridges is the Younghusband Penninsula, separating the Coorong Lagoon from the open sea: "Thus the Coorong is a sea-water-filled depression between two dune ridges" (Mawson, 1929, p.613). South of the Coorong Lagoon a number of smaller lagoons and lakes exist. The drainage of the area is underground: rainwater disappears quickly into the sand dunes. The flat areas in between the dune ridges are relatively impervious: these flats will be flooded after periods of rain. Swamps or shallow lakes develop in the winter, but most of these are not permanent and in many cases complete desiccation takes place during the dry summer months. "The sediment from one of these intermittant lakes, situated 10 miles north of Kingston ... was found by Sir Douglas Mawson (1929) to consist largely of dolomite": Alderman & Skinner (1957, p.561). Not only the Kingston Lake is known to contain dolomite of Holocene age: Bonython (1956) described dolomite from Lake Eyre, 960 km north of Kingston, and Rogers et al. (1956) reported it from a soil near Tintinara, 96 km NNE of Kingston.

Having studied the area for an extended period, Alderman & Skinner (1957) were able to report on the occurrence of an annual cycle of events, taking place in the intermittent lakes such as Kingston Lake. At the end of the summer fine white sediment is found on the surface of Kingston Lake. During the winter months rain water will accumulate to a depth of 30 to 60 cm. Plants will start growing in this shallow water, and in November or December of each year the lake becomes turbid with fine white carbonate sediment. High evaporation rates during the summer increase the salinity, and by the end of the dry season only a crust of salt remains, forming a loose layer above the carbonate deposit (of calcite and dolomite). The salt crust will be blown away in later months of the year, therefore Mawson (1929) called this salt the "cyclical salt". Only there where the lake bottom is protected by trees from the wind (or by neighbouring sand hills) the salt crust remains throughout the year. Alderman & Skinner (1957) noted, that lake beds with much dolomite contained little or no salt, even though concentrations of $Na^+$ and $Cl^-$ of the water of the lake were high.

An annual cycle similar to that of the Kingston Lake was described by Alderman & Skinner (1957) to take place in the Coorong Lagoon. In the winter months the rainfall will raise the water level, but this will be lowered again during the dry summer months. However a second factor is involved in the dynamics of the Coorong Lagoon: the water masses of the River Murray. The vast volume of water from this river will block the outflow at the open end of the lagoon. When the outflow of the river is low, the level of the lagoon will be lowered too. These two factors interact not always in a synchronous way, but generally the water level in the lagoon is high during the wet winter months and will be markedly lower during the dry summer months. The lowering during the summer periodically exposes large areas near the southern end of the Coorong.

One of the most comprehensive accounts on the dolomite from the Coorong and its associated salt lakes is to be found in the paper by Skinner (1963). As described by Alderman & Skinner (1957) the salt lakes go through pronounced annual cycles, and carbonate precipitationtakes place twice a year at maximum. During spring and autumn the lakes become
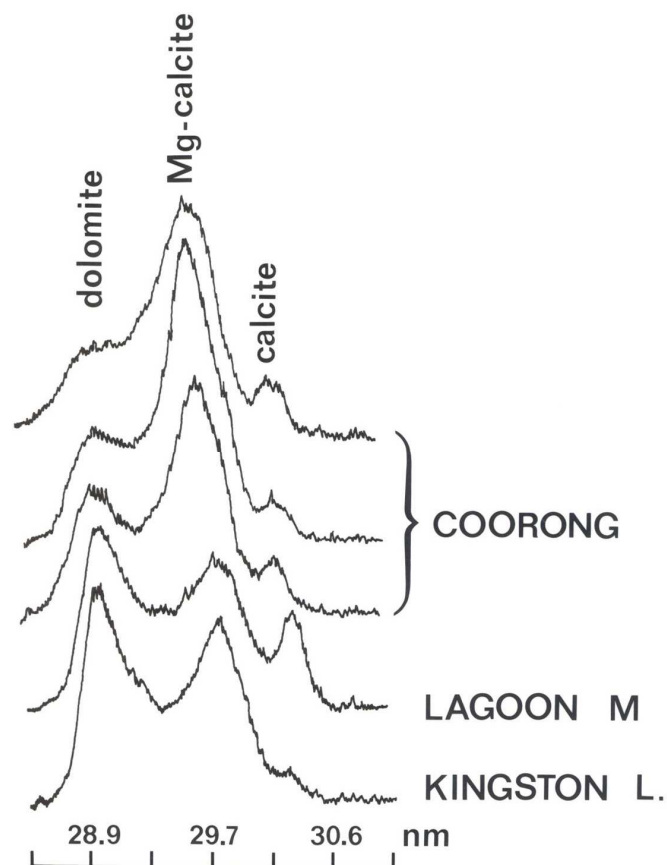
Fig.12 – X-Ray diffraction of Recent carbonates precipitating in Coorong Lagoon and two of its ephemeral lakes. Samples are arranged geographically from North to South (after Skinner, 1963).

**N.B. Here as in all subsequent X-ray diffractograms: abscissa = angle of X-ray beam to sample holder, and ordinate = relative intensity of diffracted X-rays.**
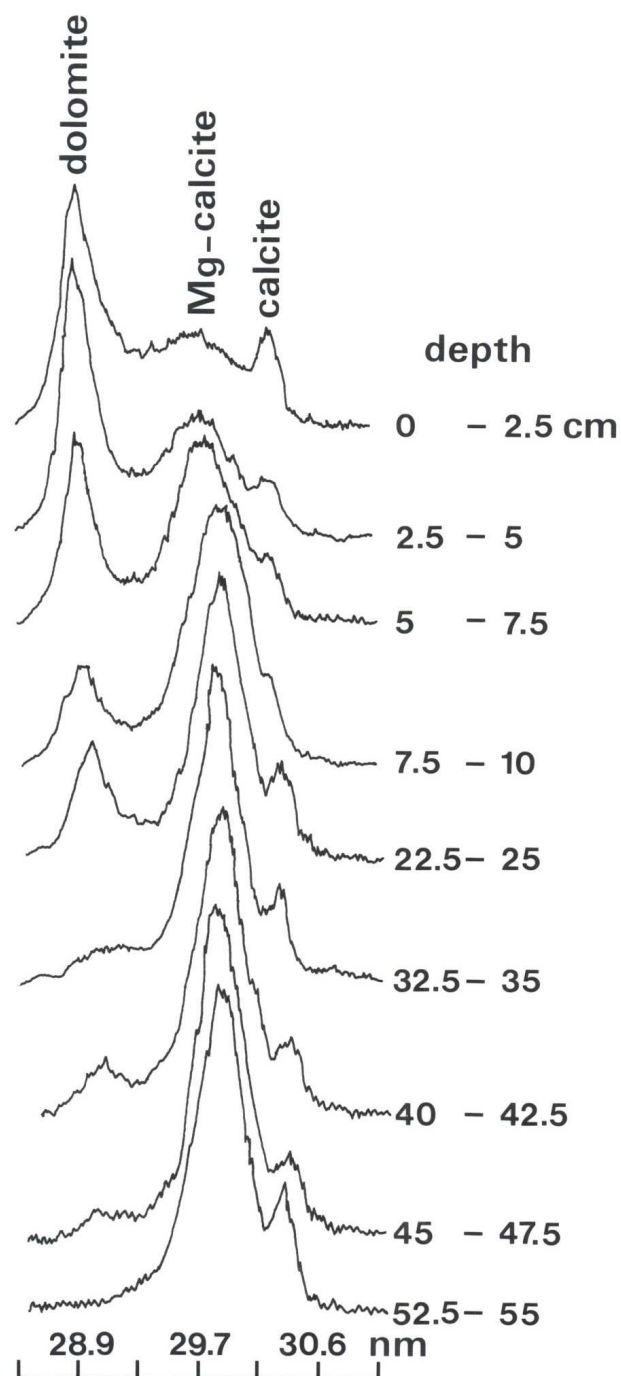
Fig.13 – X-Ray diffraction of carbonates found in core samples from the center of Lagoon M (after Skinner, 1963).

turbid with fine white sediment, which settles slowly to the bottom. The precipitate consists of magnesium calcite and dolomite. Prolonged desiccation leads to the formation of gypsum and halite. Individual crystallites of the carbonates range in size from 1 to about 20 micrometer (Skinner, 1963). The chemical composition of the magnesium calcites varies from that of pure calcite to a composition of $Ca_{77}Mg_{23}(CO_3)_{200}$ . Not only calcium-rich dolomite (with maximum 6 mol % $CaCO_3$ in excess) was found, but also the pure stoichiometric form of dolomite. Even the superstructure reflections typical of stoichiometric dolomite were observed by Skinner (1963) in X-ray diffraction.

Dolomite was always found associated with another carbonate ("In no case in this study was dolomite observed to be the only carbonate phase present": Skinner, 1963, p.453). The association between dolomite and magnesium calcite becomes especially clear, when arranging diagrams of the X-ray diffraction patterns of the carbonate samples in a sequence indicating their original geographical distribution. From Fig.12, where the samples were arranged from the north to the south, it is clear that as the amount of dolomite increases, the magnesium calcites become less magnesium-rich. But this change is not accompanied by a change in the chemical composition of the dolomite (which remains at $Ca_{56}Mg_{44}$). "The marked and consistent relation between calcite and dolomite implies that the dolomite is not secondary, and that it is not forming by the alteration of a precipitated magnesian calcite, but that it is a primary phase and is co-precipitating with a magnesian calcite directly from saline waters": Skinner (1963, p.459). Additional evidence was given by Skinner (1963), that dolomite is not forming in any secondary reaction: the distribution pattern of the dolomite in cores illustrates, that dolomite must be forming directly from solution. From an observed increase in the percentage dolomite with depth in a certain core one might be inclined to conclude, that secondary reactions would be involved in the formation of dolomite, apparently requiring long periods of time. The distribution pattern of dolomite found in the core from a drilling into Lagoon M sediments demonstrates the contrary: the dolomite disappears with depth and concomitantly the amount of magnesium calcite increases with depth (Fig.13).

The chemistry of the water of the salt lakes was summarized by Skinner (1963) with the observation, that this lake water has the same ionic proportions as that of normal sea water: salinities were found to vary seasonally from 16 ‰ to 189 ‰ ; the pH ranged from 8.4 to 9.2 . Almost all of these salt lakes go through an annual cycle of changes in salinity and pH; but one exception was found. The most northern station sampled (at Magrath Flat, in the Coorong Lagoon itself) did not contain any dolomite or magnesium calcite. At the same time the Coorong Lagoon at Magrath Flat is, according to Skinner (1963), "... not subject to the same periodic wet-dry cycle as the southern end of the Coorong and the lagoons" (Skinner, 1963, p.462).

The ephemeral lakes associated with the Coorong Lagoon go through an annual cycle of alternations between inundation and desiccation. As a direct result the salinity of these lakes fluctuates, as well as the Mg/Ca ratio of its water (Alderman, 1965). In addition the pH of the water varies from season to season, mainly as the result of the photosynthetic activity of plants in the shallow lakes. Abundant growth of water plants (e.g., *Ruppia maritima* Linn.) during the winter is responsible for an increase in pH to values as high as 10. In spring the pH values will be lowered again to values around 8 by the decline of plant growth (Alderman, 1965). Von der Borch et al. (1975) suggested that dolomite formation would be taking place at the base level of the seaward-flowing groundwater. This groundwater discharge is not a continuous process either. Von der Borch & Jones (1976) stated specifically, that dolomite was forming from ground water, which discharged seasonally into the sink zone near the coast. The samples of dolomite described by Von der Borch & Jones (1976) were taken from carbonates which had accumulated in the groundwater-fed, seasonally dry pans of the Coorong area. Although the Recent dolomite of the Coorong Lagoon seems to be correlated with annual changes between

wet and dry conditions, too much rain appears to inhibit the formation of the mineral. Von der Borch (1976, p.957) noted, that "... primary dolomite does not form in lakes in regions where rainfall is greater than 700 mm". In a publication devoted to the geological significance of the Coorong dolomites Von der Borch & Lock (1979) described, how a process of "flushing" acts in those areas, where Recent dolomite has been found. Chlorides and sulfates do precipitate in the seasonal lakes of south-east Australia, but no accumulation of these salts takes place into the dolomite-containing sediments ("... saline and sulphate evaporite minerals are conspicuous by their absence": Von der Borch & Lock, 1979, p.822). Concerning the mode of formation of modern dolomite in Lake Ormerod (an inland, ephemeral lake in the Coorong region) Von der Borch (1981, p.210) remarked, that "… it must have formed from seasonally discharging Ca and Mg bicarbonate groundwaters".

Dolomite not older than 17,000 years has been found by Draper & Jensen (1976) in the sediments of Lake Frome, a large playa (some 100 km long and 45 km wide) in the southeast of South Australia. Sub-recent dolomite has been reported from two cores taken at the margin of Lake MacFarlane (South Australia) by Förstner (1977), who also described a dolomite crust some decimeters above the water level of Lake Yindarlgooda (Western Australia). Holocene dolomite from the North Stromatolite Lake (Coorong area) has been found by Hayball et al. (1991). The dolomite occurred in a laminated mudstone unit together with magnesium calcite and aragonite. "This unit, in places up to 1 m thick, was deposited under restricted anoxic bottom conditions, as a result of density stratification ..." (Hayball et al., 1991, p.106). The laminated mudstone contained about 7 wt.% organic carbon, in the form of a sapropel consisting mainly of decomposed cyanobacteria and remains of the green alga *Botryococcus braunii*.

Mann & Deutscher (1978) found dolomite in the calcretes of the Wiluna district of Western Australia. The age of this dolomite is not yet firmly established; some of the calcretes are thought to be of Tertiary age, but others must be Quaternary. The climate of this region of Western Australia is distinctly arid, with an average annual rainfall of 204 mm and evaporation rates of as much as 2540 mm per year. In the summer months of December to February day temperatures are usually around 308 K. The dolomite was found in calcretes together with calcite, quartz, amorphous silica, talc and celestite. Bowler (1981) described modern dolomite from the Holocene sediments of Lake Keilambete (near Warmambool, Victoria). "A series of concentric wave-cut notches form steps on the exposed crater slopes, and represent a legacy of past fluctuations in high water levels within the basin": Bowler (1981, p.433).

Calcretes from South Australia (River Murray Basin and Yorke Peninsula) contain considerable amounts of modern dolomite according to Hutton & Dixon (1981). In some places the lowest horizons of these calcretes consist almost entirely of dolomite. In general a trend in Mg/Ca ratio's of the carbonate fraction (in chemical analysis) increasing with depth, exists. According to Hutton & Dixon (1981) rain water falling onto the South Australian soils would first dissolve calcium carbonate. Nearly pure calcite precipitates upon the downward movement into the soil. Because the soil itself contains magnesium (in its clay minerals), the soil solution becomes increasingly enriched in magnesium. From such pore solutions rich in magnesium dolomite may precipitate. "The amount and intensity of the rain in relation to the evaporation will control the depth to which percolating water will penetrate": Hutton & Dixon (1981, p.77). In other locations of Australia the same phenomenon in soils of an increasing amount of dolomite with an increase in depth has been observed. "The constancy of the change in the chemistry with depth strongly suggests the carbonates at a given site have been modified *in situ*": Hutton & Dixon (1981, p.77).

Handford et al. (1983, 1984) reported on modern dolomite in tepees on the shores of Lake MacLeod, a coastal salina on the west coast of Australia. The tepees consist mainly of aragonite, deposited from sea water streaming into the 2000 km$^2$ salina of Lake MacLeod,

which lies 3 to 4 m below sea level. From time to time the aragonite cements forming the tepees will be flooded by rain water. In the words of Handford et al. (1984, p.524) the characteristic layers of aragonite cement: "… may be annual varvelike records of cementation that is being driven by seasonally fluctuating evaporation." Kendall & Warren (1987) explained, that the tepees as such are typical of carbonate crusts exposed to alternating phreatic and vadose conditions.

In the Holocene sediments cored from the bottom of Pellet Lake, Coorong region, Rosen et al. (1988) found dolomite as well as magnesite. The dolomite showed in X-ray diffraction the superstructure reflections typical of dolomite *sensu stricto*. Rosen et al. (1988) returned to the question of a possible relation between the degree of ordering of the dolomite with increasing depth of burial. Crystallographic unit cell parameters showed variations greater than the error of measurement within the seven different stratigraphic horizons, which could be distinguished. Therefore no trend with increasing depth could be established. "This indicates that differences in the unit cells of each unit are the result of the chemistry of the precipitating solutions and are not related to the "maturation" of the dolomite with age": Rosen et al. (1988, p.117). Holocene dolomite from the lacustrine sediments of Lake Hayward (W. Australia) has been described by Rosen & Coshell (1992), Rosen et al. (1992, 1995). Micromorphological relations pointed towards an origin within the sediment itself of the semi-permanent hypersaline lake: its maximum winter surface area is about 1 km[2]; but during the summer it shrinks to about half this size.[2]  The two cores in which authigenic dolomite was found, had been taken from the sediment subjected to the summer / winter change in water volume. "The pH and $HCO_3$ of the lake varies seasonally as well as vertically in the water column during stratification": Rosen et al. (1992, p.664). An unconfined hypersaline aquifer of some 20 m thick of relict seawater should be considered to be the source of the necessary magnesium ions. The euhedral form of the dolomite rhombs indicates their *in situ* origin (Rosen & Coshell, 1992). In the top layer of the sediments of Lake Hayward active bacterial sulfate reduction takes place (Rosen et al., 1992).

In a review paper on the formation of dolomite in the Coorong region Rosen et al. (1989) were able to distinguish two different kinds of Holocene dolomite. The first kind is a calcium-rich dolomite, which occurs together with aragonite, calcite and/or Mg-calcite. In X-ray diffraction this type of dolomite was analyzed to possess unit cells slightly expanded in the $c_o$ direction (average of 160.8 nm) and contracted in the $a_o$ direction (average of 47.99 nm); ideal dolomite shows $c_o$ = 160.2 nm and $a_o$ = 48.12 nm. The second type of dolomite is enriched in $MgCO_3$ and was found together with magnesite and magnesium hydroxide carbonate. Samples of the second kind of dolomite showed in X-ray analysis larger than usual $c_o$ (= 161.5 nm) as well as $a_o$ (= 48.27 nm) values. Although both kinds of dolomite show superstructure reflections, those of the second type were stronger, indicating according to Rosen et al. (1989, p.664) "... a relatively homogeneous microstructure".

After coring 20 different lakes of the Coorong Lagoon area, Warren (1990) was able to distinguish three different mineral assemblages: 1) dolomite plus Mg-calcite; 2) dolomite plus magnesite; and 3) dolomite plus aragonite and magnesium hydroxide carbonate. No dolomite was found at the bottom of the perennial Coorong Lagoon itself: there the laminated sediment consists of aragonite and Mg-calcite. The differences in mineral paragenesis were explained by Warren (1990) to result from the separate development of the different lakes. Varying proportions of aragonite, magnesium calcite, dolomite, magnesium hydroxide carbonate and magnesite in general make up the Holocene sediments of the lakes. Deposits of a single mineral are not often found, with the exception of the dolomite in "Dolomite Lake". Dolomite together with magnesium calcite is the most common paragenesis found: Warren (1990) had found it in 85 % of the lakes in the Coorong area containing dolomite. "Magnesite occurs only in the uppermost few tens of centimeters of the lake sediments" (Warren, 1990, p.849).

Recent dolomite occurring in Quaternary sediments from the Lacepede shelf, adjacent to the Coorong Lagoon area, has been described by Bone et al. (1991, 1992). The sediment of the shelf consists of a mixture of carbonates made up by bryozoa and bivalves, and terrigenous clastic sediments. Up to 25 % of the mixture may consist of dolomite. Individual dolomite rhombs as well as clusters of crystallites were found. The single crystals have sharp edges in some instances, but other crystals are completely rounded, indicating perhaps different ages of formation or phases of transportation during Holocene sea level changes. From carbon isotope measurements an age for the dolomite crystals of Pleistocene to Recent was inferred. The dolomite has an excess of calcium carbonate: it contains 43 mol % $MgCO_3$ . Distinct zoning of the dolomite crystallites was observed in cathode luminiscence.[3···]

Davies (1970) described Recent supratidal dolomite from the South Gladstone tidal flats. This tidal flat is part of the Hamelin Pool, itself being part of the Shark Bay area. The South Gladstone tidal flats bear a close resemblance to the sabkha's of the Persian Gulf as described by Illing et al. (1965). Here too the intra- and supratidal carbonate sediments are characterized by a wealth of algal mats (Davies, 1970). The environment of Shark Bay has been described in detail by Logan & Cebulski (1970), Hagan & Logan (1975), and Woods & Brown (1975). The average annual evaporation rate in Shark Bay is some 220 cm, whereas the annual rainfall averages 23 cm (Hagan & Logan, 1975). Rainfall is concentrated in the month of June with an average (over a period of measurements of 45 years) of 4.9 cm. December is the driest month with an average rainfall of only 0.2 cm (Logan & Cebulski, 1970). Evaporation takes place throughout the year, but especially January is a month with a high evaporation rate (of some 27.5 cm); in June the evaporation reaches a relative minimum of ± 7.5 cm (Logan & Cebulski, 1970). The high evaporation rates are responsible for the formation of concentrated seawater brines. The salinity of the water from the Indian Ocean of 35 to 38 ‰ is gradually increased till it reaches a maximum of 50 to 65 ‰ in the hypersaline Hamelin Pool. Diurnal variation in the salinity of the water of the Indian Ocean is in the range of 1 to 2 ‰; in Hamelin Pool this diurnal variation in salinity reaches as much as 5 ‰ (Logan & Cebulski, 1970). Higher salinities exist in the concentrated pore waters of the tidal flats bordering Hamelin Pool, where salinities of 80 to 90 ‰ can be reached (Hagan & Logan, 1975). The difference between high water level and low water mark ranges from 60 to 90 cm, but during heavy storms the water level may rise by as much as 300 cm. The extensive carbonate tidal flats (carbonates that consist mainly of skeletal grainstones and unconsolidated sands) of Shark Bay and associated hypersaline lakes (such as Hamelin Pool) offer good conditions for the precipitation of evaporites. Gypsum is one of the major minerals found in the upper intratidal zone (Woods & Brown, 1975). Not only the annual changes in temperature, evaporation rates, and the tidal changes introduce fluctuations in the Shark Bay area: Woods & Brown (1975) noted how halite precipitates in the lower supratidal zone, but that it is removed every year by rain and storm tides.

Although the paper by Ferguson et al. (1982) deals primarily with cementation phenomena at Fisherman Bay, South Australia, it contains also a few words concerning the possible presence of dolomite: "The formation of protodolomite at the periphery of the lithified area has not significantly influenced the Mg concentrations in the groundwaters ..." (Ferguson et al., 1982, p.1139).

Dolomite of Recent age from One Tree Reef (southern Great Barrier Reef, Australia) has been described by Davies et al. (1975). Dolomite was found there in a small semi-permanent pool, containing an algal mat covering the bottom of the pool. Only in the algal mat dolomite was found; below it magnesium calcite and aragonite occurred.

The presence of Holocene dolomite in carbonate concretions of the predominantly siliciclastic tidal flats adjoining Broad Sound, Queensland has been described by Cook (1973). The dolomite-bearing concretions were found only in the supratidal parts of this area. The

siliciclastic supratidal flats of Broad Sound show all of the characteristics of the supratidal environment: much of the surface is salt-encrusted and mud-cracked during dry periods; during spring high tides, when the flats are inundated by sea water, algal growth is abundant. The sediment contains numerous "gas bubbles" (birdseye structures). Salt encrustation is a feature found only at the beginning of the desiccation phase: halite will be rapidly removed by wind, rain or seawater inundation. An annual cycle in pH (varying between 6.5 and 9.0) of the ephemeral accumulations of water in the supratidal zone was measured by Cook (1973). Most of the annual rain in the Broad Sound region falls in the months December to March. The annual rainfall average is ± 100 cm; the annual evaporation rate is close to 170 cm. Dolomitic concretions were found by Cook (1973) some 10 to 20 cm below the surface of the mudflats in the Charon Point area. X-Ray diffraction showed, that the dolomite present had a chemical composition varying between $Ca_{65}Mg_{35}$ and $Ca_{59}Mg_{41}$ . The presence of quantities of cations such iron (II), manganese and strontium may have influenced the d-spacing measurements. Radiocarbon measurements showed the dolomite from the Broad Sound area to be of Holocene age: the dolomite itself has an age of 2860 ± 100 years B.P. Wood samples and shell fragments found at the same place and depth as the dolomite had a radiocarbon age of 2980 ± 95 and 3450 ± 90 years B.P., respectively (Cook, 1973).

Dolomite of Holocene age has been found by De Deckker et al. (1982) in Pillie Lake, a small ephemeral lake at the southern end of the Eyre Penninsula (South Australia). The sediment of the lake consists mainly of aragonite, but small amounts of halite, magnesium calcite and dolomite are present as well. Part of the year only a thin layer (less than 1 cm) of water is present, but the presence of large-scale polygonal cracks indicates periodical desiccation. Perhaps desiccation is not complete each year, because the pore water of the sediment supports Charophyta (*Lamprothamnium* sp. and *Ruppia* sp.) as well as marginal algal mats. "The lack of mat accretion, or of preservation detectable as buried laminated organic matter indicated that colonization during wetting periods is followed by desiccation and subsequent aeolian erosion ...": De Deckker et al. (1982, p.172).

Modern dolomite occurring in several lakes (identified as Beeac, Lake at Cemetary, Lake south of Cemetary, Lake east of Cemetary, Cundare, North of Cundare, Middle Eurack, Cora, Tooliorook, Gellie, Lake southeast of Gellie, Pink, Weering, Burne, Ondit and North of Beeac) in the Western Plains District of Victoria, some 150 km west of Melbourne, has been described by De Deckker & Last (1988, 1989). The area has poor drainage and low relief; the predominant lithology is that of lava flows (olivine tholeiite and alkali olivine basalts). The numerous lakes of the region consist of shallow depressions in a lava field, or are in fact maar craters. The climate is described as semi-humid temperate: summer temperature is around 292 K and winter temperature is near 281 K. On an average 65 cm of rain falls during the year, but evaporation rates are such, that about twice this amount will be lost due to evaporation. The lakes investigated are shallow (less than 1 m deep) and saline to hypersaline. The water has in general a high alkalinity and high Mg/Ca ratio's (of 25 and more). Salinities change with the seasons as well as from lake to lake. Dolomite is present in the white to grey gelatinous muds at the bottom of these lakes. Apart from dolomite and calcite, clay minerals together with minor amounts of quartz and feldspars were found. The dolomite is virtually stoichiometric ($Ca_{48}$ to $Ca_{52}$), showing superstructure reflections. In scanning electron microscopy the dolomite appeared as anhedral to subhedral crystallites of 0.1 to 3 micrometer. This dolomite is not of detrital origin: no dolomite at all occurs in the rocks and soils surrounding the lakes. "The chemical conditions that are conductive to dolomite formation in most of these lakes are similar to those reported in other Holocene dolomite settings: high salinity, high Mg/Ca ratios, and high alkalinity. Sulphate levels are moderate and do not seem to be inhibiting dolomite precipitation. Beyond these generalizations, neither the abundance nor the composition of the dolomite exhibits any obvious relationship to specific chemical parameters or basin characteristics": De

Deckker & Last (1989, pp.234-236). Arakel et al. (1990) observed how numerous saline playa lakes in the semi-arid interior of Australia will act as effective sinks for the authigenic formation of evaporites, carbonates and silicate minerals. For example near Lake Way and Lake Miranda (Western Australia) groundwater calcretes were found to contain up to 20 wt. % of dolomite. "Petrographic observations suggest that dolomite forms within a zone of alternate solution and reprecipitation, corresponding with the local groundwater-level fluctuation zone": Arakel et al. (1990, p.8).

Dolomite not older than 4,000 years was found by Last et al. (2004) in several carbonate hardgrounds of several maars on the plains of Western Victoria. Lake Gnotuk, Lake Bullenmerri and Lake Keilambete consist of fully enclosed, isolated deep craters in the central part of the Volcanic Plains of Western Victoria. Groundwater has little or no effect on the limnology of these three maar lakes, the main factor is the accumulation and evaporation of rain water. As a result "… water levels and brine salinities fluctuate dramatically". The carbonates of the hardgrounds at the shorelines of these three different maar lakes consist mainly of dolomite, aragonite, and magnesite. In the interpretation of Last et al. (2004) field observations on algal boundstones and microbiolites may well indicate a role played by biologically-induced processes in addition to purely inorganic ones.


AUSTRIA


Authigenic dolomite from the topmost sediments of the Neusiedler See, a lake on the border between Austria and Hungary, has first been reported by Wieden (1959). Although initially the sediment samples had been analyzed by way of differential thermal analysis, confirmation of the presence of dolomite was obtained with X-ray diffraction. The sediment in the topmost layers of the Neusiedler See consists mainly of grey to brownish-black clays (montmorillonite, illite) with a high percentage (of 4 to 10 %) organic substances such as plant remains, humic substances and bitumina. Because the dolomite crystals did not show any evidence of abrasion by mechanical processes, Wieden (1959) and Schroll & Wieden (1960) were convinced, that although the river Wulka is known to transport dolomite into the Neusiedler See, at least part of the dolomite had to be of an *in situ* origin. Müller et al. (1972), Preisinger (1979) and Schroll (1979) all have confirmed the occurrence of authigenic dolomite in the modern sediments of the Neusiedler See.


BAHAMAS


In 1933 Field & Hess reported finding dolomite in core samples from a well drilled near the south shore of New Providence Island, Bahamas. The total depth reached was 120 m; the alternating beds of calcareous sand and porous cavernous limestone changed into dolomite at a depth of 48 m. From the fossils found the age of the core could be estimated to be Pleistocene to Pliocene, but not Miocene.

In cuttings from drillings into the Plantagenet Bank (southwest of the Bermuda Islands at 32° 00' N / 65° 10' W) dolomite was described by Gross (1965). The carbonate sediment sampled to a depth of some 20 m below the sedimentary interface, consists mainly of coralline algae, foraminifera, mollusca, coral fragments, and echinoid fragments. "The type and abundance of skeletal fragments in these sediments are similar to those in the modern beach sands and near- shore marine sediments from the southeast coast of the Bermuda Islands":
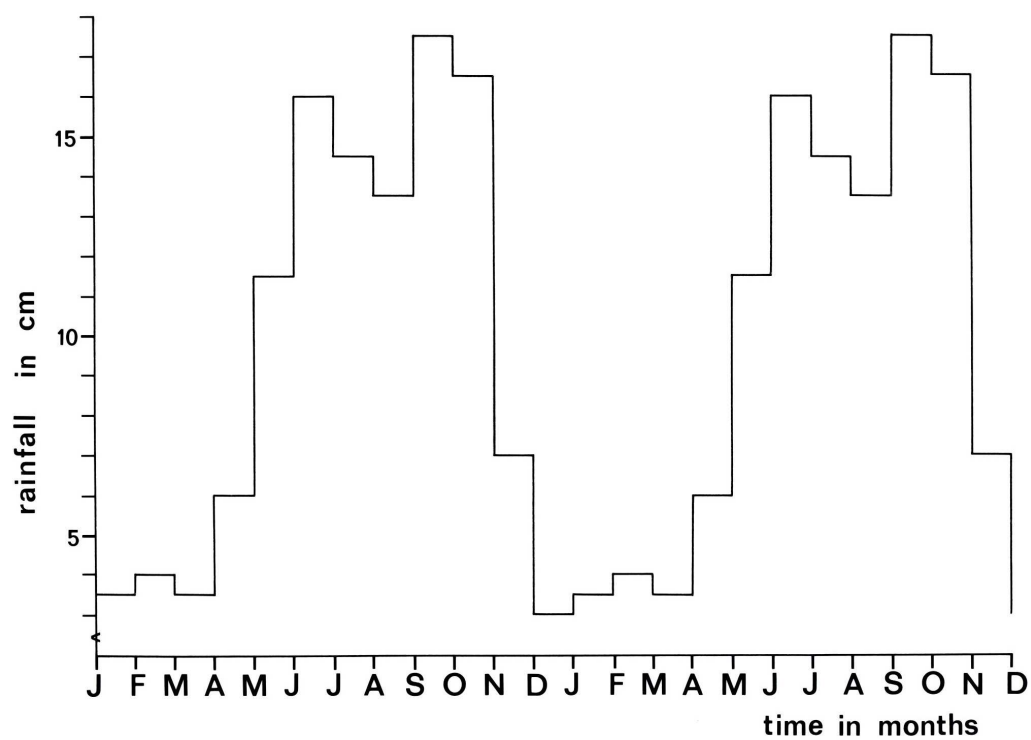
Fig. 14 – Fluctuations in monthly amounts of rainfall as measured at Nassau, Bahamas; average over 57 years (extrapolation based on data of Bourrouilh-Le Jan, 1980).
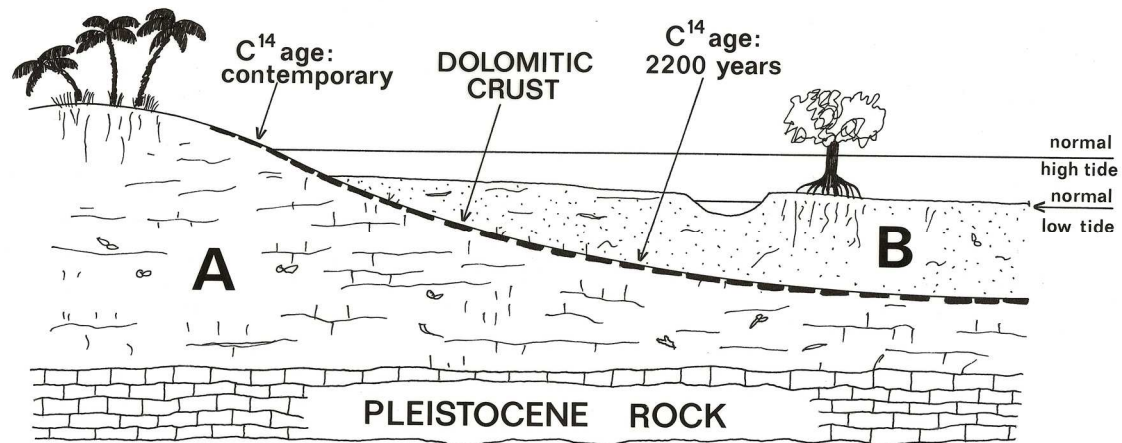
Fig.15 – Stratigraphic cross section of dolomite occurrences on the Bahamas. The dolomitic crust is diachronous (it is contemporary at the strand line and 2200 years old where buried at some 120 cm below normal high tide level) and originated in the lower supratidal zone (after Shinn et al., 1965).

Gross (1965, p.1285). The dolomite was found here in all cuttings, but at a depth of 20 m all of the sediment consists of dolomite. "Despite the prevalent destruction of textural features, recognizable fragments of coralline algae preserving the original cell outlines cemented together by dolomite are common. Tests of foraminifera and one echinoid plate were also recognized. Apparently the dolomite formed from a carbonate sand consisting largely of coralline algae": Gross (1965, p.1286).

The Recent dolomite of Andros Island and Abaco (Bahamas) occurs mainly at or near the shoreline, which lies a few centimeters above the mean high tide level (Shinn & Ginsburg, 1964; Shinn et al., 1965; Lasemi et al., 1989). At the same time it can be found in small dolines (Bourrouilh-Le Jan, 1973 A, 1980) and under "hammocks" (= vegetated topographic highs reaching elevations of 1 to 1.5 m above sea level) (Gebelein, 1977; Gebelein et al., 1980). The contemporary dolomite found at or near the shoreline, covers large areas on the tidal flats of western Andros Island and Abaco Island. In the intratidal zone only traces (less than 5 %) of dolomite were found. The dolomite is concentrated here in a crust-like layer, which crops out above normal high tide level. The crust contains between 20 and 80 % pure dolomite. The dolomite occurs in pelleted carbonate muds, that show laminations, stromatolites, mud cracks and birdseye structures. "The dolomite forms where tidal flooding and storm sedimentation is followed by many days of subaerial exposure": Shinn et al. (1965, p.112). Although evaporation rates during the periodic phases of exposure are high, no evaporates are preserved in the dolomite-containing sediments. The absence of evaporites can be understood, because the climate of the Bahamas is semi-tropical and quite humid. Cloud (1962) summarized the climate by pointing out the high humidity of the air (about 75 %) and by stressing the fact, that during 4 out of 10 days it rains on the Bahamas. Comprehensive climatological data gathered by the Climatological Branch of the Meteorological Office of Great Britain and the Meteorological Department of the Bahamas since 1853, were published in diagrams by Bourrouilh-Le Jan (1980). From that publication the diagram depicting the monthly amounts of rain, averaged over the last 57 years, has been reproduced here as Fig.14.

The dolomitic crust can be traced as a continuous layer intersecting the bedding planes of other Holocene carbonate deposits, especially on the flanks of those typical small-scale elevations of the Bahamas, the palm hammocks (Fig.15). Age determinations with carbon isotopes of pieces of this layer were made by Shinn et al. (1965). Measurements showed that for 3 out of 8 samples the total carbonate sample was older than the dolomite contained in it, and that 5 samples had the same age as the dolomite in it. All of the dolomite from these samples was definitely of Recent age (from 0 to 2200 years old). Samples taken from a continuous part of the dolomite crust above and below the sea level, revealed the diachronous (= time transgressive) character of the crust. Isotope measurements showed two samples taken only 150 m apart, to be quite different in age. The sample that came from directly above the high tide mark, was of contemporary age. The dolomite samples that had been collected from a depth of about 90 to 120 cm below the sea level, were found to be 2200 years old (Fig.16). Shinn et al. (1965) concluded therefore, that "... the formation of dolomite has been taking place slightly above normal high tide level during a gradual transgression of the sea" (Shinn et al., 1965, p.121).

In the paper of Shinn et al. (1965) photographs were given of birdseye structures present in the carbonate sediments from the Bahamas; sediments that contain dolomite. Shinn (1968 A) discussed the possible significance of birdseye structures, and Deelman (1972) explained their origin. These macropores originate in granular (or pelleted) sediments, which possess both capillary and non-capillary pores. Air will be entrapped as the direct result of the flooding of the granular sediment when dry, and the trapped air will accumulate into visible pores of several mm in diameter. Sediments that contain such birdseye structures are therefore indicative of an environment, in which periodical alternations between wet and dry predominate (tidal deposits).

In view of this evidence it may not be entirely surprising to note, that the tidal carbonates of the Bahamas contain additional evidence of alternations between wet and dry such as mud cracks (polygonal structures), laminations and stromatolites.

Dolomite of contemporary origin has been found on the east coast of Andros Island (Bahamas) by Bourrouilh-Le Jan (1973 A). The dolomite found near Fresh Creek occurs in such amounts, which without further preparation samples could be studied directly in the electron microscope. In X-ray diffraction the sediment was seen to consist of a mixture of magnesium calcite and dolomite. The dolomite of Fresh Creek occurs in small dolines, that are dry for most of the year, but that will be filled with rain water (salinity of this water = 3 g/dm$^3$) during seasonal storms. The thus formed small lakes are lined with algal mats, which are associated with carbonates such as aragonite, magnesium calcite and dolomite. After studying the water chemistry of the area in detail, Bourrouilh-Le Jan (1980) arrived at the conclusion, that a rather unusual type of hydrological regime must be involved. The numerous fresh water ponds of Andros Island are never quite dry, not even during the dry season of the year. No true fluctuations between wet and dry were found there, but instead the amount of accumulated water would fluctuate (and as a consequence the water chemistry of these lakes fluctuates).

Although Gebelein (1977) had initially claimed, that the dolomite found in the south-west of Andros Island had formed as the result of mixing between sea water and fresh water lenses, subsequent research published by Gebelein et al. (1980) could not reveal any relation between such mixing processes and dolomite formation. After X-raying numerous core samples Gebelein et al. (1980) observed, how dolomite occurred preferably in cores from the hammocks. Such hammocks were found on the tidal flats at Andros Island, and also in the interior of the tidal flats (i.e., supra tidal). "Thick diverse vegetation which colonizes the hammocks acts as a current baffle to trap sediments. The sediments are mostly lime muds, which are mixed with decaying plant material by the churning of terrestrial fauna and flora. This produces an incipient soil": Gebelein et al. (1980, p.35).

Dolomite has also been found in man-made concrete reservoirs, used for the crystallization process of salt from seawater on the island of Inagua, Bahamas. Dolomite rhombohedra were present in the sludge dump wastes from evaporation pans, which had been in service for only 8 years (Miller, 1961). Although Miller did not describe the exact procedure used on Inagua to crystallize NaCl from seawater, it must be clear, that all of the known crystallization techniques for NaCl from seawater are discontinuous. Periodic alternations between phases of complete desiccation of seawater and phases of removal of the salts are involved, followed by the inlet of new seawater into the basins. A common procedure in the crystallization of sea salt requires three steps: in the first basin calcium carbonate precipitates from the slowly evaporating mass of seawater. Calcium sulfate precipitates in the second basin ("pickle pond"). In the third basin ("saltern") halite is finally precipitated, and the concentrated brine that remains, constitutes a "bittern", that will be pumped back into the sea. A different method that is used in countries such as France, Italy, Spain and Portugal, involves a "carpet" of living algae (*Microcoleus chtonoplastes*) forming an impregnable layer sealing the bottom of the evaporation basin (Baas-Becking, 1934). The photosynthetic process of the living algae (living in spite of extreme salinities) will be able to withdraw dissolved carbon dioxide and so lead to the formation of carbonates.

Modern dolomite has also been reported from the island of San Salvador, Bahamas. Although the core samples of Supko (1977) were not particularly well dated (paleontological information was scarce and no isotope measurements were available), it may be assumed, that the upper part of the cores contained dolomite of Recent age. Supko (1977) was able to distinguish two different parageneses of dolomite according to lithology. The first type consists of a more or less well-bedded dolomite ("stratal dolomite") with evidence of a supratidal origin (intraclasts, birdseye structures). A second type of dolomite is more massive and has been

interpreted as being part of a non-bedded backreef or lagoonal facies. In both types of dolomite sediments floored interstices, birdseye structures, vadose cements and coloring by iron occurred to such an extent, that Supko (1977) concluded, that there must have been numerous stages of deposition, soil formation, submergence and re-deposition alternating with each other.


BARBADOS


Dolomite of Late Pleistocene age has been found by Humphrey (1988, 2000), Humphrey & Quinn (1989), Humphrey & Radjef (1991), and Machel & Burton (1994) on Barbados (the easternmost Caribbean Island). The original carbonate sediment here consists of an algal-foraminiferal limestone. The Golden Grove dolomite occurs not only in such skeletal grains, but also as limpid cements and as banded cements, in which layers of calcite alternate with those of dolomite. According to Humphrey (2000) dolomite formation at this loaction had to be related to the mixing of marine and rain water. Because dolomite distribution is highly localized, Machel & Burton (1994) thought seawater with variable temperature and/or variable salinity to be the cause of the conversion, without the possible mixing with rain water. Dolomite formation must have taken place upon subaerial exposure of the Golden Grove area during the Pleistocene. Barbados has a sub-humid to humid tropical climate. Mean annual temperature is 297 to 301 K. The topographically low coastal areas suffer little rainfall, and have high evaporation rates. The highlands of the Scotland District of Barbados receive more rain, and have lower evaporation rates. Rain falls especially during the months of September to December.


BELIZE


There can be no doubt, that the dolomite described by Ebanks (1975), Mazzullo & Reid (1985, 1988), Mazzullo et al. (1987, 1995) and Gregg et al. (1992) is of Recent origin: isotope measurements gave age readings of 845 to 2925 years before present. The dolomite had been found on Ambergris Cay, a low-lying peninsula of the southeastern Yucatan Platform, Belize (Central America). The climate of the region is humid tropical. The annual rainfall (of 130 to 150 cm) occurs mainly during the summer season. Temperature varies with the seasons from 297 to 300 K. Ambergris Cay is essentially a mosaic of shallow lagoons in combination with densely vegetated, broad supratidal flats. The Holocene sediments, lying on top of karsted Pleistocene limestone, consist of pelletal micrite, foraminifer-molluscan sandy micrites and some carbonate sands and gravels. The predominant mineralogy is magnesium calcite (with 14 to 17 mol % $MgCO_3$), although aragonite is found as well. Dolomite crusts are widespread on many of the supratidal flats of the northern and the central part of Ambergris Cay. These supratidal flats are only slightly above mean sea level, so that the areas of active dolomite formation are subject to rain as well as to flooding by seawater during storm tides. Concentration of dolomite exists in the form of crusts in the Holocene sediments: from 50 to 70 % of such crusts consists of dolomite. The dolomite itself has been described as "... poorly ordered, non-stochiometric calcic dolomites ... ranging from $Ca_{53}Mg_{47}$ to $Ca_{58}Mg_{42}$" (Mazzullo et al., 1987, p.227). Crust formation proved to be the result of the crystallization of dolomite, cementing the particulate carbonate sediment. According to field observations by Mazzullo et al. (1987, pp.226-227) the crust "... initially was formed at the sediment-air and/or sediment-shallow water (2-3 cm) interface at sea level, in a regime of vertically fluctuating interstitial and standing lagoonal waters." The crusts were found immediately below the surface of the

Holocene sediments, overlain by several cm's of dried-out cyanobacterial mats (made up by *Scytonema* sp.). In the algal mats too authigenic dolomite was found (along with aragonite and Mg-calcite). "Where such mats are absent, the sediments are similarly periodically desiccated and locally contain abundant gas bubbles (unfilled birdseye structures)": Mazzullo & Reid (1988, p.483).  Periodicity is not only introduced in the form of phases of flooding by autumn storms followed by long intervals of desiccation; the supratidal flats of Ambergris Cay also are subject to seasonal variation in salinity. On the Thomas Savannah supratidal flat an annual variation from 25 to 75 ‰ was measured. Ebanks (1975) measured even higher salinities in supratidal ponds on Ambergris Cay: there salinities of 76 to 123 ‰ were found. The Mg/Ca ratio varied with the seasons from 3 to 5. Virtually the whole thickness of the Holocene supratidal sediments at this location (measuring at maximum 23 cm above mean sea level) is influenced by the semi-diurnal tidal fluctuations of the pore water, since the neap-tide range measures on average 20 cm.

   According to Gregg et al. (1992) there is a linear increase in the average size of the dolomite crystallites with increasing depth in the three crusts at Ambergris Cay. But the size increase was not accompanied by a decrease in porosity. As a consequence Gregg et al. (1992) concluded, that re-crystallization must have taken place. Geochemical analyses, notably Mn and Fe measurements, suggested reducing conditions.

   Holocene dolomite was found by Teal et al. (2000) in sediments of some 6400 years old in the Cangrejo Shoals mudbank at the southern tip of Ambergris Caye, northern Belize. The dolomite was analyzed to contain 39.5 to 44.5 mol % $MgCO_3$ , and  would be closely related to active bacterial sulfate reduction taking place in the organic-rich sediment. At the same time Teal et al. (2000, p.659) noted how the dolomite formation "… at Cangrejo Shoals is/was episodic. Other workers likewise have suggested that dolomitization typically is episodic rather than continuous..".


BONAIRE


   Deffeyes et al. (1964) were the first to describe Recent dolomite from the island of Bonaire (Antilles, Caribbean Sea). This dolomite is definitely of Holocene age: isotope measurements indicated ages of 1480 ± 140 and 2190 ± 150 years. The dolomite had been found in a hypersaline lake, located on a tidal flat at the southern tip of the island. In the northern part of Bonaire a somewhat different occurrence of Recent dolomite was found; there dolomite occurred in marine Plio-Pleistocene rocks, without any apparent relation to the bedding planes. Deffeyes and co-authors devoted their attention almost entirely to the dolomite found in the Pekelmeer salina. The dolomite occurred there exclusively in finely laminated carbonate crusts, often cut by mudcracks. In the course of their investigation Deffeyes, Lucia & Weyl (1964) had to observe, that the hydrology of the Pekelmeer is not static; it was found to be a dynamic system controlled by the volume of sea water inflow, the volume of rain water added, the rate of evaporation, and the possible outflow through the bottom of the lake (the latter phenomenon was named "reflux").

   Like in so many other places on earth the rainfall on Bonaire shows a marked annual variation: most of the total amount of rain falls in the months October to January (Fig.16). Measurements of the level of the Pekelmeer by Rooth (1965) showed an annual pattern of fluctuations, with almost weekly variation (Fig.17). At the same time Rooth (1965) measured an annual pattern of changes in chlorinity. Earlier Westermann & Zonneveld (1956) had concluded from their hydrological investigation, that fluctuations form the most prominent aspect of the
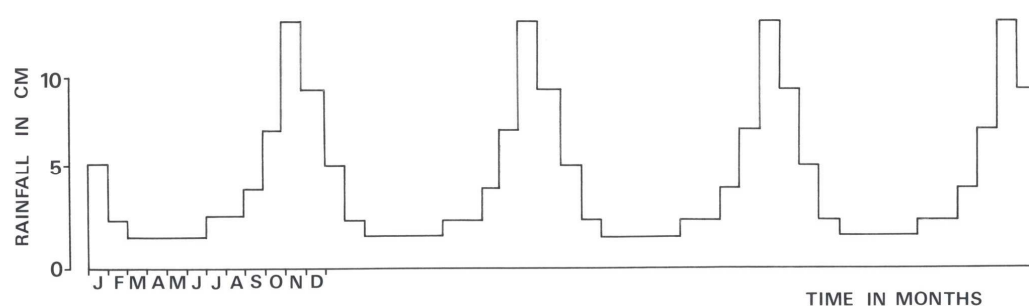
Fig.16 – Annual variation in the amount of rainfall on the island of Bonaire. Diagram obtained by extrapolating the 1-year data published by Westermann & Zonneveld (1956).
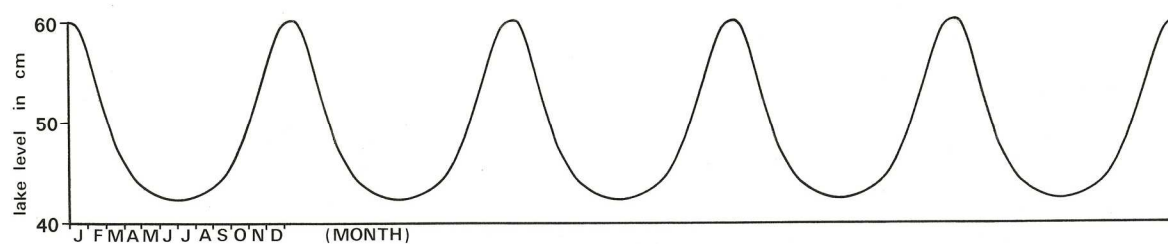
Fig.17 – Annual fluctuations in the water level of the Pekelmeer on Bonaire (extrapolation based on the 1-year diagram published by Deffeyes et al., 1964).

hydrology of Bonaire. At least in the areas near the coast the level of the pore water follows the tidal movements of the open sea.

The "reflux" model of dolomitization advanced by Deffeyes et al. (1964), is of course identical with that proposed by Adams & Rhodes (1960). Support for the application of this particular model seemed to be supplied by Murray (1969), who founded his hydrological conclusions on the work of Rooth (1965). Murray (1969) re-calculated the water level measurements of Rooth into pressure values at 1 meter below the sediment surface, where a layer of clay and/or volcanic ash occurs. The calculations led Murray (1969) to suppose, that during a short period each year in early summer the brine accumulating in the Pekelmeer would return (or "reflux") to the open sea. This would mean a temporary reversal of the inflow of seawater through numerous flow channels and seepages of the underlying Pleistocene terrace rock. Such an underground supply of sea water from the surrounding ocean had been established by Westermann & Zonneveld (1956) and confirmed by Rooth (1965). Because salinas such as the Pekelmeer possess high rates of evaporation, their level is below that of the sea throughout the year. As a consequence a slow, but continuous flow of seawater streams into the salinas. As Rooth (1965) pointed out, there are three different ways in which the Pekelmeer receives its supply of water from the sea: 1) through the wall of coral debris, which separates the Pekelmeer salina from the open sea; 2) through underground channels, that possess circular openings ("eyes") in the bottom of the Pekelmeer; and 3) through cracks and joints acting as seepages.

It must be stressed, that Murray (1969) inferred the possible existence of a "reflux" event solely from his theoretical calculations. No such return flow had actually been observed or measured by him. The only form of evidence supplied, consisted of Murray's observation on the absence of halite crystals outside some of the rubble walls surrounding "eyes" in the Pekelmeer area. Rooth (1965) had not found any evidence in support of the "reflux" of Pekelmeer brine into the Caribbean Sea: his measurements showed, that even at extremely low ebb tide levels the sea level would not become lower than the level of the Pekelmeer, and therefore "... no brine flowed away to the sea" (Rooth, 1965, p.27). Evidence against the suggested "reflux" model has been supplied by Lucia (1968). After taking various core samples and analyzing the pore water contained in it, Lucia (1968) came to the conclusion, that in the underground below the salina "... there was *no* hypersaline water" (Lucia, 1968, p.852). Therefore the conclusion was drawn, that the heavy brine of the Pekelmeer is capable of leaving the salina in much the same way as sea water comes into it from the surrounding sea: through the rubble ridges surrounding the Pekelmeer.

Bandoian & Murray (1974) were able to distinguish at least two episodes of dolomite formation in the Plio-Pleistocene carbonates of Bonaire. "No evidence for deposition of sediments in the supratidal environment was found. ... The distribution of the dolomite is consistent with the evaporative reflux model, but conclusive evidence for this origin was not obtained": Bandoian & Murray (1974, p.1247). Even so, Major et al. (1992) have explained the formation of Holocene dolomite in the Pekelmeer of Bonaire in terms of hypersaline fluids, but their conclusions were based on oxygen isotope studies.


BOTSWANA


Recent dolomite from calcretes in the soil of the Kalahari Desert (Botswana, southern Africa) has been described by Watts (1980). The dolomite seems to be related to present-day processes of soil formation in the semi-arid climate. At the same time magnesium calcite (with up to 17 mol % $MgCO_3$), authigenic kaolinite, palygorskite and sepiolite have formed. X-Ray
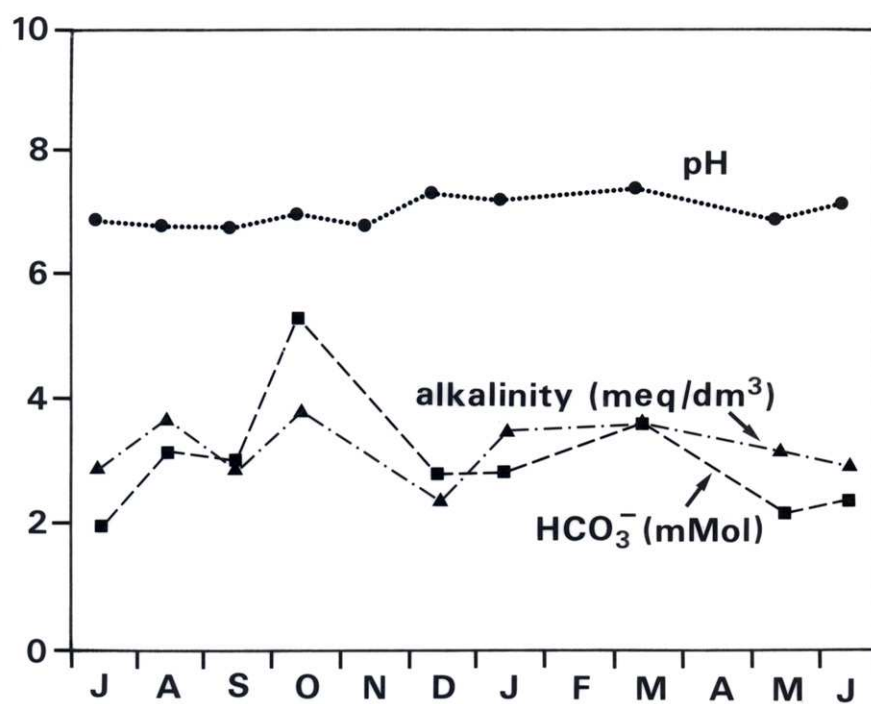
Fig.18 – Bicarbonate concentration (---), alkalinity (-.-), and pH (…) of the Lagoa Vermelha water during the months July 1996 to June 1997 (modified after Van Lith, 2001).

diffraction applied to the dolomite crystals showed, that it was well ordered, and not "protodolomite". The dolomite was found as euhedral rhombs lining solution channels, in some instances overgrown by a layer of calcite, as well as small (5 to 20 micrometer), cloudy rhombs associated with authigenic sepiolite and/or palygorskite. The climate of the Kalahari Desert in Pliocene and Recent times possessed distinct dry-wet-dry fluctuations, and Watts (1980) stressed the importance of these rapid alternations of climate ("... an environment with high evaporation and periodic flushing by rain water": Watts, 1980, p. 680). At least the euhedral dolomite crystals were, in the view of Watts (1980), related to groundwater movements.


BRAZIL


Dolomite of Holocene age has been found by Moreira et al. (1987) in the Lagoa Vermelha, a hypersaline lagoon located about 100 km east of Rio de Janeiro. The lagoon measures about 4.4 km in length and its width varies from 250 to 850 m. Details on the setting and climatological conditions of this particular location have been published by Höhn et al. (1986), Vasconcelos & McKenzie (1997), and Santelli et al. (2006). Water depth of the Lagoa Vermelha varies on an average between 1 m in summer to about 1.7 m in winter. The mean annual temperature fluctuates between a maximum of 305 K and an annual minimum of around 290 K. The average rainfall in the area is some 900 mm per year, most of which falls in the months of April and May and from October to December.

The Lagoa Vermelha came into existence after a ridge, made up from shells, accumulated to such an extent, that it could separate the lagoon itself from the main body of the Atlantic Ocean. That this separation took place in Recent times, is proven by the radiocarbon age of the shells. Two samples measured by Höhn et al. (1986) showed an age of 3800 and 4200 years before present. Algal mats cover those areas of the Lagoa Vermelha, which are flooded periodically (in particular the intratidal and adjacent supratidal environments). These algal mats consist of a gelatinous layer of 3 to 6 cm thick of predominantly blue-green algae. They cover the shores as well as the bottom of the lagoon to a depth of 30 to 40 cm. Presumably these algal mats are responsible for periodically recurring "bicarbonate booms" depicted by Van Lith (2001) (Fig.18). Under the top layer of active blue-green algae a $H_2S$-rich, black anaerobic zone is found. Analyses of pore water samples by Höhn et al. (1986) showed that the sulfate content of the lagoon water disappears gradually with depth. Bacterial sulfate reduction was thought to be responsible for that fact. Cores taken showed the following sequences: 1) top layer (of about 4 cm thick) of algal mat. 2) A laminated sequence of carbonates and organic material extending from 23 cm to a depth of 41 cm. 3) A bed of sand mixed with marine Pelecypoda from 41 cm to the maximum core depth of 60 cm. The algal mat itself contains at maximum 25 % carbonates, but especially the second layer is very rich in carbonates: from 65 to 89 wt. %. The carbonates found in that second part of the cores, are aragonite, magnesium calcite and "protodolomite". Carbon-14 isotope dating by De Oliveira Vasconcelos & McKenzie (1991) showed the sediments in the upper 1 m of core samples from Lagoa Vermelha to be younger than 5000 years. From the observation that in the top of their cores magnesium calcite with minor amounts of aragonite predominated, and that only in the deeper parts of the cores the percentage dolomite became more substantial, De Oliveira Vasconcelos & McKenzie (1991) concluded, that the magnesium calcite had been the initial precipitate and that it had only later been changed into dolomite. From carbon-13 isotope distribution the conclusion was drawn, that "... dolomitization likely occurred in association with bacterial sulfate reduction" (De Oliveira Vasconcelos & McKenzie, 1991, p.60).

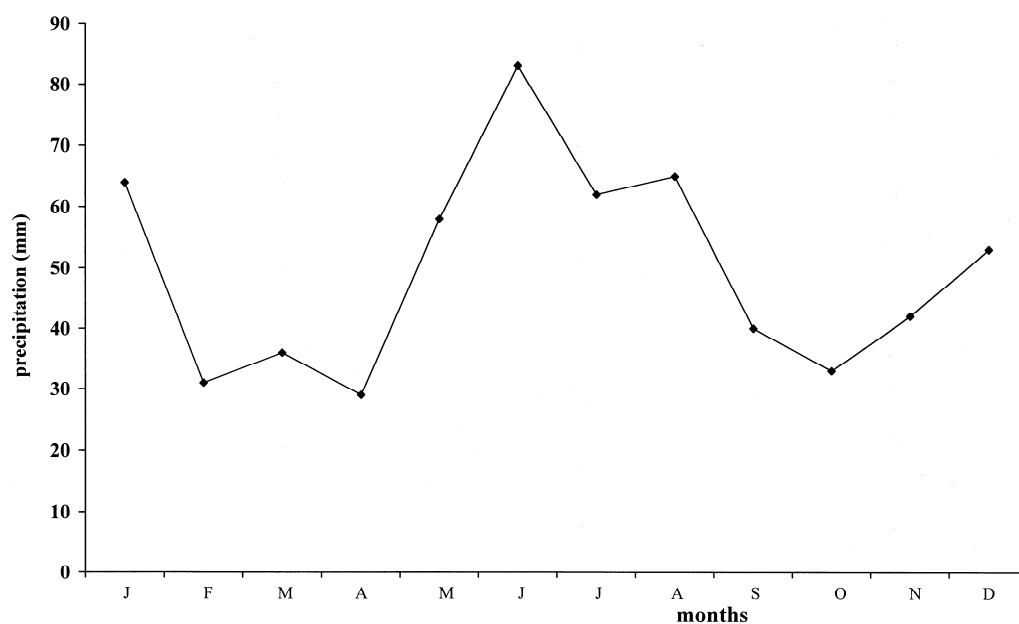Holocene dolomite has also been found in the Brejo do Espinho lagoon located near the

Fig.19 – Periodicity in monthly precipitation at the southern Cariboo Plateau, Canada (average for the years 1951 to 1980) (modified after Renaut & Long, 1989).

Lagoa Vermelha by Van Lith (2000), Van Lith et al. (2002; 2003 A,B) and Sánchez-Román (2006). Brejo do Espinho is located between the Atlantic Coast and the Lagoa Araruama in Riode Janeiro state. It is a very shallow (depth less than 0.5 m) hypersaline coastal lagoon. Evaporation rates exceed precipitation due to the semi-arid climate at this location. Thick microbial mats flourish in its water during flooding phases during the wet season. Much like the nearby Lagoa Vermelha the water of the Brejo do Espinho goes through an annual cycle, in which for example salinity anf the concentrations of $SO_4^{2-}$ , $Br^-$, $Ca^{2+}$ and $Mg^{2+}$ fluctuate. The upper 10 cm of a 25 cm deep core was seen to contain magnesium calcite and what was described as a dolomite with 47 to 52 mol % $MgCO_3$.

## CANADA

Probably the first description of Holocene ("postglacial") dolomite found in Canada was published by Rostad (1975). Amounts of very fine-grained dolomite had been found in the sediments of Lake Sturgeon and in a soil profile near Debden (Saskatchewan). In particular the latter site contained considerable amounts of fine grained dolomite, and its authigenous origin could not be doubted: "Since it is highly unlikely that the dolomite in the finer fractions ... was derived from the surrounding glacial material, it is postulated that the finer dolomite was formed in situ from aragonite or calcite": Rostad (1975, p.802).

The Basque lakes of British Columbia (Canada) are made up of several little lakes, located in small valleys at an average altitude of 670 m above sea level. The bedrock of this area consists of basic and ultrabasic rocks. The lake water contains relatively high concentrations of magnesium sulfate; the magnesium having been derived from the weathering of serpentines, olivines and pyroxenes. The sulfate content could be traced to the oxidation of sulfides (Eugster & Hardie, 1978). In the mud of Basque Lake 2, the lake with the highest salinity of the area, epsomite ($MgSO_4.7 H_2O$), bloedite ( $Na_2SO_4.MgSO_4.4 H_2O$ ) and gypsum are present. Alkaline earth carbonates found in the sediments of Basque Lake 2 are: calcite, magnesium calcite with 30 - 32 mol % $MgCO_3$, "protodolomite" (with 43 mol % $MgCO_3$) and magnesite (Eugster & Hardie, 1978). The remaining amount of dissolved calcium in the lake water precipitates in the form of gypsum. What remains in solution are essentially magnesium, sodium, sulfate and chloride. Continued evaporation may eventually lead to the precipitation of epsomite and bloedite (Eugster & Hardie, 1978). The presence of magnesite and dolomite in several of the seven different Basque Lakes has been confirmed by Nesbitt (1990) and Burton et al. (1992).

In the Holocene sediments of Waldsea Lake (Saskatchewan)  Last & Schweyen (1985) and Last & Slezak (1986) found dolomite along with magnesium calcite, magnesite, mirabilite and gypsum in organic-rich silty clays. Waldsea Lake is one of the hundreds of saline lakes in the Prairie region (a very large area with internal drainage) of western Canada (Last & Ginn, 2005). Climate is of a cold, semi-arid continental type: average day temperature in January is 255 K and during the summer month of July the average day is 292 K. Annual precipitation is about 360 mm, and the annual evaporation rate is about twice that amount (Last & Schweyen, 1985). The lake sediments (reaching a maximum thickness of 4 m) are well laminated, with distinct packages of varve-like couplets especially in the upper 2 meters of sediment. The lake water is populated by colonies of phototrophic bacteria (*Chlorobium* sp.); the water near the bottom of this lake is strongly reducing (- 300 to - 400 mV) and contains high amounts of dissolved $H_2S$ (150 to 200 $mg/dm^3$). Pronounced fluctuations in hydrology and water chemistry are recorded in the Late Holocene sediments in the form of changes in organic productivity (Last & Slezak, 1986). That at least part of the dolomite at this location is authigenous, is illustrated by the occurrence of dolomite-cemented hardgrounds in the laminated units. In the

view of Last & Schweyen (1985) the dolomite (plus magnesite) must have been formed, when the Waldsea Lake was a shallow hypersaline lake. The laminae of gypsum and carbonate minerals would have originated at the margins of the shallow playa.

Modern dolomite has been described from a number of neighbouring saline lakes on the Cariboo Plateau, British Colombia, by Renaut & Long (1989) and Renaut (1990). For example in the Meadow Lake, Goodenough Lake and Clinton Lake dolomite (described as "protodolomite" with a composition of $Ca_{45-52}$) has been found, accompanied by aragonite, calcite, Mg-calcite, magnesium hydroxide carbonate and magnesite. The basins in which the saline lakes developed after the retreat of an ice cover some 10,000 years ago, are bordered by wooded hill slopes. The climate of the region is semi-arid to sub-humid, with relatively small amounts of rain (neighbouring mountains receive more than 100 cm precipitation, but on the Cariboo Plateau only 30 to 40 cm of rain and snow precipitates each year) (Fig.19). Temperatures range from annual averages of about 286 to 290 K in July to averages of 264 to 262 K in January. The lakes can be divided in most instances into a mud flat (saline or dry) and a perennial or ephemeral lake. Carbonate precipitation takes place especially in the mud flat area. Groundwater levels fluctuate according to the season by as much as 1 m. Evaporites (including for example trona, nahcolite, gaylussite, thenardite, hexahydrite, and epsomite) are being precipitated in the upper parts of the mud flat during the summer retreat of the water level. The alkaline earth carbonates precipitate in many of the saline lakes: cores taken demonstrated the presence of calcite, aragonite, and dolomite with silty, organic-rich muds. Black siliciclastic muds mixed with carbonates and smelling of hydrogen sulfide are common in cores from the margins of these saline lakes. According to Ferris et al. (1994) (cyano-) bacteria would be involved in the precipitation of dolomite and magnesite in the alkaline lakes of the Cariboo Plateau.

Kohut et al. (1995) described modern dolomite from a sulfate-containing saline soil in Alberta, Canada. The dolomite is well-ordered and of stoichiometric composition, and must be authigenic: $C^{14}$ measurements gave age readings of 1270 to 5270 B.P. Detrital dolomite from the Devonian era present in the larger size fractions lacked any $C^{14}$ activity. Isotope analysis showed that the dolomite must have been formed by way of direct precipitation and not by a reaction with pre-existing calcite.


CHAD


Modern dolomite from Lake Yao, a saline lake in the northern part of Chad, has been described by Gac et al. (1977). High evaporation rates induced by the arid climate of the region, lead to salt crystallization on the beaches of the lake. A sequence according to increasing concentration of the brine was found, extending from the water body up the beaches. The sequence consists essentially of calcite, aragonite, magnesium calcite, dolomite, huntite, magnesite, sodium carbonates, sodium sulfates, and at the outer edges of the beach sodium- and potassium chloride.


CHINA


Dolomite of Holocene age has been described by Xia & Li (1986) from beach rock at the Xiaochaidan Salt Lake (Qinghai Province, China). Some of the dolomite was found in algal lumps, and possibly algae were involved in the precipitation of dolomite at this location.

Dolomite of obvious Holocene age has been found by Hui et al. (2005) in drainage wells in the base of the Baozhusi Dam, near Guanyuan city, Sichuan province. The presence of dolomite (along with quartz, calcite, albite, microcline and chlorite) was established in X-ray diffraction. In addition samples of neighbouring rocks and building materials from the dam itself were X-rayed, and were found not to contain any dolomite. Because of the presence of $H_2S$ in these deposits, Hui et al. (2005) attributed the precipitation of calcite and dolomite to the alkaline pH values caused by the process of sulfate reduction.

In the Qinghai Lake (northeastern Qinghai – Tibetan Plateau) dolomite was found by Dong et al. (2006) in lacustrine sediments not older than Pliocene. Annual evaporation rates (of some 1400 mm) exceed by far the mean annual precipitation (some 400 mm), thereby leading to a very large (4300 km$^2$) saline lake.

Small amounts of dolomite, together with large amounts of magnesium calcite (with up to 38 mol % $MgCO_3$) and aragonite, were found by Han et al. (2008) in sediments from the South China Sea. Dissolution was analyzed to be a common phenomenon in these mainly biogenic carbonates, leading to for example partially dissolved clam shells. But the exact sequence of dissolution phases and intervals of carbonate precipitation was found to be different for samples from different sites (Han et al., 2008).


COLOMBIA


Recent dolomite occurring on the slopes of a small cliff on the island of San Andres, Colombia has been described by Kocurko (1979). An irregular layer of Pleistocene limestone bordering the seaward periphery contains the dolomite rhombs (that range in size from 5 to 10 micrometer). Dolomite crystals with alternating layers of dolomite and calcite were found. The outer surface of the Pleistocene accumulation consists predominantly of dolomite, in clear contrast to the underlying magnesium-free limestone. Apart from dolomite, gypsum crystals were found as euhedral crystallites lining voids. The hypersaline brines responsible for the formation of dolomite originated in the spray zone of the supratidal environment, and evaporation will have increased the salinity. "Sea water splashing against the cliff face causes pools of water to accumulate in dissolution cavities on the rock surface. The periodic wetting and drying gives rise to brines that percolate inward...": Kocurko (1979, pp.211-212). In addition to concentration of trapped seawater due to evaporation followed by renewal of the seawater in the small pools and cavities by new splashes, other periodic phenomena take place on the cliff's surface. Kocurko (1979) described, how the water in the small pools is being warmed up during the day time (to temperatures of 323 K) and cools down again during the night. Because of abundant algal activity in the pools and splash cups, the pH of the enclosed water will be fluctuating. In pH measurements changes from pH = 8 to pH = 10 were found. "These figures fluctuate on a daily basis and are controlled primarily by surf action, exposure to sunlight, rain and activity of photosynthetic algae": Kocurko (1979, p.212).


DENMARK


Scuba divers of the *Frederikshavn Dykkerklub* discovered sandstone concretions as large as 4 m long and 1 m wide, standing up in water depths of 10 to 12 m near Hirsholmene Island in the Kattegat, Denmark. Jørgensen (1989) obtained several samples, and performed a detailed mineralogical analysis. The concretions consisted of the quartz sand (medium grained

and well sorted), that makes up the sediment at the bottom of this part of the Kattegat, cemented by dolomite. Water temperatures at the site vary from approximately 276 K in winter to about 289 K in summer. Salinity is relatively constant at 30 ‰. Such carbonate-cemented sands were found in places uncovered, but usually occurred as slabs or a more or less homogeneous pavement of 10 to 30 cm thickness at depths of 1 to 3 m below the sediment's surface. Concretions in the form of vertical pillars of several meters, apparently well braced in the sediment, form the most spectacular aspect. "The surrounding seabed is characterized by numerous gas seeps and occasionally gas leaks are observed through vents in the sandstone pillars. The submarine gas seeps observed in the Kattegat originate from a shallow gas field, which extends from northeastern Jutland into the Kattegat area... ": Jørgensen (1989, p.72).

Carbon-14 age determinations of the dolomite gave readings of 19,100 ± 500 and 18,300 ± 370 years B.P. In X-ray diffraction traces of magnesium calcite and pyrite were observed. The dolomite itself showed sharp diffraction peaks, including superstructure reflections. Microprobe analyses gave percentages $MgCO_3$ of 43 to 50 mol %, with an average of 47 mol %. In scanning electron microscopy the size of the dolomite rhombohedra could be measured as 10 to 30 micrometer.

In explaining the mode of formation of the mineral dolomite in the quartz sand of the seabed of the Kattegat, Jørgensen (1989) followed the example of Hathaway & Degens (1969) and suggested, that a process of methane oxidation would be involved. "Methane oxidation occurs when methane migrates upwards through the diagenetic zones of the sedimentary column. The oxidation is believed to take place either in the anoxic environment by sulphate-reducing bacteria or in the oxic environments through the activities of aerobic methane-oxidizing bacteria ... Methane oxidation increases alkalinity in the interstitial brine which subsequently may result in carbonate precipitation": Jørgensen (1989, p.77). Especially the formation of the pillar-like concretions would be indicative of the role played by the oxidation of methane gas, emanating from the sediment below. The internal structure of the sandstone pillars had to be the result of outbursts of methane. The association between dolomite and pyrite suggested an anoxic environment, created by the activities of sulfate reducing bacteria.

EGYPT

Beachrock along the southern shores of the Bardawil Lagoon, Egypt was found to consist almost entirely of (non-stoichiometric) dolomite (Levy, 1974, 1977, 1980; Friedman, 1991). Age determinations gave readings of less than 5700 before present. The Bardawil Lagoon is located on the eastern coast of the Mediterranean Sea near the Sinai Penninsula. The large water body of the lagoon (some 600 $km^2$) is separated by a sand barrier (some 500 m wide) from the open water of the Mediterranean Sea. On the southern shores sabkha's have developed, where dolomite is present. Locally salt pans have been formed in which gypsum and halite have precipitated. Much more dolomite is present in the form of beachrock, together with small amounts of aragonite and calcite (accompanied by quartz, feldspar, plagioclase, pyrite and sylvite). Varying amounts of fossils such as the pelecypod *Glycymeris*, fenestrate bryozoans and worm tubes were found. Based on isotope analyses Friedman (1991) suggested a mode of formation of the beachrock dolomite as being related to the oxidation of methane. The production of methane would have been brought about during bacterial sulfate reduction.

FRANCE

In samples dredged from a depth of 150 to 300 m in the Mediterranean Sea south of Marseille, Froget (1972) found dolomite of Pleistocene age. The Pleistocene samples consist of *Halimeda* limestone, often encrusted with iron in the form of the mineral goethite. The dredged rock samples had to be of an authigenic origin, because similar rocks do not occur within at least 100 km from the coast line land inward. The limestone is made up from mainly *Halimeda*, but fragments of benthic formaminifera, corals, molluscs and echinodermata were present as well. Indications for the dissolution of the aragonite originally making up the *Halimeda* fragments and its replacement by dolomite, were found in thin-section examinations. Other minerals present were magnesium calcite (with 12 mol % $MgCO_3$) and dolomite. At present calcareous algae of the *Halimeda tuna* species grow in the Mediterranean Sea at a depth of about 40 m below the surface of the water. Therefore Froget (1972) suggested, that the dolomite must have formed in the supralittoral zone of the Mediterranean Sea, when (during the Pleistocene) its surface was some 270 m below the present level.

Bréhéret et al. (2003, 2008) have found dolomite in the Holocene sediments of the former Lake Sarliève, Massif Central, France. The dolomite lacked superstructure reflections and was analyzed to contain between 35 and 54 mol % $MgCO_3$. At least some of the dolomite found at this location must be of detrital origin, but the main part would have originated *in situ* in microbial mats (Bréhéret et al., 2008).

GERMANY

Dolomite rhombohedra occurring in the siliciclastic sediments of tidal flats adjoining the North Sea near Wilhelmshaven (northern Germany) were reported by Lüneburg (1958) and Gadow (1970). The carbonate fraction of the mainly siliciclastic sediments of these tidal flats is clearly of biogenic origin, as Lüneburg (1958) pointed out. A small proportion (about 10 %) of this carbonate fraction consists of dolomite, which in the view of Maschhaupt (1948) and Van Straaten (1954) had to be authigenic. Lüneburg (1958) noted a decrease of the total amount of the carbonate fraction with increasing depth, and explained this to be the logical result of anaerobic conditions prevailing in the deeper parts of the tidal flat sediments. The production of gases such as carbon dioxide and hydrogen sulfide would be responsible for the gradual dissolution of any carbonates present. Gadow (1970) was convinced, that the dolomite found by her would be authigenic. This suggestion is supported by evidence in the form of a photomicrograph published in the paper by Gadow (1970). This particular photograph (her Fig.20) shows an idiomorphic dolomite crystal without any signs of mechanical abrasion. The absence of traces of mechanical wear on a carbonate crystal from a siliciclastic environment, characterized among others by cross-bedding and other high-energy sedimentary structures, must be considered as evidence of an authigenic origin.

GHANA

In the cored Quaternary sediments of Lake Bosumtwi, a meteorite impact crater in the forests of southern Ghana (West Africa), authigenic dolomite was found by Talbot & Kelts (1986). Together with the dolomite calcite, aragonite and magnesium calcite (with up to 18 mol

% $MgCO_3$ as measured in X-ray diffraction) were analyzed. The dolomite appeared to possess superstructure reflections in X-ray diffraction. The lake is almost circular and measures 8 km in diameter; its maximum depth is 78 m. Surface water has pH 9.1 to 9.6, but the lake water from the anoxic zone at depths of more than 10 m has pH 8.1 to 8.5 . The anoxic conditions are the result of a large influx of organic matter from the surrounding forests (organic content of the sediments 8 to 20 %) in combination with the activities of methane-producing bacteria. "Dolomite has been recorded at several levels in Zone C. It occurs both in lamellae and as small (< 50-μm diameter) clusters of 1-5 -μm diameter grains ... Each of these grains is typically composed of interpenetrating submicron-sized dolomite rhombs, sometimes apparently arranged in a spiral pattern, perhaps due to step growth. Only rarely are single rhombs of a size comparable to that of the compound grains observed": Talbot & Kelts (1986, p.913).


GREECE


        Recent dolomite has been found to occur on the island of Naxos, Greece. From the geological setting near the Ormos Agiassou lagoon Koppenol et al. (1977) concluded, that the sediments accumulated there to a thickness of about 2.4 m, must be of Holocene age, probably not older than a few thousand years. Occurrences of pumice in these deposits could be correlated to eruptions of the volcano of nearby Thira (= Santorini) in historical times. The sediment itself consists of a top layer of organic mud, where active methane production takes place, followed by clays with a few wedges of sand. All layers contain quartz, illite and albite. Carbonates such as aragonite, calcite, and small amounts of dolomite were found. Aragonite, in the form of shell debris, is present especially in the top, but its percentage decreases rapidly with depth. The calcite found contains $MgCO_3$ , especially near the top of the cores, where percentages of about 10 mol % $MgCO_3$ were measured. The percentage $MgCO_3$ incorporated in the calcite fell to some 3 to 4 mol % at greater depths. From a number of pore water analyses Koppenol et al. (1977) concluded, that a marked degree of dilution by meteoric water must be taking place, and that the shores of the lagoon are determined by evaporation of normal sea water. No additions of dissolved species into the pore water took place, with the exception of calcium bicarbonate coming from landward springs near the lagoon. Koppenol et al. (1977) remarked, that the Ormos Agiassou lagoon (which measures at times 100 x 500 m) on Naxos usually dries up completely during the summer season.
        Authigenic dolomite and magnesite of Holocene age has been reported by Kyriakopoulos et al. (1990) to occur in the Soussaki area, about 65 km West of Athens, near the Canal of Corinth. The 10 m thick mass of unconsolidated secondary minerals has been formed on top of an ophiolite complex under the influence of post-volcanic emanations of hydrogen sulfide, carbon dioxide and water vapour. The magnesite was found in particular near serpentinites together with opal-CT. Dolomite occurs here together with magnesite, opal-CT, quartz, epsomite, gypsum, low-cristobalite, and volcanic glass.


HUNGARY


        Lindner (1947) described dolomite, occurring together with aragonite and calcite, in a hot-water spring in the city of Budapest, Hungary. In the muds of the Turkish Spring at the Rudas bath large amounts of dolomite together with barite, some aragonite and quartz along with minor amounts of pyrite and limonite were identified. The water of this particular hot

spring has a temperature of 315 K.

Dolomite and magnesite of Holocene age were described by Kriván (1953) in lacustrine carbonates ("*Teichkreide*") from the area in between the rivers Duna (Danube) and Tiszo. Leaching of carbonate from aeolian sand dunes was thought to have been the main source for the neoformation of the modern carbonates. Occurrences of Holocene dolomite and magnesite from various lakes of the same Danube-Tisza Interfluve region have been described by Molnár (1980, 1991) and Molnár & Botz (1996).

In 1970 Müller reported on an occurrence of "protodolomite" ($Ca_{56}Mg_{44}$ to $Ca_{58}Mg_{42}$) in the clay-sized fraction of the Quaternary sediments of Lake Balaton. Müller (1970) pointed out, that at least magnesium calcite must have formed in an authigenic way. Even so the possibility of an introduction of clastic carbonates (including dolomite) from nearby rocks can not be excluded. Every year during the warm summer months (this region of Hungary possesses a pronounced continental climate) fine-grained magnesium calcite was seen to form in the lake. Instrumental in the precipitation was an annual maximum in the growth of phytoplankton. In addition to the seasonal change in photosynthetic activity definite periodical changes in the water mass of Lake Balaton would lead to marked changes in the chemistry of the lake water. Earlier (in 1969) Müller had described the aquatic chemistry of Lake Balaton. The water of the lake contains somewhat less $Ca^{2+}$ and $HCO_3^-$ than the water of the river Zala, the supply river of Lake Balaton, but it is notably enriched in $Na^+$, $Mg^{2+}$, $Cl^-$ and $SO_4^{2-}$. The decrease in calcium bicarbonate showed, according to Müller (1969), that *in situ* precipitation of carbonate must be taking place. More details on Lake Balaton geochemistry were given by Müller & Wagner (1978), who also provided evidence on the age of the lake sediments. Lake Balaton must have been formed at the beginning of the Holocene era, as was found by way of pollen analysis.

Another occurrence of Recent dolomite in Hungary has been described by Molnár & Molnár-Murvai (1975). In the Holocene natron lakes of Fülöpháza, Kiskunság National Park, dolomite together with calcite was found. In X-ray diffraction the dolomite proved to be calcium-rich: $Ca_{55}Mg_{45}$ was measured (Molnár et al., 1980, 1995). The carbonate that precipitates initially is a magnesium calcite, to be changed later into dolomite. The various natron lakes vary in size from season to season, as the result of the interaction between rainfall and evaporation. Only the two largest lakes are permanent; two of the smaller lakes desiccate completely each summer. During the dry summer season the lakes are definitely alkaline (pH= 9 to 10), due to the presence of dissolved amounts of $NaHCO_3$ and $Na_2CO_3$. In winter the lakes loose their alkaline nature as the result of dilution with rainwater. In addition to seasonal changes in water chemistry caused by winter/summer volume changes, there are marked changes in the bicarbonate/carbonate balance related to plant growth and photosynthesis. Withdrawal of dissolved carbon dioxide takes place by green plants in spring and summer. Especially in the summer, aided by higher temperatures and increased evaporation rates, plants will cause the precipitation of the two carbonates (calcite and dolomite). High concentrations of dissolved carbon dioxide in the lake water in the autumn and winter may even dissolve again part of the previously precipitated carbonates. A detailed investigation of one of these lakes, the ephemeral Lake Péteri, has been published by Molnár & Schneider-Lüpkes (2001).


INDIA


Small amounts of modern dolomite have been found by Durgaprasada Rao et al. (1978) in carbonate lumps from the Lawson's Bay area, Visakhapatnam (East coast of India). The carbonate nodules that contain this dolomite, were found on the beach and in the intratidal zone of a small and shallow bay, where conditions for the inorganic precipitation of carbonate are

given, because of the prevailing high temperatures (Lawson's Bay lies not far from the equator). Water temperatures exhibit two maxima each year: one around April, when an average of 300 K is reached, and a second even higher maximum of 302 K in October. Salinity of surface water from Lawson's Bay ranges from 17.4 to 34.96 ‰. In the view of Durgaprasada Rao et al. (1978) the most likely cause for the precipitation of carbonate nodules and coatings of carbonate on beach pebbles can be found in the photosynthetic activities of two species of lime-secreting algae (*Amphiroa fragilissima* and *Chaetomorpha* sp.). In other parts of the Visakhapatnam coast no such carbonate coatings were found, most probably because of the absence of lime-secreting algae in those areas. A distinct seasonal rhythm in the process of carbonate deposition in the Lawson's Bay area has been noted. This periodicity finds its origin in seasonal successions in maximum growth, decline and regeneration of the algae. X-Ray diffraction applied to the carbonate fraction of the lumps showed, that mainly high Mg-calcite (with 23 mol % $MgCO_3$), smaller amounts of aragonite, and a trace of dolomite were present. Although no direct age measurements on the basis of isotope distributions were made, the Holocene age of the deposited carbonate could be inferred from circumstantial evidence: carbonate coatings occur on most pebbles and boulders of the present beach and the intratidal zone. The high percentage carbonate (66 to 87 %) of the lumps containing dolomite in comparison with the surrounding beach sand (with a carbonate content of only 2.0 to 3.5 %) suggests an authigenic origin (Durgaprasada Rao et al., 1978).

Sambhar Lake and Didwana Lake are two of the largest playa lakes in the arid Rajashtan state of NW India. Sambha Lake ($27^o$ 58' N / $75^o$ 55' E) measures some 22 km in length and is 3 to 11 km wide (Jakher et al., 1990). Its maximum depth (in 1984/1985) was only 3 m. The surrounding area is sandy and virtually devoid of plant growth. The salinity of the lake water fluctuates greatly: from an initial 5.14 ‰ (February 1984) to as high as 267.3 ‰ (May 1985) (Jakher et al., 1990). Didwana Lake is situated some 70 km to the west of Sambhar Lake and measures about 6.5 x 2.5 km; its maximum depth at the time of investigation by Jakher et al. (1990) was some 5 m. The presence of dolomite in Didwana Lake has been described by Wasson et al. (1984) and Roy et al.(2006).

The Holocene sediments at this location have recorded frequent large-scale fluctuations in for example salinity. Average air temperature is about 302 to 305 K during the summer months (July to September), and around 290 K during the winter time. Only during the summer months rain will fall (some 330 mm on average). Wasson et al. (1984) did not discover any direct source of magnesium ions in the catchment area, but were certain, that the authigenic carbonates were usually Mg-calcites. High percentages of dissolved magnesium ions did occur at times however, and these must have "... allowed dolomite formation apparently as a primary phase" (Wasson et al., 1984, p.355) to crystallize directly from the water of Lake Didwana. At the same time Wasson et al. (1984) reported on the presence of northupite ($MgCO_3.Na_2CO_3.NaCl$) in the sediments of the Didwana playa. Recent dolomite from the hypersaline Sambhar playa lake (Thar Desert) has been described by Roy et al. (2006). The two supply rivers of this lake, the Mendha and the Rupangarh rivers, carry water only during the monsoon months. During the rest of each year the water volume of Sambhar Lake decreases to a large extent, leading to salt deposits of even potassium salts. Four different concentric zones could be distinguished in the evaporites. Halite and calcite were found throughout all four zones. Dolomite was found exclusively in the outer ring (subject of course to the most pronounced fluctuations between wet and dry).

Dolomite has been found in the playa lake sediments of Sambhar Lake not only in surficial duricrusts (Roy et al., 2006; Sinha & Raymahashay, 2004), but also deeper down in the sediments (Sinha & Raymahashay, 2000, 2004; Sinha & Smykatz-Kloss, 2003). The Sambhar Salt Lake undergoes complete desiccation every summer, upon which an efflorescent crust forms, consisting of halite with minor amounts of dolomite, carnallite, polyhalite and sylvite

(Roy et al., 2006). The salt crust dissolves again during the next rain season. The parent rock of the neighborhood of Sambhar Lake playa does not include any ultrabasics, and the soils surrounding it only contain Mg-calcite. Therefore Sinha & Smykatz-Kloss (2003) inferred an authigenic origin for the dolomite found in Sambhar Lake sediments. Small amounts of what appeared to be Recent dolomite have been found by Glennie & Evans (1976) in the tidal sediments near Paccham Island in the Ranns of Kutch. The supratidal flats known as the Great Rann extend for some 300 km from east to west, with a maximum width of some 100 km, on the borders of the Arabian Sea, at the mouth of the Indus river near the border of India and Pakistan. Annual floodings during the Southwest Monsoon have given rise to an area of some 30,000 km$^2$ just above high tide level to be described as salt-covered desert areas (sabkhas). In general the Holocene sediments of the Ranns of Kutch contain little or no carbonates, with the exception of Paccham Island (Glennie & Evans, 1976).

Dolomite in algal mats dredged from Late Pleistocene carbonate sediments at the outer continental shelf off the northwestern India (near the Gulf of Khombat) were described by Rao et al.(2003). The samples had been collected at depths between 60 and 90 m, and radion carbon ages varied from 21,000 to 6,730 years BP. The carbonates are made up predominantly from aragonite faecal pellets, coral fragments, bryozoa and bivalves. Dolomite crusts present showed laminations, but in thin-section especially replacement of fossils by the mineral dolomite was noted. The laminations could have resulted from the actions of an algal mat biotope or cyanobacteria.

INDONESIA

According to López de Azcona et al. (1979) the living coral reefs in the Indian Ocean near Sanur, on the southeastern coast of the island of Bali, not only contain dolomite, but magnesite as well. There can be little or no doubt as to the age of these bioherms, because the reefs are being formed by living organisms at the present day. Although differential thermal analysis had been used as the main analytical tool, the identification of the relatively small amounts of magnesite and dolomite took place with X-ray diffraction. Amounts of magnesium calcite (with some 10 to 12 mol % $MgCO_3$) were found as well. The pure magnesite had been detected in tests of foraminifera.[4]

Holocene dolomite (with superstructure reflections) has been found by Middelburg et al. (1990) in the marine sediments of Kau Bay on the Island of Halmahera (eastern Indonesia). Dolomite is accompanied there by calcite and aragonite, and is often found in association with pyrite and apatite. At present the sediment is distinctly reducing as the result of bacterial sulfate reduction, but during late Pleistocene times Kau Bay must have been a fresh-water lake.

IRAN

Baltzer et al. (1982) found modern dolomite in the fine-grained sediments of the delta of the Mehran River (Iran). Although a large part of the dolomite present in all samples from the delta sediments must have a detrital origin, several indications point toward an authigenic origin for this dolomite. For one thing there is the intimate relation between algal filaments and the small dolomite crystals (of some 2 micrometer). The algae form the top layer of most sediments in the littoral part of the Mehran delta. In contrast to the rest of the sediments, the sediment underlying the algal mat has a dark color. The dolomite content of these sediments increases

with depth (to about 50 cm at maximum), in contrast to all other sampled locations. The most convincing argument for an authigenic origin of the dolomite was supplied by scanning electron microscopy: thin fibres of attapulgite not only on, but also *in* the dolomite rhombohedra. Partial etching clearly showed the clay mineral fibres actually penetrating the dolomite rhombs. The high percentage of attapulgite (up to 55 %) in the sediments under the algal mat contrasts markedly with the much lower percentages (of about 5 to 15 %) of attapulgite in other samples from the delta sediments. It is therefore likely, that both dolomite and attapulgite are to a large extent authigenic minerals. Dolomite formation seems to depend largely on the seasons of the year. Because of Precambrian salt diapirs emerging in the Hinterland, the water flowing through the Mehran River normally is very saline (more than 100 $g/dm^3$). The amount of dissolved salts changes abruptly, as soon as one of the heavy rainstorms sets in. Large amounts of sediments are being transported during the torrential rains, often in the form of flash floods, although these occur only a few times a year.

More dolomite of modern origin has been reported by Kelts & Shahrabi (1986) from Lake Urmia, one of the largest salt lakes in the world (measuring some 50 x 150 km) in northwestern Iran. The continental climate of this region causes winter temperatures as low as 293 K and summer temperatures near 313 K. The lake itself receives some 300 mm rain each year, but the evaporation rate (of 1500 mm) exceeds it by far. The shallow salt lake (maximum depth 13 m) undergoes an annual fluctuation in water level of about 1 meter. Organic productivity shows a distinct seasonal alternation, in which mainly leafy green algae and brine shrimps (*Artemia* sp.) participate. "The seasonal biologic cycle induces the precipitation of aragonite in surface waters ..."; and "... precipitation of aragonite or calcite can be induced by changes in temperature and evaporation, but more importantly in combination with shifts in $CO_2$ balances due to biological activity": Kelts & Shahrabi (1986, p.113). Dolomite probably of Holocene age, was found mainly in marginal eulittoral mudflats inhabited by blue-green algae.


ISRAEL


Recent dolomite occurring in a small lake on the borders of the Gulf of Eilat has been described by Aharon et al. (1977), Krumbein & Cohen (1977), and Lyons et al. (1984). The Solar Lake, located 18 km south of Eilat on the western coast of the Gulf of Eilat, measures some 140 m in length and about 65 m in width. Its maximum depth is 5 m. The lake is separated from the sea by a barrier, consisting of sand and pebbles of igneous and metamorphic rocks mixed with numerous molluscan shell fragments. Although the barrier is some 60 m wide and 3.5 m high, it cannot prevent seawater from entering the Solar Lake during high tides and strong winter storms. Solar Lake is hypersaline (especially during the summer months, when salinities up to 170 $kg/m^3$ are measured) due to the arid climate. In winter the in-flowing seawater mixes with rainwater and forms a layer of relatively low salinity on top of the highly saline brine. The changes between summer and winter cause an annual fluctuation in water level of 50 to 60 cm. According to Gerdes et al. (1985) seepage through the coastal barrier must be responsible for the observed inverse water stratification during most of the year (September to May). The high evaporation rates of the summer months are responsible for a marked lowering of the level of Solar Lake, so that a seasonally flooded littoral zone of considerable width borders the permanent pool in the middle of Solar Lake. From the observation that the average salinity had not changed significantly during the 6 years preceding their investigation, Aharon et al. (1977) concluded, that underground transport of pore water ("seepage reflux") must exist in the hydrological regime of Solar Lake.

Isotope measurements conducted by Aharon et al. (1977) showed how a large part of the
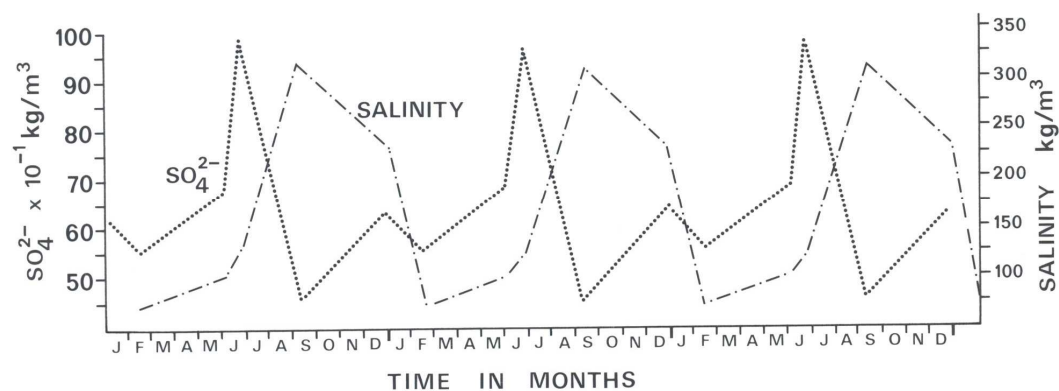
Fig.20 – Seasonal fluctuations in salinity (-.-) and sulfate concentration (…) in the water of a sea-marginal pool at Ras Muhammed, Sinai (extrapolation based on the 1-year diagram published by Friedman, 1980).

carbon of the carbonate sediments of Solar Lake has been derived from the decomposition of bicarbonate solutions under anaerobic conditions, presumably caused by the action of sulfate reducing bacteria. This aspect became clear from the composition of a layer of anoxic water near the bottom of the Solar Lake; a layer that is rich in dissolved $H_2S$. The origin of the organic compounds required as nutrient for the sulfate reducing bacteria is not hard to find: the shallow margins of the Solar Lake are covered by algal mats. The predominance of algae has to be contributed, in the view of Aharon et al. (1977), to the high salinity of the lake's water, which will prevent grazing by metazoans. The floor of the lake is covered by a crust of gypsum and aragonite crystals. The bottom sediments consist of black mud and loose gypsum crystallites. The deeper bottom sediments consist of laminations of alternating light bands (consisting mainly of aragonite and magnesium calcite) and black laminae of high organic content (as much as 40 wt. % organic compounds) in combination with iron sulfides. Deeper still the cores were seen to change into gypsum layers alternating with thin laminae of an algal mat origin. Dolomite was found in the cored bottom sediments only at depths of more than 30 cm below the sedimentary interface, and here exclusively in the carbonate laminae. Percentages of up to 90 % dolomite were found in these light-coloured carbonate layers. It is not an ideal dolomite that formed there: X-ray diffraction showed it to be a poorly ordered dolomite, with excess calcium carbonate (56 mol % $CaCO_3$). Its authigenic origin can not be doubted, since no possible sources of detrital dolomite can be found in the vicinity of the Solar Lake. Since the lake itself is less than 6000 years old (Aharon et al., 1977), the authigenic dolomite must be younger than that. In fact radiocarbon measurements by Friedman et al. (1973) and Krumbein & Cohen (1974) showed it to be around 4500 years old. In their study of the Recent sediments of the Dead Sea  Neev & Emery (1967) did not find any dolomite; but Begin et al. (1974) did report on dolomite (along with aragonite, gypsum and diatomite) from the lower member of the Lisan Formation, which originated in the Pleistocene precursor of the Dead Sea.

Recent dolomite together with magnesium calcite has been described by Magaritz & Kafri (1979) from carbonate nodules, occurring in the soil of the Zevulan Plain, North of Haifa. Usually these carbonate nodules have only small amounts of incorporated $MgCO_3$, but exceptionally high magnesium contents (reaching up to that of dolomite) were found in nodules, which formed near saline springs in the hydromorphic grumosols of the Zevulun Plain. These hydromorphic grumosols have a very shallow water table, so that during the wet winter season the soils are usually entirely flooded.

Dolomite of Quaternary age has been reported by Magaritz et al. (1980) from wells drilled into the coastal aquifer of Israel (Mediterranean coast). From mineralogical and isotopic investigations it could be concluded, that this dolomite must have formed in the zone of mixing between the fresh ground water and intruding seawater. The fresh water/sea water interface was found to be anything but a stationary level. In most of the cores two levels of dolomite formation could be distinguished. The upper level corresponds with presentday processes. The lower level must represent the interface between fresh water and sea water level of the coastal plain during the Pleistocene, when the level of the Mediterranean Sea was much lower. The actual precipitation of dolomite near these two different levels would be related to fluctuations in the fresh water/sea water interface due to seasonal changes in the water table.

Dolomite crystals in Quaternary sediments accumulating in a brine pan sabkha near Ras Muhammed[5]     on the southern tip of the Sinai Penninsula, have been described by Gavish (1980) and Gavish et al. (1985). The small pool (some 200 m in diameter) is fed by high tide flooding with water from the nearby sea, as well as by sea water from tidal lagoons close to this pool. The depth of the Ras Muhammed Pool and the size of the pool changes considerably with the seasons. High evaporation rates during the summer and fall minimize the pool: its salinity may rise to more than 300 ‰. During the wet winter months the pool's size is at maximum, and its salinity drops to about 100 ‰ (Gavish, 1980). The bottom of the pool is covered with algal

mats, which exhibit typical hexagonal patterns caused by desiccation cracks, rupturing the algal mat during dry intervals. Below the algal mat layer (of some 30 cm thickness) a layer of large gypsum crystals is found alternating with layers of fine-grained carbonate mud. This carbonate mud is made up from aragonite, magnesium calcite and dolomite.

More information on the hypersaline pool at Ras Muhammed has been published by Friedman (1980) and Friedman et al. (1985). They found, that the mechanism for replenishing the rapidly evaporating water from the Ras Muhammed pool (in the order of 3 m per year) would consist entirely of underground percolation through the highly permeable reef carbonate, which separates the pool from a narrow inlet of the Red Sea. The floor of the pool is covered by microbial mats and it was there, that Friedman and his colleagues found the modern dolomite. The large-scale seasonal changes in volume of the Ras Muhammed pool noted by Gavish (1980), lead to pronounced annual fluctuations in water chemistry. Samples taken during the years from 1977 to 1979 showed, that between the months of February 1978 and July of that same year the salinity of the water had increased from 80 to 260 g/dm$^3$ (Friedman et al., 1985). During the same period of time the concentration of dissolved sulfate increased from 6.4 to 11 g/dm$^3$. The salinity increased further in September 1978, but the sulfate concentration showed a sharp decrease. After that both factors would decrease again in a pronounced manner (Fig.20). Earlier measurements made during the years 1970 and 1971 had shown the Mg/Ca ratio of the pool water to change with the seasons from 2.4 to 19.8. Comparable seasonal changes were noted to take place in the microbial mats covering the floor of the pool. The algae flourish when water is high in winter and early spring (the water possesses a low salinity at that time of the year), but deterioration sets in during the fall of the water level and the accompanying increase in salinity during the months from spring to late fall. As Friedman et al. (1985) noted, the carbonate is deposited during the phase of abundant algal growth, when the water has a low salinity. Later in the year, when the water has become much more saline, carbonates no longer form, but gypsum and halite are being deposited. The marked annual fluctuations in concentration of dissolved sulfate would be caused by the phases of gypsum precipitation. In addition microbial sulfate reduction will influence the concentration of dissolved sulfate. The traces of this process in the sediment of the Ras Muhammed pool are not easy to miss ("... no one who has worked in these pools can avoid noticing the presence of H$_2$S gas": Friedman et al., 1985, p.234). Bicarbonate ions (from the decomposition of algal material) in combination with calcium ions (which remain behind after removing the sulfate anions from dissolved calcium sulfate) would unite to form calcium carbonate and dolomite.

Dolomite in association with anhydrite, gypsum, aragonite, calcite and magnesium calcite, found under a halite crust of some 30 cm thick, has been described by Gavish (1980) from a sabkha near Nabq, Gulf of Eilat. Sea water supply to this seasonal lake takes place, according to Gavish (1980), almost entirely through the coarse sediment, which forms the barrier between this sabkha and the Gulf of Eilat. During the dry summer months high evaporation rates increase the salinity of the enclosed water body to a considerable degree. In the following winter months the salinity decreases gradually as the result of renewed supply of seawater mixed with rain. Gavish (1980) distinguished three different zones in the sediment of this sabkha. In Zone I halite is found as a seasonal precipitate; formed during the summer, but dissolved again during the following winter rains. Dolomite was found especially in the deposits of Zone II, nearer to the central part of "Sabkha Gavish". In this central part the ground water table is only a few centimeters below the sediment's surface. The salt crust remains in place here, even during the wet winter months.

ITALY


In the city of Bologna dolomite has been found on the weathered marble surfaces of various buildings. Evidently this dolomite is of modern age. At the same time its origin must be authigenic, since the unweathered rock underneath does not contain any dolomite. As Del Monte & Sabbioni (1980) explained, there is a possibility, that the low-magnesium calcite (with ± 2 mol % $MgCO_3$) originally present in the marble has gradually changed into dolomite, but this conversion leaves open the origin of the required amounts of magnesium cations. The magnesium might have been supplied by components of the air pollution (for example as fly ash from coal or as industrial fall-out). This possibility seems the more likely because of the presence of metals such as Zn, Cu, V and Pb on the outer surface of the marble. These metals typical of the industrial revolution are not found in the non-weathered rock below the altered layer (of a few mm's thick). Accepting the idea, that atmospheric pollution caused the weathering of the marble (authigenic gypsum was found too, indicating a supply of sulfate ions from acid rain), will not fully explain the mode of formation of the mineral dolomite. Del Monte & Sabbioni (1980) aptly remarked that a high salinity is obviously not involved. The role of microbes (algae, lichens and fungi were found on the weathered surface) remains problematical, much as the possible significance of the pH of pore water. The presence of dolomite was established by way of X-ray diffraction. The dolomite was found to be calcium-rich: $Ca_{53}Mg_{47}$ . Electron microscopy convinced Del Monte & Sabbioni (1980), that the dolomite, unlike quartz and K-feldspar at the weathering surface, was not a wind-driven soil derivative. The dolomite could not have been older than the buildings: a few centuries at the most.

In the sediments of Lake Specchio di Venere, Pantelleria Island (SW of Sicily)  Azzaro et al. (1983) have found modern dolomite. Most of the sediment at this site consists of aragonite and dolomite. The lake water was measured to possess pH = 9.0 , but two different springs feeding the lake showed slightly acidic pH values (around pH = 6.3 to 6.9).

The possible formation of modern dolomite in sea-floor sediments in the Grotto Azzurra, Capo Palinuro (South of Naples), has been suggested by Stüben et al. (1996). However the host rock of this cave is a Jurassic limestone containing dolomite. Details concerning this dolomite found in the Recent sediment of this underwater cave are lacking at present.


JAMAICA


Land & Epstein (1970) described Recent dolomite, occurring in Late Pleistocene reefs on the northern coast of Jamaica. The dolomite was found in red algae of the Falmouth Formation, but not all red algae contained dolomite. Calcite and dolomite were intimately intergrown with the cell walls of the algae. The original mineralogy of magnesium calcite had been (secondarily) changed into calcite plus dolomite. The *c*-axes of the calcite and dolomite crystallites possess the same orientation as that of the initial magnesium calcite crystals. From isotope measurements Land & Epstein (1970) were able to conclude, that $C^{12}$ and $O^{16}$ isotopes had been added to the carbonate sediment from $CO_2$ transported by rain water into the Falmouth Formation. In a second paper on the same subject Land (1973) no longer ascribed dolomite formation to the actions of rain water in the vadose zone,[6]  but expressed the view, that since the dolomite-containing parts of the Falmouth limestone are enriched in magnesium, this magnesium must have been added to the system from sea water. Dolomite formation was explained to be the result of the dissolution of aragonite and Mg-calcite by $CO_2$-rich groundwater.[7]      The carbon dioxide would be dissolved in higher concentrations than that

which results from the equilibrium with atmospheric carbon dioxide only. Upon the escape of the excess $CO_2$ into for example seawater, precipitation would take place. Thus dolomite formation would be favoured by the mixing of ground water with seawater.

In the Holocene hardground overlying the Pleistocene Falmouth Formation on the northern coast of Jamaica, Mitchell et al. (1987) found modern dolomite. Age determinations by way of $C^{14}$ analyses gave readings of 1200 to 7630 years. Samples were taken at a water depth of 8 m and consist of pore fillings within corals, found in growth position. Most of this fine-grained material consists of magnesium calcite with 14 tot 18 mol % $MgCO_3$. In electron microscopy thin rims (of about 5 µm thickness) surrounding the magnesium calcite particles were noted; quantitative wavelength dispersive analysis showed these rims to contain up to 39 mol % $MgCO_3$. After selective leaching had been used to concentrate the material, Mitchell et al. (1987) were able to apply X-ray diffraction. This technique confirmed, that the dolomite contained only 39 mol % $MgCO_3$. Whether or not superstructure lines were found in the diffractograms was not made clear, but Mitchell et al. (1987) did report finding superstructure reflections in electron diffraction. Regarding the mode of formation of this particular occurrence of dolomite Mitchell et al. (1987) suggested mixing of seawater with meteoric water, but more likely "... the respiration of organic matter is suggested, possibly accompanying sulfate reduction, within the microenvironment of the coral skeleton" (Mitchell et al., 1987, p.560).


JAPAN


Dolomite of Pleistocene age was found on Okinawa (Ryukyu Islands, Japan) by Konishi et al. (1972). In several abandoned quarries north of Koza City the Pleistocene Naha Limestone was sampled. The carbonate rock is made up mainly from calcareous algae, corals and molluscs (such as *Ostrea*, *Chlamys*, *Anadara* and *Cypraea*). In thin section sand-sized fragments of these nannofossils were recognized in addition to fragments of older sedimentary rocks. Dolomite was found "... forming anhedral to subhedral interlocking aggregates, which replace original aragonitic skeletons (of *Halimeda*, hermatypic corals, molluscs, Ectoprocta, and serpulid tubes) and occupies the interparticle and interseptal voids as cement. Rim cementation by dolomite appears to be abundant": Konishi et al. (1972, p. 21). In X-ray diffraction magnesium calcite, calcite, aragonite and dolomite were recognized. Because in most cases the superstructure reflections typical of dolomite were absent, the samples from this location should according to Konishi et al. (1972) be described as "protodolomite".

Recent dolomite (not older than 10,000 years) has been found by Seki (1977) in pyroclastic rocks, which border the Seikan Undersea Tunnel, Japan. Contact with seawater initiated in these lava's the neoformation of clay minerals, siderite and dolomite. The formation of these authigenic minerals was explained by Seki (1977) to be the result of the introduction of sodium, potassium and magnesium cations from the sea water, and the gradual removal of calcium cations. After discussing in more detail the origin of the dolomite of the Seikan Tunnel, Liou & Seki (1980) confirmed the conclusion, that an interaction between sea water and penetrating meteoric water must have been responsible. Those interactions were, according to Liou & Seki (1980), of a periodic nature: compositional variations of the seepage waters correlated with the formation of the carbonates.

Aizawa & Akaiwa (1988) analyzed the "protodolomite" of Minamidaitojima Island, and found the iron content (12.8 ppm) to be present solely in the form of the bivalent cation: this Mg/Ca carbonate must have formed under reducing conditions.

KENYA

In the Holocene sediments of Lake Bogoria dolomite has been found by Renaut et al. (1986). Not as much as in the lacustrine sediments of the lake itself (which is a saline closed lake fed by hot springs), but especially in the stromatolitic carbonates on the shoreline dolomite was found. Although the water of Lake Bogoria is strongly alkaline (pH = 10.2), rain water was measured to be slightly acidic (pH = 6.23) and the water from one of the warm springs (Maji Moto) was near neutral (pH = 6.7).

In the exposed Holocene deposits of Lake Turkana small amounts of dolomite are present according to Owen & Renaut (1986). The level of the lake at this particular site is subject to large-scale fluctuations (Owen et al., 1982).

LIBYA

Rouse & Sherif (1980) found dolomite in Holocene sediments of the coastal sabkha in the western Gulf of Sirte, Libya. This enclosed coastal sabkha is flooded only during the winter, when the sea reaches higher levels than in the summer. Subsequent evaporation of the seawater leads to the precipitation of halite, gypsum, magnesite and dolomite.

MEXICO

In the Laguna Ojo de Liebre, one of several lagoons on the Pacific coast of Baja California (Mexico), dolomite of Holocene age has been found by Kinsman (1969). The Ojo de Liebre consists of three different coastal lagoons; the lagoons form the seaward edge of the Vizcaíno basin, a basin without runoff by rivers and without a detectable drainage pattern (Phleger & Ewing, 1962; Phleger, 1969). The prevailing climate is arid (maximum annual precipitation is about 2 cm), and high evaporation rates of about 150 cm per year prevail (Phleger & Ewing, 1962). Maximum temperatures range from 293 to 302 K, and minima of 281 K have been measured. The nearby Pacific Ocean causes humidity higher than in most desert regions. The Ojo de Liebre lagoon extends inland for more than 65 km; the lagoon is connected to the Pacific Ocean by a narrow inlet of some 3 km wide and only 12 m deep. The difference between high and low tide in the lagoon is approximately 1.5 m, with a maximum of 2.7 m (Phleger, 1969). Small lakes and ponds containing hypersaline water, are located on the border of the inner part of the lagoon. These ponds are separated from the lagoon by barriers of sand, silt and shell material built up by wave action in the lagoon. Tidal channels extend at several points through these levees and the tidal channels will overflow each time during high water tide. The inner edges of the intratidal flats form marshes populated by *Spartina* and *Salicorna* plants. The brine pans and basins are thought to be of Late Pleistocene age, but in the lagoon itself deposition of Recent evaporites takes place (Phleger, 1969). The bottom of the brine pans is usually covered by rubbery algal "pads"; a layer which consists of filamentous algae and diatoms. The living algae influence, through photosynthesis during the day time, the pH of the brine to a considerable degree: water entering the lagoon has a pH of 8.2 , but water in the brine pans may reach pH = 9.2 during the day. The brine ponds are situated in the high intratidal and seaward supratidal environments. Minerals deposited include aragonite, gypsum (but not anhydrite: Phleger, 1969; Kinsman, 1969), polyhalite (Holser, 1966), magnesium calcite,

magnesite, and dolomite (Kinsman, 1969). Although much halite is present in the top layers of the sediment, and may even reach several meters thickness locally, it is apparently not incorporated into the deposits of the Laguna Ojo de Liebre. To explain this discrepancy, Kinsman (1969) pointed out, that marine shells and other, more modern flotsam can be found many kilometres land inward of the lagoon. Any salt precipitated would be washed away by heavy storms, during which the sea floods the whole of the tidal environment (possibly aided by rainwater). Pierre et al. (1984) have confirmed the occurrence of modern dolomite in the south-eastern edge of the evaporite flats bordering the Ojo de Liebre lagoon, but they found the dolomite only in a grayish-green siliciclastic mud below the water table. The dolomite is well ordered with superstructure reflections.

Dolomite of Late Pleistocene age from the northeastern margin of the Yucatán Peninsula has been described by Ward & Halley (1985). Most of the coralline limestone here consists of Mg-calcite. "The distribution of the replacement dolomite is patchy, apparently being related to the irregular distribution of cavities. In many places, the rock is most dolomitic, adjacent to larger vugs, becoming less dolomitic away from cavities. This suggests that permeability was a major control on dolomitization"; Ward & Halley (1985, p.409). The majority of the dolomite crystals are glass-clear, but in a number of samples zoned dolomite crystals (in which thin layers of dolomite alternate with calcite) were found. According to Ward & Halley (1985, p.416) the complex mineralogy of such zoned dolomite crystals indicates ground water "... characterized by fluctuating chemistry."

Lock et al. (1991) found dolomite cementing a Holocene quartzose sand in the supratidal part of the Bahai Adair Bay, western Sonora, Mexico. The dolomite occurs at a depth of 15 to 50 cm below a top layer of algal (cyano-bacterial) mat. Immediately below this algal mat gypsum has been precipitated in the quartz sand. The percentage of gypsum decreases with depth, while at the same time the amount of dolomite increases. The supratidal part of the sediments in Bahia Adair Bay is covered by a white layer of sodium chloride. But little or no NaCl has been found in the underlying sand. The difference between high and low tides is quite large at this location: some 10 m. The climate of the region is arid, with an average rainfall of only 7 cm each year.


NAMIBIA


In the interdune areas of the Namib Sand Sea  Teller et al. (1990) have found modern (i.e., Late Quaternary) dolomite. This dolomite (together with aragonite and magnesium calcite) is present in a fragmented, case-hardened sandy carbonate crust forming the topmost sediment of the interdune playa's.

Dolomite from the Otjomongwa Pan, NNE of Aminius in the southwestern Kalahari, Namibia has been reported by Mees (2001). The salt lake contains thenardite and halite; its sediments consists mainly of quartz sand, carbonates (calcite and dolomite), and clay minerals (Mg-smectite and sepiolite). The Late-Quaternary deposits were deposited by run-off  from all sides of the pan. Earlier, in 1930, Gevers had described finding dolomite in the surface sediment of the Etosha Pan (an inland playa measuring 72 x 105 km) in northern Namibia. During the rainy season (January to April) the Etosha Pan will become filled with rain water, after which most of the water evaporates again during the rest of the year. The shores of the Etosha Pan are usually covered with salt deposits. Although dolomite rocks do occur in the neighbouring Otavi hills, Gevers (1930) was convinced to have found authigenic dolomite in Recent carbonate crusts. The carbonate crusts near to the outcrops of magnesium-rich rocks contained little or no dolomite, but the carbonate crusts on top of the sandy deposits typical of Ovambo Land did

contain dolomite. More recently Buch & Rose (1996) have confirmed the presence of modern dolomite in the (Quaternary) sediments of the Estosha Pan. The pedogenic calcretes containing this dolomite were often found associated with stromatolites in the seasonal playa lakes of the Etosha Pan.

## THE NETHERLANDS

Considerable quantities of dolomite have been described from the siliciclastic tidal mud flats south of the Dutch island of Schiermonnikoog by Crommelin (1943). In certain samples taken as much as 32 % of the 10 - 25 micrometer fraction of the sediment consists of dolomite crystallites. Crommelin (1943) refused to believe, that this dolomite had been transported by the Eems, Weser or Elbe rivers into the tidal flat environment, because the tidal flat sediments here lack the glass-like particles, fragments of industrial waste, typical of the sediment of these three rivers. In addition the overall mineralogical composition of the sediment from the tidal flats would be different from the continental mineralogy of the sediments carried by the Eems, Weser and Elbe rivers. After separating the dolomite from the rest of the carbonate fraction by way of acid treatment, Crommelin (1943) observed, how the individual dolomite crystallites possess a clear rhombohedral form. The authigenic origin of this dolomite hinted by Crommelin (1943), was endorsed by Van der Marel (1950). The latter author thought it unlikely, to explain the presence of dolomite in the Dutch tidal flats of the Waddenzee merely by a supply of wind-blown dolomite during the Riss-Würm interglacial: at least part of the dolomite had to be of an *in situ* origin. This observation has been confirmed by Van Straaten (1954), who had also found "dolomite in greater quantities" at this location. Chemical precipitation from sea water could not be ruled out, because, as Van Straaten (1954) stressed, even precipitation of halite takes place in summer on these tidal flats (but this salt will disappear again during the following autumn / winter).

## NEW ZEALAND

Orpin (1997) found dolomite (described as non-stoichiometric, calcium rich) in concretions dredged from the continental slope off Otago Penninsula, New Zealand. Radiocarbon measurements of a dolomite sample from this location gave an age of 33,000 ± 550 years B.P. Biogenic oxidation of methane leaking from the sediments was thought to be responsible for the formation of the carbonate (Ritger et al., 1987).

## PACIFIC ATOLLS

In 1896 a drilling up to a depth of 340 m into the carbonate sediments of the Funafuti Atoll[8] (Ellis Islands) was carried out. Judd (1904) noted in his description of the cores, how the organic matter rapidly decreased with depth. After 30 m almost all of the organic matter had disappeared. The carbonate sediment near the surface of Funafuti contains an average of 1 to 5 % $MgCO_3$ , but at a depth of 7.5 m about 16 % $MgCO_3$ was analyzed. Between 7.5 and 194 m the percentage magnesium carbonate decreases to values between 1 and 5 %. But it starts rising again at 194 m to reach a maximum of 40 % at a core depth of 201 m. This high value persists
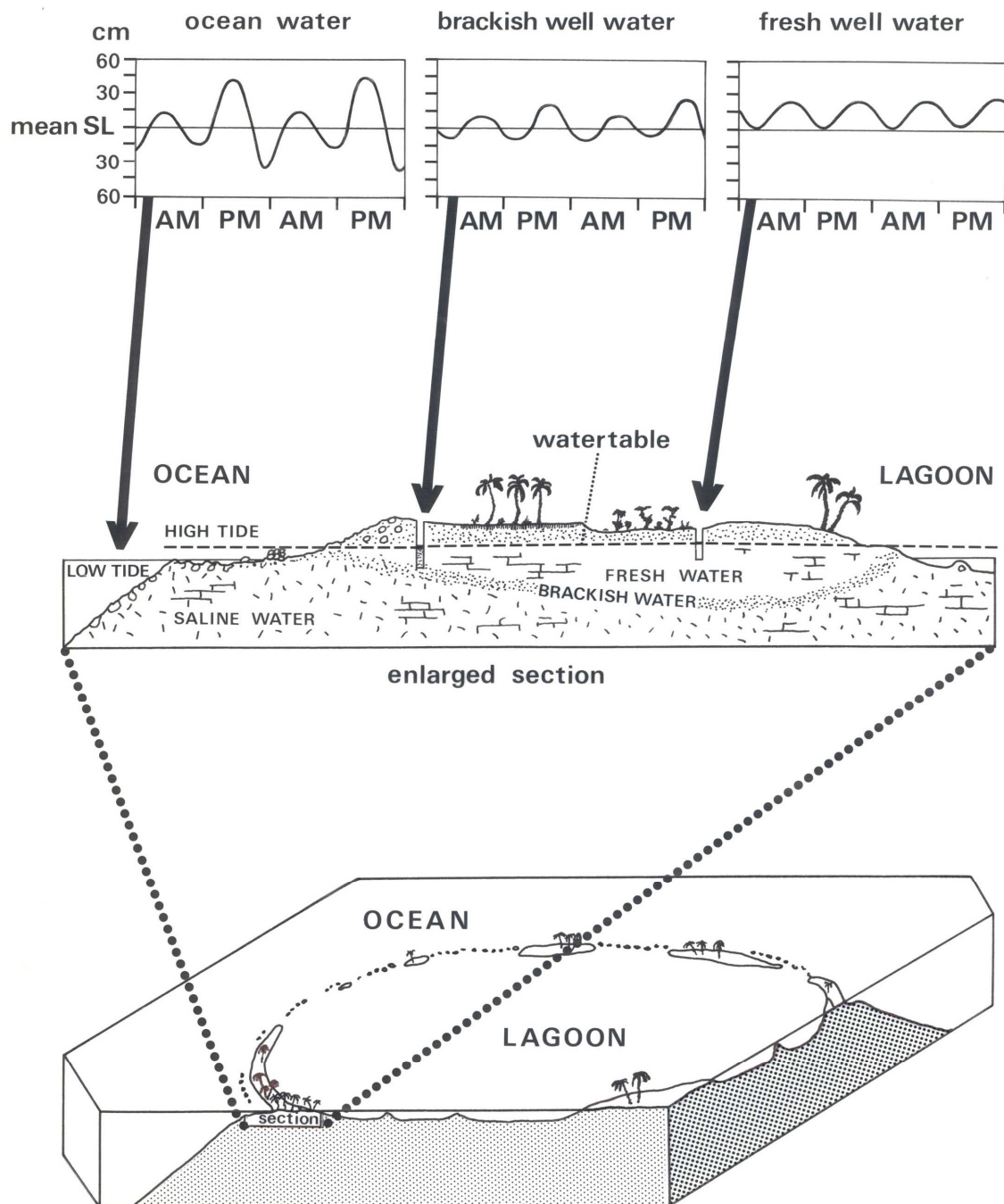
Fig.21 – Tidal periodicity controls the hydrology of atolls: the changes between low- and high water levels are most pronounced at the sea shore, but the brackish water layer and even the fresh water lens (if present) are subject to cyclic variations of their levels too (after Davis & DeWiest, 1966).

up to the maximum bore-hole depth of 340 m (Judd, 1904). The mineralogical examination of the same core by Cullis (1904) showed the presence of calcite, aragonite and dolomite (the three minerals could be recognized in thin sections due to the colouring technique developed by Lemberg, 1888 and Meigen, 1901). Crystals of dolomite were detected in the cores from Funafuti only in samples from depths greater than 194 m. The upper part (from 0 to 30 m) of the cores contained predominantly aragonite. The middle part (30 to 45 m) contained mainly calcite, and at depths exceeding 194 m dolomite was the predominant carbonate. Schmalz (1956) has repeated the mineralogical analyses of the Funafuti core, and by using X-ray diffraction confirmed the findings of Cullis (1904). In addition Cullis (1904) noted that the magnesium-rich carbonate of the lower part of the core did not consist of pure dolomite. The magnesium carbonate percentage of about 40 found in chemical analyses, was explained to be the result of a magnesium-rich limestone, because pure dolomite had to contain 45.65 wt. % $MgCO_3$ . From similar analyses of rock samples from Matea,[9]   Dana (1872) had been able to calculate an average composition of 38 % $MgCO_3$ and 62 % $CaCO_3$ . Some of the cores studied by Skeats (1905) contain dolomite "... from top to bottom", such as the cores from Vatu Vara. The presence of dolomite in core samples from the Pacific atolls Funafuti, Vatu Vara, Christmas Island, Mango, Namuka and Eua has been established by Skeats (1903, 1905). Other cores drilled into the coralline limestones of the Pacific atolls did not contain any dolomite (for example those from Nive, Vavau, Tongatábu, Niau, Guam and Makatea[10]  ). Cores from Christmas Island, Mango, Namuka and Eua contained only small amounts of dolomite. From his mineralogical analyses Skeats drew the conclusion, that little or no $MgCO_3$ would be incorporated into the younger carbonate reefs, which fringe the coral islands at present. Only samples from "deeper horizons" showed the presence of dolomite, and several ways for its distribution would exist. In a second paper devoted to dolomite formation in coral islands, Skeats (1905) repeated his view, that dolomite formation would not require concentrated brines (as Dana, 1872 had postulated), but that normal sea water would suffice, and that great depths of burial were not required either.[11]   Summarzing his observations Skeats (1905) stated, that not only shallow and $CO_2$-rich waters would lead to the formation of dolomite, but that the carbonate rock of the coral island had to be porous enough to allow for "... the percolation of seawater through the mass of the rocks" (Skeats, 1905, p.138).

Support for the theory of Skeats came from Van Tuyl (1918), who agreed on the explanation, that the dolomite of Funafuti and Christmas Island must have originated in shallow water. But not all of the dolomite found on the Pacific atolls could have had such an origin: Van Tuyl (1918) pointed out, that in the core of Vatu Vara dolomite does not occur at depths of less than 314 m. This observation showed according to Van Tuyl, that certain dolomites must have formed in the deeper parts of the ocean, the more since Van Tuyl (1918) considered sea level changes of 150 to 300 m to be unlikely.[12]   After a critical re-examination of the data from the Funafuti drilling Reuling (1934) reached a somewhat different conclusion as the origin of the dolomite. In Reuling's view dolomite formation was controlled by the rate of precipitation (*Ablagerungsgeschwindigkeit*) of the $CaCO_3$ phase, because the seawater "needed its time" to react with the calcium carbonate.

Dolomite presumably of Quaternary age has been found in cores from Kita-daito-jima, at least in the upper 100 m (as described by Ladd et al., 1948, p.53: "... cavernous, indurated, dolomitic limestone, containing reef-building corals, calcareous algae, and Foraminifera."). The dolomite content in this upper part of the core from Kita-daito-jima was high: from 78 to 90 %.[13]   Quaternary dolomite was found as well in samples from Eniwetok Atoll, Marshall Islands. The drillings on Eniwetok Atoll reached a maximum depth of 1400 m. First considerable deposits of soft, Quaternary reef limestones had been encountered. Deeper sections contained thick deposits of a more consolidated Tertiary carbonate (limestone with minor amounts of dolomite). Below this Tertiary limestone the volcanic core of the guyot was drilled.
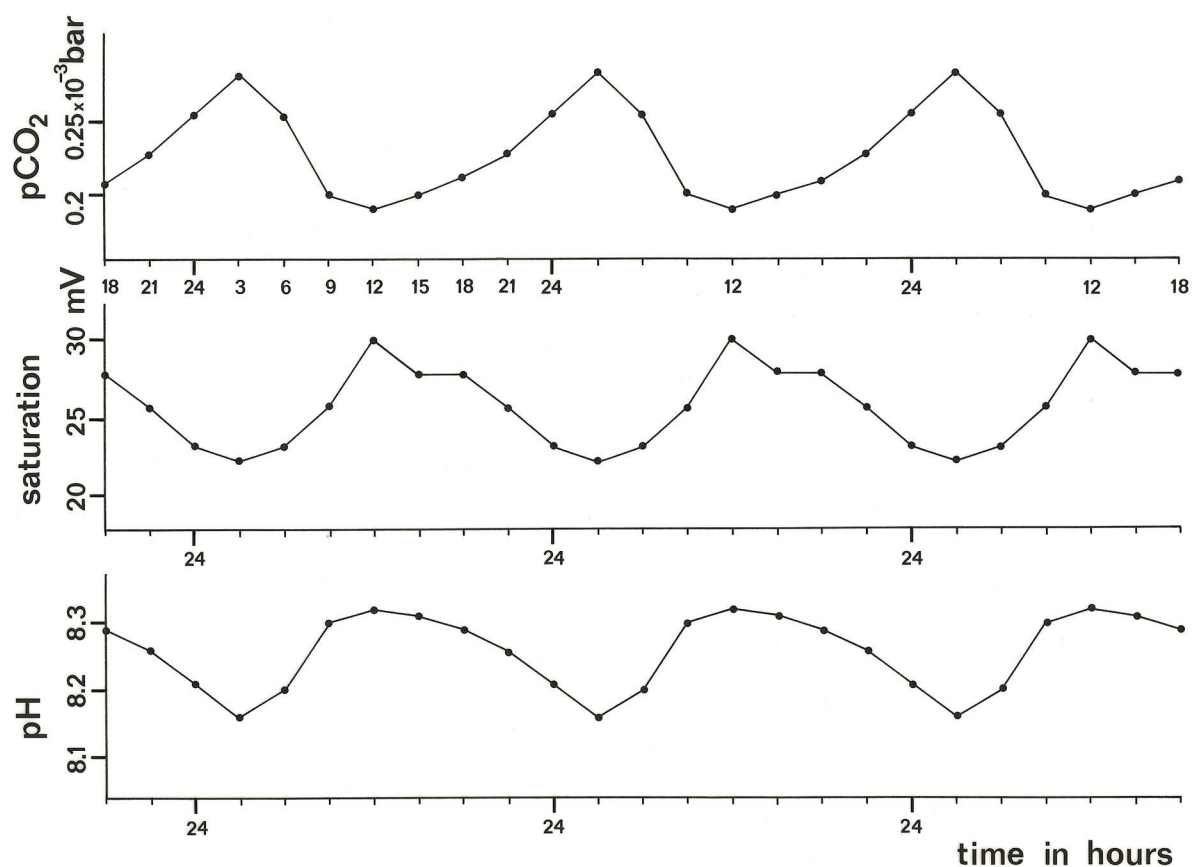
Fig.22 – Diurnal variations in dissolved $CO_2$, in carbonate saturation (measured relative to standard aragonite sand), and in pH in a surge channel of the ocean reef of Eniwetok Atoll (extrapolation based on data published by Schmalz & Swanson, 1969).
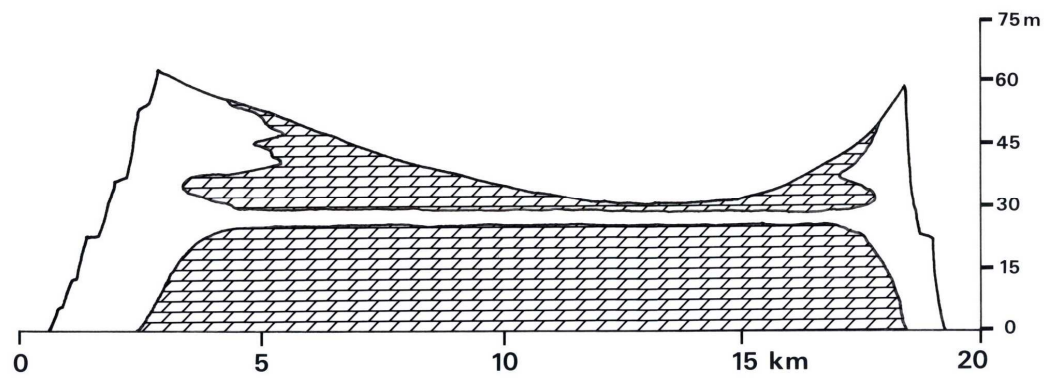
Fig.23 – Dolomite distribution in schematic cross-section of Niue Island (after Schofield & Nelson, 1978).

Fig.24 – Annual periodicity of rainfall (average from 1906 to 1978) and calculated evapo-transpiration (….) (average from 1948 to 1957) at Niue Island (modified after Jacobson & Hill, 1980).

The soft Quaternary and Tertiary limestones were found to be very porous, and to possess an extremely high permeability. Evidence came from measurements made in one of the bore holes after completion of the drilling itself: water pressure in drill hole F-1 on Eniwetok followed closely the ebb and flo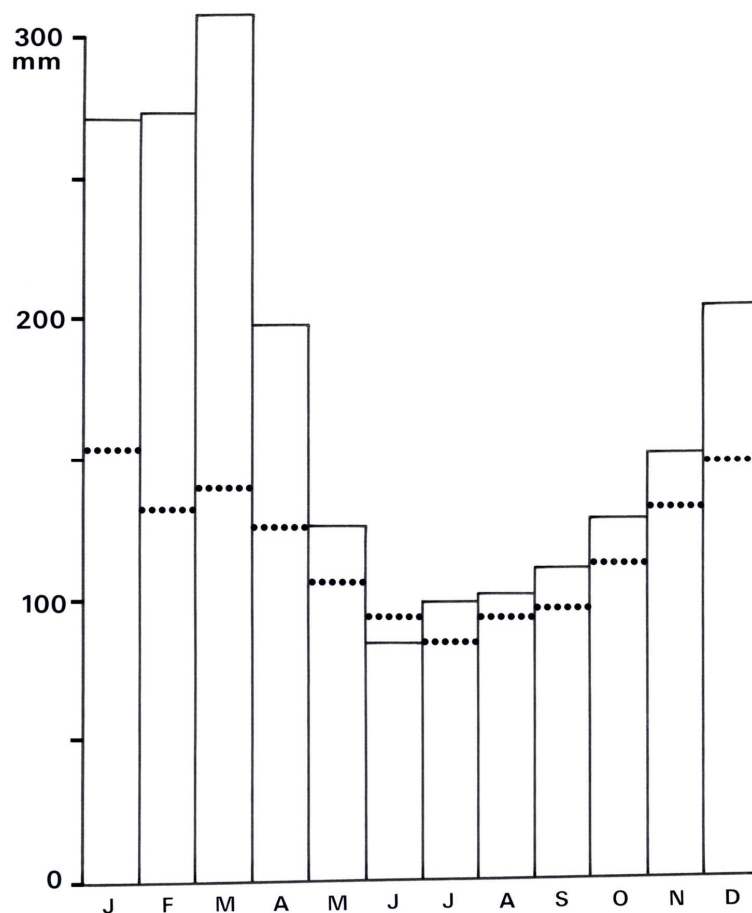w movements of the surrounding sea. Ladd et al. (1953) considered this observation the more surprising, because the drill hole had been cased solidly from the very surface down to a depth of 600 m. Hydrological measurements on other atolls have confirmed the observation made on Eniwetok: Davis & DeWiest (1966) stated, that the ground water of atolls is always subject to marked fluctuations.

Ground water forms by infiltration of rainwater, and then floats on the heavier seawater in the pores of the carbonate sediments. But this seawater moves in and out of the sediment under the influence of the tides. The relatively high permeability of the reef material of the atoll is the cause of the phenomenon that the whole mass of pore water, fresh and brackish water alike, fluctuates in unison with the ocean's tides (Fig.21). The existence of such large-scale fluctuations in the water table of Eniwetok has been established by Buddemeier & Oberdorfer (1986), thereby confirming the observations made earlier by Ladd & Schlanger (1960) and Swartz (1958). Using a direct measuring technique Lewis (1987, p.1168) observed how "… groundwater flux onto corals on the west coast of Barbados varies spatially, fluctuates with the tidal cycle, and is generally higher in the wet season than in the dry season." Saller (1984) argued, that the dolomite present in the Eocene strata of Eniwetok cores postdated the brittle compaction stage of lithification. Because dolomite formation took place at depths of more than 900 m below sea level, Saller (1984) inferred, that undersaturation with respect to calcite of the contacting cold seawater must have played an important role. Goldstein et al. (1991) studied the freezing points of fluid inclusions in the Eocene strata from Eniwetok. The inclusions showed evidence of salinity about twice as high as that of normal sea water at the moment of sedimentation.

Ladd et al. (1953) could not discern any specific pattern in the stratigraphic distribution of dolomite on the Pacific atolls. In only one of the three cores from Eniwetok known to Ladd et al. (1953) dolomite was present, and there only below a depth of 1340 m. No dolomite was found in the cores from the Fiji Islands. The drilling of Funafuti reached a maximum depth of 347 m.

Dolomite was found only from 183 to 347 m in this core. Dolomite is present in the upper 122 m of the cores from the atoll of Kita-daito-jima. On Midway Atoll (Hawaiian Islands) dolomite occurred in a layer between 130 and 150 m depth; from 171 to 285 m some dolomite interspersed in the Miocene limestone was found (Ladd et al., 1970). On Bikini the drillings could only reveal the absence of dolomite; similarly drillings on Michaelmas Cay and Heron Island (Great Barrier Reef, Australia) (Ladd et al., 1948) and Maratoea (Borneo, Indonesia) (Kuenen, 1947) did not bring any dolomite to light. As a consequence any theory postulating a relation between dolomite formation and water depth (such as the theories of Skeats, 1903, 1905 and Van Tuyl, 1918) had to be abandonned in the opinion of Ladd et al.(1953). (The same argument goes against the theory of Saller, 1984.)

From his studies of the cores from the atolls of Funafuti, Kita-daitô-jima and Eniwetok, Schlanger (1963) drew several conclusions regarding the formation of dolomite. In the first place Schlanger (1963) observed, that the presence of dolomite in the cores was not a simple function of depth or pressure. In the second place no relation between the duration of immersion of pre-existing limestones in the surrounding seawater and the presence or absence of dolomite existed. In this respect Schlanger noted, that "... mere soaking in sea water does not cause the formation of dolomite" (Schlanger, 1963, p.1011). Nor could a relation be discerned between porosity of the pre-existing limestones making up the atoll and the presence or absence of dolomite. Neither did the fossil content correlate with the occurrence of dolomite. All that could be concluded, was that "Each atoll displays a unique pattern of distribution of dolomite, and the
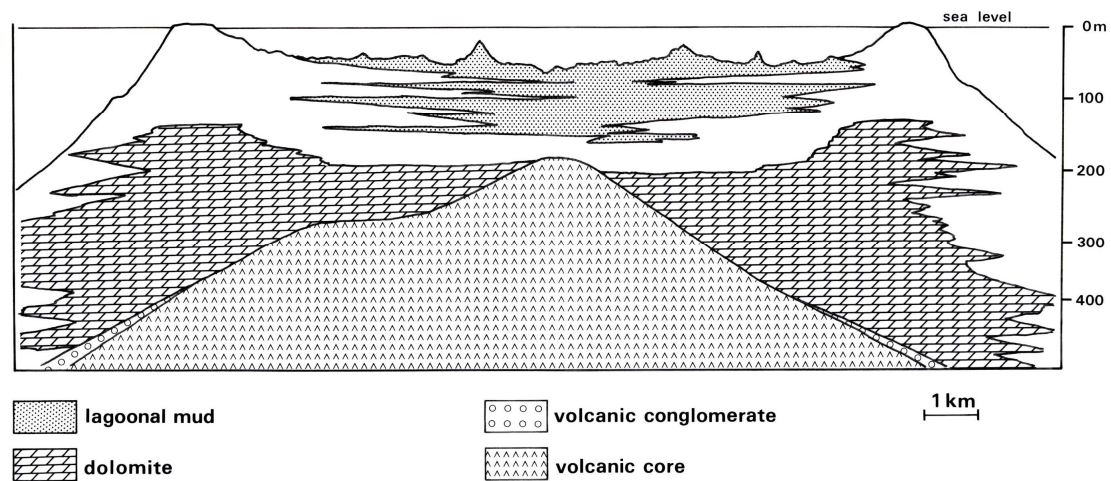
Fig.25 – Distribution of dolomite in the underground of Mururoa Atoll (after Aïssaoui et al., 1986).

cause of the alteration must be sought within the atoll itself": Schlanger (1963, p.1008). Berner (1965 B) claimed to have found a model to explain all of Schlanger's observations: the dolomite of the Pacific atolls would have been formed as the result of a reaction between hypersaline brines and the pre-existing skeletal limestones. The irregular pattern of distribution of the dolomite within the cores indicated, that not as much the chemistry of the solution in contact with the submerged limestones or the duration of this contact, but solely the pre-existing mineralogy would determine whether or not dolomite would form. In addition Berner (1965 B) pointed out, that the observed thin interlayers of calcite and dolomite within zoned dolomite crystals must have resulted from fluctuations in chemistry of the sea water. Such fluctuations were found especially in a shallow water environment, such as in hypersaline lagoons, where the salinity fluctuates as the result of seasonal changes in evaporation and rainfall. One addition must be made at this point: not only in hypersaline lagoons the physico-chemical parameters fluctuate, as Berner pointed out. Such fluctuations can be found in virtually all tropical and subtropical marine waters, as for example Schmalz & Swanson (1969) have described. This periodicity finds its ultimate origin in day / night alternations, and can be measured for example by way of periodical changes in dissolved carbon dioxide, in carbonate saturation, and in pH (Fig.22). Photosynthesis by algae in particular leads to a marked decrease in the amounts of dissolved carbon dioxide, reaching a minimum in the late afternoon; the pH reaches its maximum at this time. Each night respiration creates amounts of dissolved carbon dioxide, and the pH therefore falls again. The overall effect of these diurnal changes on for example the carbonate sediments of Eniwetok Atoll, is that dissolution takes place at night followed by re-precipitation during the day.

On several other Pacific atolls modern dolomite has been found. Elschner (1913) reported finding dolomite on top of the youngest carbonate deposits on the atoll of Nauru. Skeats (1918 A) stated, that the atolls Yathala and Kambara consisted "... from top to bottom" of dolomite. At different places on Atiu and on Mangaia (Cook Islands) dolomite was found by Marshall (1930). (Marshall, 1930, p.57 noted: "The infillings in the lacunae of a few coral skeletons show alternating layers of calcite and dolomite. There is every reason to think that all these mineralogical changes have taken place at or near the sea level.") Dolomite formation was described by Daly (1945) as taking place on the island of Lau (Fiji Islands). Schlanger & Tracey (1970) described dolomite from Jarvis Atoll. Chevalier & Repellin (1978) found modern dolomite in the carbonate sediments of Fangataufa Atoll: it occurred in very limited amounts in the upper 100 m of the core, but massive amounts of dolomite were found from 100 m to the end of the core at 383 m depth. In contrast to the core samples from nearby Mururoa, amounts of calcite were not found below the dolomite. In chemical analyses the rather exceptional composition of the dolomite from Fangataufa was established. The dolomite contained in several instances more $MgCO_3$ than the usual 50 mol % (as much as 57 mol % was measured). From the limited number of samples studied by them, Chevalier & Repellin (1978) drew the conclusion, that dolomite formation must have been accompanied by dissolution phenomena and by a pronounced change in organic substances.

Dolomite from the former atoll of Niue Island has been described by Fieldes et al. (1960), Schofield & Nelson (1978), Rodgers et al. (1982) and Aharon et al. (1987). There the process of dolomite formation did not affect the whole of the upraised former atoll: only the "core" has been changed into (secondary) dolomite (Fig.23). A relation between dolomite formation and radio-active elements was found.[14]   The hydrogeology of Niue Island has been described by Jacobson & Hill (1980). The former rim of the atoll can be recognized as a virtual circular ridge some 60 m above sea level; the original floor of the atoll now is an internal basin some 35 m above sea level. Limestones up to Miocene in age, rest on a volcanic core. Resistance measurements showed the freshwater lens to extent to a depth of 40 to 80 m below the centre of the island and to depth of 50 to 170 m below the rim of the former atoll. Annual
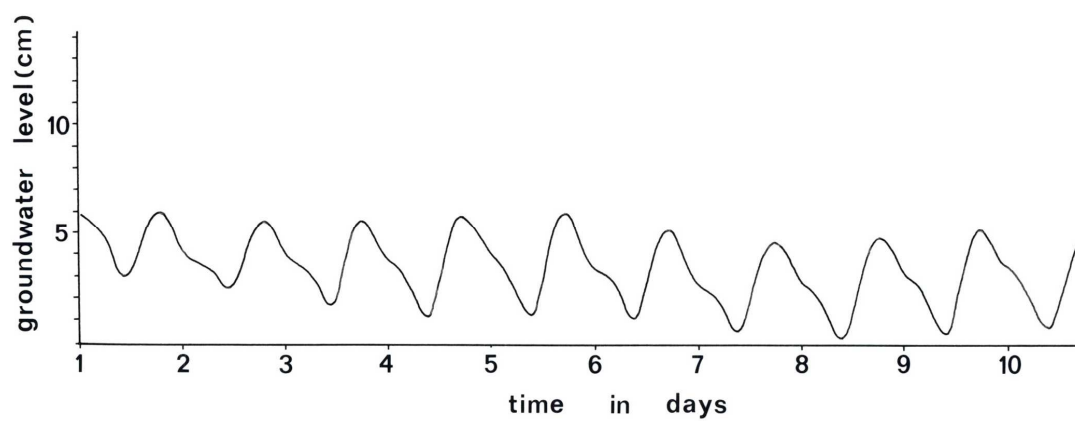
Fig.26 – Tidal fluctuations in level of the groundwater table (arbitrary scale) at "site 1" of the Abu Dhabi sabkha (after McKenzie et al., 1980).

rainfall recorded at Alofi ranged from 1065 to 3185 mm; the mean value is 2041 mm (measured from 1904 to 1979). Throughout the year most rain falls in the months of December to April, and only occasionally in June a temporary deficit in the supply of rainwater causes evaporation to predominate (Fig.24). High permeability of the porous and fissured limestone can be witnessed after each heavy rainfall: the ground of Niue Island is dry again after only a few minutes (Jacobson & Hill, 1980).

Recent dolomite has been found by Bourrouilh (1973 A) on the pseudo-atoll of Clipperton. That island consists of an outcrop of trachyte, rising up to a few meters above the sea, completely surrounded by a living, circular coral reef. The reef measures some 50 to 200 m across, and encloses a large body of standing water. The water attains a maximum depth of 45 m, and its salinity varies considerably (from 3.6 to 5.3 $kg/m^3$ at the surface, through 13.4 to 17.9 $kg/m^3$ at the bottom, to as high as 33.7 to 34.5 $kg/m^3$ in an intermediate lens: Bourrouilh, 1973 A). The enclosed water is dark, smells of $H_2S$ and possesses a pH, which ranges from 7 to 11. Little or no animals live in this water, but an abundant micro- and macro flora is present. The atmosphere of Clipperton is extremely humid and most of the annual rainfall takes place in the summer months. A small percentage (about 5 %) of the carbonate sediments accumulating at the bottom of the stagnant water body consists of dolomite.

Dolomite in the Recent carbonate sediments on the island of Lifou-Lifou (Loyalty Islands, New Caledonia) has been described by Bourrouilh (1973 A,B; 1975). The occurrence of dolomite on Lifou-Lifou was found to be closely related to the fluctuating water table of the carbonate sediments (Bourrouilh, 1973 B). On the island not only seasonal fluctuations in the level of the ground water occur, the concentration of dissolved salts in the ground water also changes annually. On the nearby atoll of Maré dolomite of Quaternary age has been found by Carrière (1987).

From the drilling into the calcareous reef limestone at Grand Tenia (a small island in the St. Vincent Bay of New Caledonia) dolomite was reported by Coudray (1971) and Chevalier (1973); the dolomite was found especially at depths from - 130 to - 226 m. But the main part of the one core drilled at this site consists of organic limestone, made up from fragments of foraminifera, radiolaria, echinodermata, calcareous algae, corals, gastropoda and lamellibranchiata. The mineralogy of the bioclasts measuring between 0.2 and 2 mm is predominantly that of magnesium calcite (with some 10 % $MgCO_3$) and aragonite (Coudray, 1971).

The Mururoa Atoll (Tuamotu Archipelago, French Polynesia) consists essentially of an ancient volcano, which ceased its activities at the end of the Miocene, covered by a mass of carbonates, including a thick lens of dolomite. Numerous drillings (described for example by Lalou et al., 1966; Chauveau et al., 1967; Chevalier, 1973; Repellin, 1977; and Trichet et al.,1984) have shown, that the dolomite lens has its maximum thickness at the periphery of the carbonate sequence and thins out towards the top of the former volcano. At the same time the dolomite lens was seen to disappear rather abruptly at the outer perimeter of the carbonate deposits (Fig.25). The coralline limestone of the reef reaches down to 350 to 450 m, but its maximum depth is 900 m. The climate of Mururoa is tropical humid with a total rainfall in for example 1965 of 1350 mm. The average temperature in that same year was 298 K (Repellin, 1977). The ring-shape of the atoll is not continuous, but actually consists of a series of islets ("motu"). These small islands are not exactly flat; on many of the motu depressions, often filled with rain water, are found. The small lakes are 1 to 2 m deep at maximum; the water contains large amounts of organic material in suspension and it smells of $H_2S$ . The organic material must have been derived from the plant growth (coconut palms and palms of the *Pandanus* species). The limestone associated with the dolomite lens, which occurs at a depth of 125 to 374 m, consists of biocalcarenite and locally even a conglomerate. The dolomite itself is quite compact and shows in thin section little or no porosity. Carbon isotope measurements failed to

give any results, and therefore this dolomite must be older than 35,000 years. This relatively old age of the dolomite might well be related to the occurrence of two different instances of a considerable hiatus in the coralline deposition. These discontinuities in coral growth correspond to Pleistocene falls of sea level (Trichet et al., 1984). Mineralogical details of the Muroroa dolomite have been published by Trichet et al. (1984): the dolomite contains 40 to 45 mol % $MgCO_3$ . No relation between eustatic sea level changes during the Quaternary and dolomite formation could be inferred from the cores taken on Mururoa; which excludes at the same time a relation between the mixing of fresh water (or brackish water) and sea water (Trichet et al., 1984). A different conclusion in this respect was drawn by Aïssaoui et al. (1986) after a re-examination of the cores from Mururoa. Mainly petrographic evidence was used in support of the conclusion, that "... dolomitization is essentially a process involving dissolution-precipitation" (Aïssaoui et al., 1986, p.45). The hydrological model responsible for dolomite formation at Mururoa would be controlled by the differences in porosity between the fine-grained, chalky sediments of the inner platform and the more open biogenic network typical of the peripheral (reef) wall. Sea water would be pumped upwards to the centre of the carbonate platform, where mixing with fresh water from the meteoric lens would take place. The driving force would be a temperature difference between the underground core of the atoll and the surrounding seawater. Exactly in the zone of mixing of seawater and fresh water the dolomite would form. The relief of the land controls to a large degree the dimensions of the fresh water lens. In order to form measurable amounts of dolomite, the meteoric aquifer must have a minimum size, as Aïssaoui et al. (1986) stressed. This model would explain why the Mururoa sediments contain dolomite up to that level, where an initial platform island changed into a true atoll with a lagoon in the centre. In a similar way marked lowerings of the world sea level during the Pleistocene would have been responsible for various levels of dolomite formation. Small islands and atolls emerged during those phases, and obtained fresh water lenses of considerable dimensions. High-magnesium calcite would have been dissolved and would have been instrumental in bringing about dolomite formation at Mururoa (Aïssaoui, 1988).


PERSIAN (or ARABIAN) GULF


In the carbonate sediments of tidal flats (sabkhas) bordering the Persian (or Arabian) Gulf dolomite of Holocene origin has been found. The sabkhas are inundated only a few times a year, when spring tides reach over the lagoonal sediments or when the *shamal* storm wind drives masses of Gulf water over it. Each sabkha is bordered seaward by abundant algal vegetation, marking the limit of the intratidal zone. The tides of the Persian Gulf are diurnal with a spring range of 2.10 m and a neap range of about 0.75 m; the maximum tidal range in vertical sense is about 1.20 m (Schneider, 1975). The pore water of the sabkha sediments follows to a marked degree the tidal fluctuations: "The crucial question regarding the height of the water table relative to sea level was difficult to resolve because both levels fluctuated" (Hsü & Schneider, 1973, p.419) (Fig.26).

The dynamic aspects of the hydrology of the sabkha were explained in some detail by Patterson (1972). The water table of the broad, gently sloping planes of the sabkhas is never more than 1 to 1.5 m below the surface. During storms onshore winds will drive sheets of seawater several kilometers inland over the sabkha. This accumulated seawater is rapidly concentrated by strong evaporation during the daytime. In the explanation of Patterson (1972) these desiccating quantities of brine are responsible for the formation of dolomite, magnesite and gypsum/anhydrite.

The authigenic minerals of the sabkha sediments include aragonite, magnesium calcite,

gypsum, celestite (Evans & Shearman, 1964; Kendall & d'E Skipwith, 1969 A), anhydrite (Kinsman, 1965, 1969; Cuff, 1969; Bush, 1973), dolomite (Wells, 1962; Curtis et al., 1963; McKenzie, 1981; Kenig et al., 1991; Baltzer et al., 1982, 1994), magnesite (Kinsman, 1965; Bush, 1973), huntite and polyhalite (Kinsman, 1965; Butler, 1969). Kendall & d'E Skipwith (1969 A) recognized three parallel zones of mineral parageneses in the intra- and supratidal sediments of the sabkha bordering the Khor al Bazam lagoon on the coast of Abu Dhabi: 1) above the high water line (= supratidal) anhydrite is found in the capillary zone of the sediment, and gypsum plus dolomite are found below the water table; 2) anhydrite, hemihydrate, gypsum, halite and dolomite precipitate near the mean high water line; and 3) gypsum, celestite, plus dolomite are found in the upper part of the intratidal zone.

According to Illing et al. (1965) dolomite is found only in the topmost layers of the sabkha deposits, and it is especially abundant in the top 60 to 90 cm of the sediment. Dolomite was seen to diminish rapidly with depth and to disappear towards the open sea. Away from the shoreline the percentage of dolomite increases at the expense of aragonite. The dolomite crystals found in the sabkha consist in general of true dolomite with superstructure lines rather than "protodolomite". The chemical composition of this Holocene dolomite varies between $Ca_{53}Mg_{47}(CO_3)_{200}$ and $Ca_{55}Mg_{45}(CO_3)_{200}$ (Illing et al., 1965). Gypsum was found abundantly on the sabkha, especially in those deposits that contained dolomite. The size of the gypsum crystals was noted to increase landward, coinciding with an increase in dolomite content. Little or no anhydrite was found by Illing et al. (1965), but Shearman (1963) reported layers of anhydrite up to 30 cm thick from the Abu Dhabi sabkha.

The climate predominating in the Persian Gulf area is hot and dry: the average air temperature of the region is 314 K, with an average minimum of 286 K (Schneider, 1975). According to measurements published by Bush (1973) the average rainfall in the area is some 3.7 cm/year, and the net evaporation averages about 124 cm/year. As a result the net evaporation rates on the sabkha are extremely high. The high rate of evaporation does not lead to the precipitation of soluble salts, but it does raise the salinity of the pore water to extreme values. Salinity of the nearby open sea is 38 ‰, but the salinity of the groundwater of the sabkha averages 60 ‰, and extensive evaporation in the supratidal environment may lead to salinities as high as 830 ‰ (Schneider, 1975). Although in the latter case the saturation limit for halite precipitation has been surpassed, no halite or other salts are known in large quantities from the sabkhas. The reason for this fact can be found in the drastic changes in humidity of the air following the day/night rhythm. Illing et al. (1965) noted, that the thin crust of halite, which precipitated during the day on the sabkha sediments, would vanish again during the night: dew dissolves the salt. Schneider (1975) reported, that the relative humidity of the air in this area changes from 40 % during the day to more than 90 % at night. Removal of halite by dew answers the question raised by Hsü & Schneider(1973), why no deposits of halite could be found on the sabkha ("the amount of halite is far less than it should be...": Hsü & Schneider, 1973, p.421). Another possible mechanism of removal has been suggested by Kinsman (1969): some halite will be blown away by the wind and some of it will dissolve again in the sea water of the masses which flood the sabkha during storms.

In the cored Holocene and Late Pleistocene sediments of the Gulf of Oman dolomite has been found by Stoffers & Ross (1979). Other carbonates present include calcite, Mg-calcite (with 8 to 10 mol % $MgCO_3$ ), and aragonite. The dolomite present was identified as "protodolomite" in some cases, but pure dolomite was found as well. Even in dust samples collected on board the research vessel *Atlantis II* nearby at sea, dolomite (along with illite, chlorite, palygorskite, quartz and calcite) was detected.

Patterson & Kinsman (1982) were quite specific concerning the conditions, under which dolomite is being formed in the Abu Dhabi sabkha: 1) chloride concentrations between 3.25 and 3.75 mol/kg; 2) Mg/Ca = 6 or more; 3) pH between 6.3 and 6.9 ; 4) a minimum $pCO_2$ of $10^{-2}$ to

$10^{-3}$ bar; 5) temperature between 298 and 313 K; 6) saturation with respect to gypsum; and 7) a reducing environment in association with hydrogen sulfide. The dissolution of aragonite formed an essential part of the process of dolomite formation, because Patterson & Kinsman (1982) had found partly dissolved aragonite cerithid shells and moulds of cerithids lined with dolomite. Even more convincing is the large-scale tendency for the percentage of aragonite in a core to vary inversely with the percentage of dolomite. No correlation could be found between the amount of dolomite and the distance from the shoreline. But Patterson & Kinsman (1982) observed how sediments with high amounts of authigenic dolomite were filled-up remnants of intertidal channels of the sabkha. Kenig et al. (1991) found a distinct correlation between Holocene dolomite (less than 1,000 years old) and mangrove vegetation at Ras Ghanada, Abu Dhabi. Dolomite was found there, where anoxic pore water (made anoxic by decaying organic matter) is being oxidized in microbial mats overlying aragonitic mud. This view has been repeated by Baltzer et al. (1994), who had studied the dolomite lens present at shallow depth (less than 1 m) in the northeastern part of the Abu Dhabi sabkha. Porosity created by root canals of mangrove trees would influence the re-oxidation of organic matter present in the solutions of the paleosol. The roots of living mangrove trees (*Avicennia* sp.), in combination with bacterial decomposition of organic material, would be responsible for a reducing environment with slightly acidic pH.

The presence of dolomite in the Recent sediments of Kuwait Bay has been recorded by Mohamed & Al-Shamlan (1979). Virtually all of the 10 samples from the tidal flat sediments contained dolomite (in addition to calcite and aragonite). Dolomite of Holocene age from the sabkhas of Kuwait (especially the Al-Khiran lagoon) has been described by Gunatilaka (1991), Gunatilaka et al. (1984, 1987 A) and El-Sayed et al. (1991). The Al-Khiran lagoon is connected to the Persian (= Arabian) Gulf by way of a small tidal channel. Two to three times each year the lagoon dries up completely: it obviously belongs to the subtidal environment, as spring tides subsequently fill the lagoon again with seawater. In addition there is a marked effect of winter rainfall: during thunderstorms heavy rains dilute the lagoon water. As a result salinities range from 16 ‰ (after heavy rain) to 52 ‰ (during the dry July & August months). Dolomite is particularly abundant in the upper 5 to 10 cm of the lagoon sediments. Sulfate reduction takes place to a remarkable degree. Core samples show evidence of bacterial sulfate reduction to a depth of about 1 m. The dolomite from Al-Khiran was analyzed to be somewhat richer in magnesium carbonate than most Holocene dolomites. (According to Gunatilaka et al., 1987 A it contained 51 to 54 mol % $MgCO_3$. But not all dolomite was enriched in magnesium carbonate: only 8 out of 204 samples were.) Such "calcium-poor dolomite" had previously been found only in the Coorong area (Von der Borch, 1965). "The Ca-poor dolomite is mostly (but not exclusively) found very near to or within the seasonally fluctuating ground-water table": Gunatilaka et al. (1987 A, p.1005). Dolomite has been found within crustacean burrows occurring in the Quaternary siliciclastic sediments of tidal sand-bars in Northern Kuwait by Gunatilaka et al. (1987 B). The dolomite must have an authigenous origin, because the host sediment consists of loose, well-sorted fine sand with a composition of some 85 % quartz and about 15 % feldspar without any dolomite or other carbonate present. Dolomite in calcareous duricrusts in the south of Kuwait was studied by El-Sayed et al. (1991). Only in the coastal regions the calcretes contain dolomite (and attapulgite); landinward the siliciclastic sand grains of the host sediment are cemented by calcite.

Dolomite of Holocene age, together with Mg-calcite, calcite and palygorskite, has been found by Aqrawi (1995) in lakes and marshes of the Tigris-Euphrates Delta, southern Iraq. "The dolomite reaches its highest values within the playa and sabkha evaporitic units of the borehole cores, where it is associated with high gypsum contents": Aqrawi (1995, p.262).

Spontaneous precipitation of dolomite from interstitial brines at a depth of about 70 cm below the surface of tidal flats at Umm Said, Qatar has been claimed by Swart et al. (1987).

Initially the pore water streaming into pits on the sabkha of about 1 m deep had been clear, but it quickly turned milky and frothy, indicating the escape of dissolved gas. The precipitate from these solutions turned out to be dolomite. Salinity of the brine was between 300 and 330 ‰. The concentration of magnesium cations was measured to be 0.480 mol/dm$^3$ and that of the calcium cations was 0.085 mol/dm$^3$ ; carbonate alkalinity was 0.4 mMol. The dolomite must have originated by the dissolution of fine-grained, detrital eolian dolomite present between the sand grains by seawater enriched in carbon dioxide. Upon exposure the solution would loose most of the dissolved carbon dioxide, the alkalinity would be increased and "... spontaneous precipitation of dolomite occurs" (Swart et al., 1987, p.862).

Modern dolomite has been found by El-Sayed (2001) in the Umm Az Zimul-Al Wijan area in the southeastern part of the United Arab Emirates (near the borders of Saudi Arabia and Oman). In between the sand ridges typical of this region there are many (inland) sabkha's: salt flats not supporting any plant growth and dry for most part of the year. The topmost layer of sediment here consists of alternations between sand and silt layers (about 2 cm total thickness) intercalated with thin layers of aeolian dust ("This may reflect an alternation between wet and dry periods of deposition": El-Sayed, 2001, p.212). The very fine grained (2 to 20 μm) Holocene dolomite would have been formed by direct precipitation, in a way described by Burns & Matter (1995) from the neighbouring Oman Mountains: weathering of ultramafic rocks would lead to surface water with Mg/Ca ratio's of 2 or more, causing the precipitation of cements of magnesium calcite and dolomite. Episodic rain floods created according to El-Sayed (2001) a dynamic environment, in which repeated flushing would take place.


RUSSIA


Recent dolomite has been found in the Alakul Bay, the eastern part of Lake Balkash, by Teodorovich (1946). The salinity of the lake water increases rapidly from the south (where river water flows into Lake Balkash) to the northeast. The sediment at the lake's bottom reflects this change: from mainly detrital in the south to more than 70 % carbonates in the northeast (of which about two-thirds consists of dolomite). The annual surface temperature in the area varies between 263 and 298 K. The carbonates containing dolomite invariably smelled of $H_2S$. The presence of dolomite in the Lake Balkash sediments has been confirmed by Zalmazon (1951), Levchenko (1966), Turuvskii & Sheko (1973) and Levchenko et al. (1975). The precipitation of dolomite in Lake Balkash would take place, in the explanation of Levchenko (1966), because the activity coefficients of magnesium carbonate and calcium carbonate "...had reached equality". Attempts were subsequently made to illustrate this view with laboratory evidence. However the experiments carried out by Levchenko and his colleagues have shown, that under laboratory conditions no dolomite whatever precipitated from the water of Lake Balkash. Earlier Beremzhanov & Pokrovskaya (1964) had had to make the same observation: when evaporating water from Lake Balkash at 303 K no dolomite at all formed. Instead aragonite, nesquehonite, thenardite and halite were formed. Strakhov (1958) described dolomite from neighbouring salt lakes, which contained high concentrations of magnesium. Even in the sodium lakes of Tanartarsk Strakhov (1958) had found Recent dolomite.

Vakhrameeva (1956) and Teodorovich (1958) noted the widespread occurrence of Recent dolomite near the mouth of the Kara Bogaz lagoon. The Kara Bogaz Gol is a large salt sea (it measures some 130 x 170 km) forming an appendix on the eastern side of the Caspian Sea. A geographic barrier separates the large masses of the Caspian Sea water from a neighbouring depression, now transformed into a salt flat. The barrier is not complete; amounts of Caspian Sea water stream through a narrow (100 to 500 m wide) and shallow (from 1 to 6 m

deep) channel.[15]     The Kara Bogaz is about 3 m below the water level of the Caspian Sea, and evaporation rates in the prevailing arid climate are so high, that the water level of this depression is being lowered from year to year. According to analyses given by Kusnetzow (1898) water of the Kara Bogaz contains especially the cations Mg and Na, and mainly sulfate and chloride as the anions; the brine is concentrated to 22 - 23° Beaumé.[16]     Throughout the year water from the Caspian Sea flows through the channel, but its velocity changes with the seasons. Polyakov (1959) pointed out, that the inflow of water into the Kara Bogaz Gol is a distinctly periodic event: only high levels in the Caspian Sea would cause an overflow into the neighbouring salt flat. The salt flat is known for its huge deposits of sodium chloride, sodium sulfate and magnesium sulfate. Its water shows a distinct zoning with respect to salinity: the water coming through the channel (with 200 ‰ salinity) will subsequently desiccate. Salt minerals such as glauberite ($Na_2SO_4.CaSO_4$), bloedite ($Na_2SO_4.MgSO_4.4\ H_2O$), carnallite ($KCl.MgCl_2.6\ H_2O$), kainite ($KCl.MgSO_4.3\ H_2O$), and picromerite ($K_2SO_4.MgSO_4.6\ H_2O$) are being formed. Glauberite is not being deposited throughout the year; it is a seasonal mineral. Only during the cold winter months, when water temperature is about 278.7 to 279.0 K, glauberite will be deposited (Popkopaev, 1927). The observation that other salts, especially mixed salts, are formed during fluctuations in brine composition has been emphasized by Vakhrameeva (1956).  Polyakov (1959) noted, how the sequence of salt minerals deposited, changed during the year from glauberite to bloedite via carnallite and kainite to picromerite.
The presence of dolomite and magnesite in the Kara Bogaz salt deposits has been confirmed by Andriyasova et al. (1973). Not only in the salt deposits of the Kara Bogaz Gol modern dolomite has been found: Nuryagdyev & Sedelnikov (1966) reported on dolomite from the sediments collected at stations in the inlet zone, where sea water entering through the channel mixes with the concentrated brines of the salt lake. In the inlet zone indication of bacterial sulfate reduction was found: a strong odour of $H_2S$ emanates from the dolomite-containing sediments.

In a review on the formation of modern dolomite (and magnesite) in various Russian lakes and lagoons, Strakhov (1958) stressed the significance of alkalinity in combination with salinity. Magnesite would be a primary precipitate, but dolomite could only be formed during diagenesis. Older dolomites might have been primary precipitates, because in early geological epochs the partial pressure of carbon dioxide in the atmosphere would have been higher than today.

The soils of the Chu River Valley (Kazakhstan), especially those of the Gulyaevsk and Ulanbelsk flood plains, contain carbonate concretions, which consist of dolomite, magnesite and calcite (Akhanov, 1965). In this area the flooding is of a seasonal nature and regular intervals of high salinity of the pore water of the soil alternate with periods of dilution with rainwater.

Authigenic dolomite has been found by Stoffers & Müller (1978) in the lower part of the cored Black Sea sediments at DSDP Sites 380 and 381. Stoffers & Müller (1978) described, how the Plio-Pleistocene sediments of the Black Sea record distinct oscillations between oxidizing and reducing conditions, possibly related to influx events of sea water from the Mediterranean sea. The rhythmic sequences of carbonate-free sapropelic (reducing) sediments and carbonate layers (oxidizing conditions) would illustrate large-scale fluctuations in the Mg/Ca ratio of the water of the Black Sea (as much as it illustrates, that no secondary changes have since affected these deposits).[17]     Additional evidence for these frequent changes in physicochemical conditions has been supplied by Deuser et al. (1978), who studied the oxygen and carbon isotope distributions of these sediments. Trimonis et al. (1978) drew much the same conclusion: variations in physicochemical conditions would find their origin in sea level fluctuations, which in turn were the result of changes in overall climate. The varved Black Sea sediments of the Holocene were, in the explanation of Degens et al. (1978), the result of alternations between seasonal plankton booms and the subsequent prevalence of reducing conditions. The white bands of these Black Sea varves consist of coccoliths; the black bands of
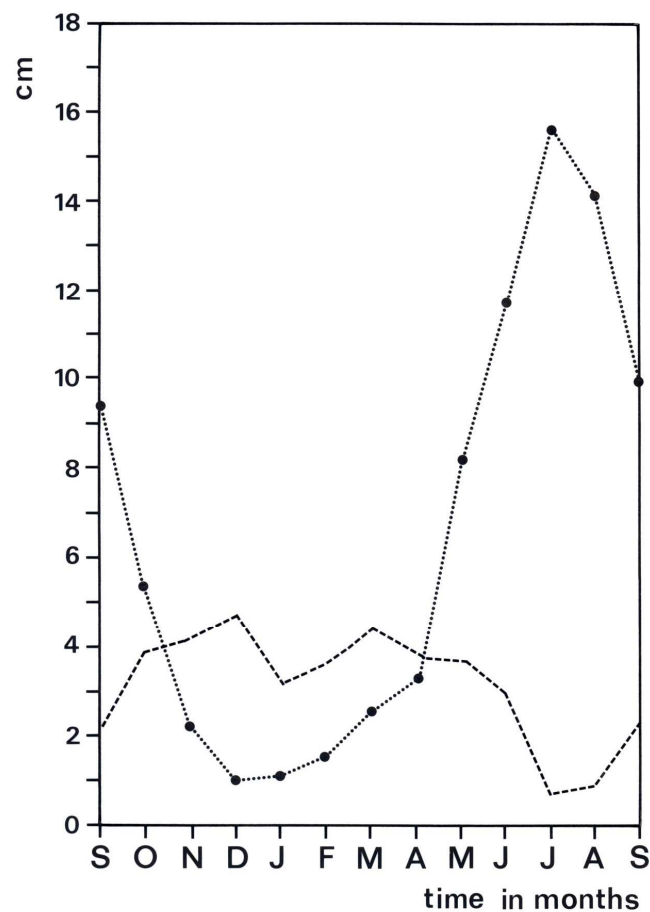
Fig.27 – Seasonal variation in precipiation (---) and evaporation (…) based on averaged meteorological data for the years 1958 to 1973 for the region of Alcázar de San Juan, Spain (after Soriano et al., 1977).

sapropel. A somewhat different conclusion has been formulated by Hsü & Kelts (1978): those two authors were convinced, that the Quaternary deposits of the Black Sea must have formed under periodically changing chemical conditions. In their explanation the Black Sea had been a lake during most of Late Neogene times, and brackish during only a few occasions. The precipitation of calcite took place, when the Black Sea was a deep, fresh water lake. Aragonite and magnesium calcite would have been formed, when the lake became a brackish, marine to hypersaline basin. The dolomite layers of the Black Sea sediments would have been formed during the transitions from a brackish lake to a hypersaline basin. Hsü (1978) went even further and suggested, that the Quaternary Black Sea dolomite must have formed under supratidal conditions in a salt lake.


## SOUTH AFRICA


Dolomite of Neogene age has been found by Botha & Hughes (1992) in ephemeral (paleo-) lakes in Transvaal Province, South Africa. The dolomite mineral is accompanied here by palygorskite. The occurrence of dolomite is restricted to the margins of the lakes, where fluctuations between wet and dry prevailed ("lacustrine environments, which undergo periodic shoreline regression”: Botha & Hughes, 1992, p.150).


## SPAIN


Perhaps the oldest description of modern dolomite (that is to say of Quaternary age) is to be found in the paper by Le Play (1834) on the geology of Estramadura and northern Andalusia. Near the city of Badajoz a sequence of Tertiary limestones had been found. Because these limestones contained fossil shells of organisms known to be lacustrine, Le Play (1834) interpreted the limestones to be of lacustrine origin. The dolomite, interbedded with shaly units, was found on top of the limestones. From the relations in the field Le Play (1834) concluded, that the dolomite too must have had a lacustrine origin.[18]     Intrusions of an "euphotide" or magmatic rock known to be of Quaternary age, intruded through all these formations, including the dolomite.

In thin sections of Quaternary limestones from the island of Fuerteventura (Canary Islands) Müller & Tietz (1966) found dolomite of Recent origin. The dolomite occurred in a terrace-forming layer of a consolidated biocalcarenite, which extended for about 10 km along the Barlovento coast, Jandía Penninsula, Fuerteventura. The dolomite is restricted to those parts of the biocalcarenite, which lie in the supratidal breaker zone or in the breaker zone along the beach. Especially fragments of calcareous algae, which consisted originally of magnesium calcite, had been changed into dolomite. Large euhedral crystals of dolomite also occurred in the pore space of this limestone. Müller & Tietz (1966) called attention to the numerous shallow depressions (of a few cm wide to a maximum diameter of about 1 m) on the surface of the indurated biocalcarenite rim: during occasional heavy seas these depressions are filled with sea water and as the sea water evaporates, crusts of gypsum and salt minerals are left behind. In the explanation of Müller & Tietz (1966) the thus formed small quantities of brine with high Mg/Ca ratio's would start "percolating" through the carbonate rock and so form dolomite.

According to Yébenes et al. (1973) dolomite of Quaternary age (Pliocene or younger) can be found in a layer of white earth ("tierra blanca") in lacustrine deposits near La Roda (Albacete Province). This deposit consists of a travertine-like layer of some 4 m thick with a rather

restricted horizontal distribution in the form of an ancient lake. In the overlying layers several fossils (*Characea*, ostracods, and molluscs) were found, indicating a shallow and quiet lake as the former environment. Electron microscopy of samples from this location revealed, that the dolomite was not well crystallized and that it was accompanied by considerable amounts of sepiolite-attapulgite. No traces of salts could be found, not in X-ray diffraction and not in electron microscopy. The absence of any detrital material in the "tierra blanca" dolomite deposits proved, that its origin was not fluviatile, but lacustrine. The origin of the mineral dolomite itself was explained by Yébenes et al. (1973) in terms of a secondary change of magnesium calcite, which would have been the primary deposit. No trace at all of magnesium calcite had been found by Yébenes et al. (1973) however. In the Laguna de Pétrola, in the same region near La Roda, Ordóñez et al. (1973) have found modern dolomite. The brine measured pH = 8.9 to 9.2 near the middle of this relatively small pond; but lower pH values occurred in the shallow water near the margins (and especially at the margins the sediment was anoxic, and H$_2$S escaped from it). In an isolated part of the lake, used as a salt pan, pH = 6.7 was measured. At the end of each summer the water of the lake almost completely disappears, and during winter only a few cm's of water remain.

Dolomite was reported by Marfil et al. (1975) as occurring in two seasonal lakes (Saladar and Corral Rubio) near La Higuera (Albacete Province). During the winter (January) minimum water temperatures of 280 to 282 K were measured; in spring (May) the amount of water reaches its maximum; and in the summer (July, August) maximum water temperatures of 294 K occur (with air temperature maxima near 317 K). The amount of water in these two seasonal salt lakes reaches its minimum in August or September of each year; complete desiccation is often observed. Since antiquity salt is being excavated from the La Higuera playa; the sodium chloride is found associated with hexahydrite, epsomite, gypsum, kieserite, loeweite, coelestine, dolomite and magnesium calcite.

Soriano et al. (1977) found dolomite in the Recent deposits of the Laguna de Salicor and the Laguna de los Pájaros, two playa lakes north of Alcázar de San Juan (Ciudad Real, Spain). These playas do not possess any effluents or any springs: no escape route exists for accumulated water except for evaporation. The meteorological data cited by Soriano and his co-authors for the years 1958 to 1973, show a pronounced phase of desiccation during the dry summer months (Fig.27). X-Ray diffraction of numerous samples showed, that gypsum, hexahydrite, epsomite, kieserite, bloedite and a little halite, along with dolomite and calcite as the carbonates, as well as some quartz and clay, make up the lacustrine sediment. It is of some importance to note the doubt expressed by Soriano et al. (1977) with regard to the actual authigenic nature of the carbonates calcite and dolomite. These carbonate minerals may have been transported into the playa from nearby Triassic rocks, but the possibility of an authigenic formation for the dolomite could not be excluded either.

In the Laguna de Quero, a playa lake near Alcázar de San Juan (La Mancha) dolomite has been found by Bustillo et al. (1978). Much like the other playa lakes in the arid heartland of Spain, the Laguna de Quero goes through a pronounced annual cycle of inundation by spring rains followed by gradual (and often complete) desiccation during the dry summer months. In addition Bustillo et al. (1978) measured a distinct annual fluctuation in pH values in the water of the Laguna de Quero: it changed from 6.5 to 8.0 during the year. Modern dolomite from the Laguna de Pájaros (near Alcázar de San Juan, Ciudad Real) has been described by Garcia Palacios et al. (1978).

The presence of dolomite in sediments of the Laguna de Gallocanta (on the border of the Zaragoza and Teruel Provinces) has been described by Calvo Betes et al. (1978); Comin et al.(1990), Pérez et al. (2002) and Corzo et al. (2005). X-Ray diffraction established the fact that the Quaternary sediment at the lake bottom consists mainly of (detrital) quartz, carbonates (calcite and dolomite) and clay minerals (illite and kaolinite). The clay minerals too would be of

detrital origin. Chemical analysis of water samples showed the lake to be alkaline (pH = 7.5 to 9.3) and to contain excess magnesium over calcium (Mg/Ca = 5.3 to 14.2). Comin et al. (1990) noted, how the precipitation of carbonates in Lake Gallocanta was a distinctly periodic event. From August to October 1987 carbonates precipitated in large amounts and the Mg/Ca ratio of the water increased from 7 to 50. In May 1987 carbonate precipitation had taken place as well, but from May to August no carbonates appeared to precipitate and the Mg/Ca ratio remained constant at about 7. More chemical analyses of the water from the same lake have been published by Gonzalez Lopez et al. (1983), who made a comparison between the chemistry of the water of the lake itself and that of several little rivers feeding it. From that comparison it followed, that the lake water contains less sulfate and less chloride ions than the rivers. The loss of sulfate ions must be due to bacterial sulfate reduction in the topmost layer of the lacustrine sediment. Responsible for the activities of the sulfate reducing bacteria is no doubt the abundant supply of organic material from living plants such as *Ruppia maritima* and *Chara* species, forming a thick carpet on the sediment. The disappearance of chloride ions, at least their diminution, had to be caused by the precipitation of halite. Other salts found in Lake Gallocanta sediments are epsomite, mirabilite and gypsum. Detrital minerals include clay minerals and feldspars. The calcite contains only minor amounts of magnesium calcite (less than 3 %). Comin et al. (1990) noted, how calcite and aragonite occurred mainly at the shores of the lake, and that dolomite and gypsum were found especially in the centre of Lake Gallocanta. The percentage dolomite increased with increasing depth of the cores (cores reached a maximum depth of 100 cm). In the cores magnesium calcite was found in the top layers; high-Mg calcite and dolomite at depths between 30 to 70 cm; and gypsum deposits were found only at depths from 80 to 100 cm (which was the maximum depth reached). According to Gonzalez Lopez et al. (1983) the dolomite showed in X-ray diffraction a variable content of $MgCO_3$ : some samples contained excess $CaCO_3$ , other samples had excess $MgCO_3$ . There can be little or no doubt concerning the periodic nature of Lake Gallocanta: "Due to the extreme flat topography of the lake, they are subjected to episodic or periodic fluctuations in the water level" and "At the present time, carbonates predominantly form during the annual flooded periods whereas salts precipitate during dry periods": Corzo et al. (2005, p.285).

Dolomite, most probably of Quaternary age, has been found by Bustillo et al. (1978) and De la Peña et al. (1982) in the Laguna de Tirez, a small (less than 1 km$^2$) playa-lake in La Mancha Province. The climate of La Mancha is semi-arid. There are considerable seasonal changes in temperature. The annual amount of precipitation is less than 400 mm. The high rate of evaporation is even enhanced further by strong and frequent wind. The Laguna de Tirez is a salt lake, covered most of the year by a salt crust of at least 10 cm thick. Only during a few months in autumn and winter a layer of water, with a maximum depth of 50 cm, temporarily turns the Laguna into a real lake. Field observations made during the summer months, made it possible to distinguish three concentric zones of salt parageneses. An outer zone is characterized by deposits of gypsum in combination with halophytic vegetation. The intermediate zone of "capillary-induced saline efflorescence" contains dolomite together with gypsum, halite and hexahydrite. The presence of modern dolomite in the intermediate zone of the Laguna de Tirez has been verified in X-ray diffraction. The third and innermost zone consists of stratified salt crusts of halite hopper crystals, epsomite, polyhalite, mirabilite, thenardite, hexahydrate and bloedite. Underneath this central salt crust a layer of some 8 cm thick was found, consisting of algae-derived sapropel.

Dolomite of obvious modern origin (< 400 years) has been found by Rodríguez-Navarro et al. (1997) on walls of the cathedral at Jean (Analusia, southern Spain). Although few blocks of a Jurassic dolomite are incorporated into this building, it consists predominantly of limestone (95 % calcite). On the limestone blocks black crusts were found, consisting of fly ash and soot containing (selenitic) gypsum, calcite, quartz and clay minerals together with small amounts of
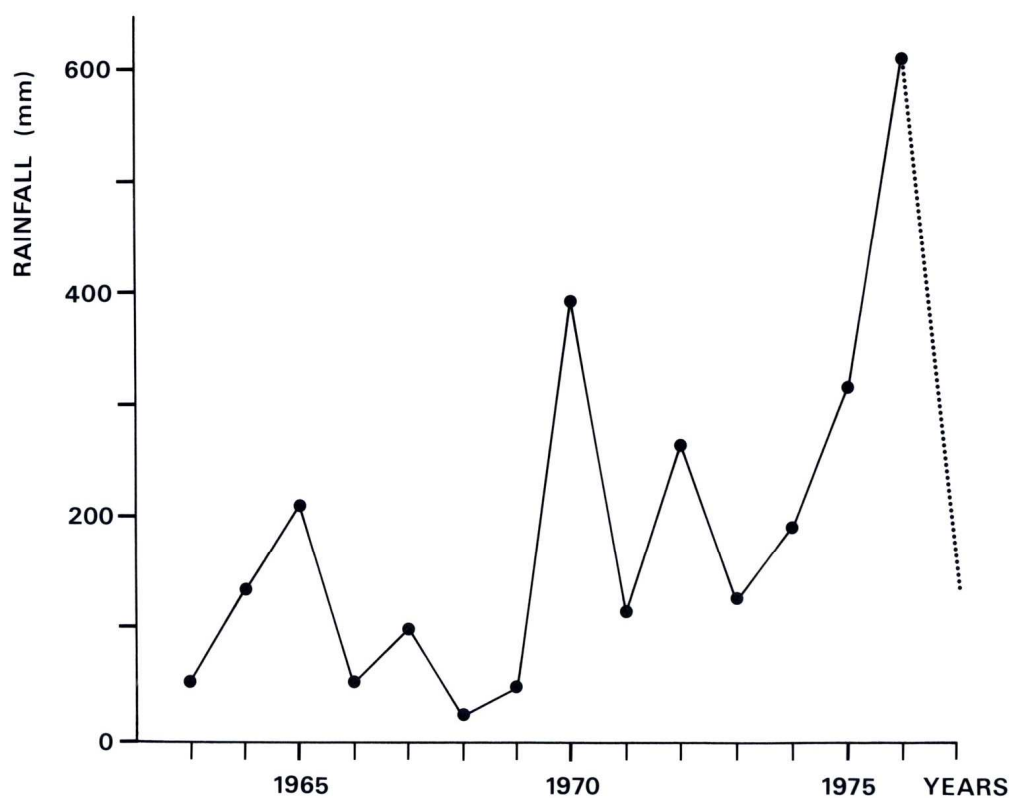
Fig.28 – Annual variation in rainfall near the Bahiret el Biban sabkha, Tunisia (as measured in the Ben Guirden-Zarzis area) (after Medhioub & Perthuisot, 1981).

dolomite."Multiple gypsum + carbonate layers are visible …. indicating that the process of crystal precipitation is probably episodic": Rodríguez-Navarro et al. (1997, p.4).

Carbonate chimneys containing not only ankerite, calcite, goethite, hematite and pyrite but also dolomite, have been discovered by Diaz-del-Rio et al. (2003) at various locations in the Gulf of Cadiz (Atlantic Ocean SW of Spain). The chimneys found at depths between 500 and 1200 m were explained to be the result of leakages of oil or gas from underlying sediments, but $H_2S$ may have been involved as well. (Compare the observations made by Jørgensen, 1989 and Stakes et al., 1999 one the same subject.)


## TANZANIA


Authigenic dolomite of Plio-/Holocene age has been found by Hay & Reeder (1978) in calcretes on volcanic ash in the Olduvai Beds of northern Tanzania. The calcretes developed on the youngest of aeolian tuffs at the eastern margin of the Serengeti Plain. The "calcretes of the Olduvai Beds" are at maximum 600,000 years old. "Aeolian tuffs of the Olduvai Beds were altered in a highly alkaline soil and shallow subsurface environment, resulting in authigenic phyllosilicates, zeolites, and … dolomite": Hay & Reeder (1978, p.660).


## TUNISIA


Perthuisot (1974) reported dolomite (of approximately 5200 years old as determined by isotope measurements) occurring in the Quaternary sediments of sabkha El Melah near Zarzis (S.W. Tunisia). The sabkha is a sediment-filled coastal lagoon, which is connected to the Mediterranean Sea by a narrow channel. The sabkha's present surface lies at or slightly below sea level. A salt crust covers much of the underlying carbonates and evaporites, which were deposited on top of fluvio-marine deposits marking the end of the (Pleistocene) Würm transgression. The carbonates, mainly calcite and Mg-calcite of organic origin, not only contain Recent dolomite, but also magnesite and huntite (Perthuisot, 1971). In addition to large amounts of gypsum, polyhalite and carnallite were found. Much of the organic carbonate sediment has been deposited under euxinic conditions: the sediment was dark colored and it smelled of $H_2S$. Perthuisot (1974) noted, how magnesium-containing carbonates are especially plentiful in the euxinic layers typical of the central part of the sabkha. The sediments near the borders are light coloured carbonates mixed with gypsum.

The Paleogene sediments at Foum Selja (Metlaoui, Tunisia) were studied by Lucas et al. (1979). The lower part (of some 80 m thick) of the Metalaoui Formation was found to contain mainly dolomite together with layers of gypsum. The central part of this formation (about 47 m) consists entirely of phosphate. The dolomite contains slightly less magnesium carbonate than ideal dolomite (46 mol % instead of 50 mol % $MgCO_3$). The mineralogy of the clay minerals (montmorillonite, attapulgite, and sepiolite) found together with the phosphate, are magnesium-rich, and indicate in the view of Lucas et al. (1979) a primary origin for the dolomite. At the same time a detrital origin for a small part of the sediments of the Metlaoui Formation could not be excluded. Because phosphate and dolomite (together with the Mg-containing clay minerals) were known to be more or less mutually exclusive, Lucas et al. (1979, p.17) interpreted the Metlaoui section to be "at the boundary of equilibrium" ("... *on se trouve à la limite de l'équilibre*").

Recent dolomite has been described by Medhioub & Perthuisot (1981) from the Bahiret

| ion | spring 1967 | summer 1968 |
|:---:|:---:|:---:|
| $SO_4^{2-}$ | 6 - 8   kg/m$^3$ | 31 - 54  kg/m$^3$ |
| $Ca^{2+}$ | 0.4 | 0.2 |
| $Mg^{2+}$ | 2.6 | 34 |
| $HCO_3^-$ | 0.08 - 0.12 | 1.4 |
| $K^+$ | 1.0 | 12.1 |

**Table III - Annual changes in ion concentration measured in water samples from the Tuz Gölü salt lake, Turkey (from Irion, 1970).**

el Biban lagoon: a lagoon on the Gulf of Gabès, measuring some 32 x 8.5 km. The coastal plain of southern Tunisia possesses a distinctly arid climate. Summer temperature averages about 301 K, and winter temperatures are usually near 288 K. Mean annual precipitation is some 200 mm. Heavy rains (with catastrophic flooding) are followed by irregular intervals of intense drought (Fig.28). Although Medhioub & Perthuisot (1981) did not exclude the possibility, that much of the dolomite found in the Bahiret el Biban lagoon is of detrital origin, at least part of the dolomite might well be of authigenic origin. The more so because aragonite and Mg-calcite time the biological production of sea grasses in particular would give rise to abundant bacterial sulfate reduction in the carbonate sediments, much like the situation found by Perthuisot (1971, 1974) in the nearby Sabkha El Melah.

TURKEY

Recent dolomite, together with huntite, magnesite and polyhalite, has been found in the Tuz Gölü salt lake by Irion & Müller (1968). Details on this location have been given by Irion (1970). An intra-montane basin in Central Anatolia (about 140 km south of Ankara) forms the source area for the Tuz Gölü. The salt lake is relatively young: it must have been formed in Neogene times. Its size is relatively large: some 50 x 80 km. A number of small rivers is responsible for a constant supply of fresh water into the closed basin. The climate of Central Anatolia is semi-arid: total annual precipitation is about 340 mm, with rain concentrated in the months of October to June and very dry summer months (July, August, and September). Mean annual temperature is 284 K; in January temperature is around 268 K, and in June 295 K. Temperature during the summer months seldom exceeds 303 K. The depth of the Tuz Gölü changes with the seasons. In spring time, after inflow of water from snow melting in the nearby mountains, the salt lake is about 30 cm deep, and nowhere is it deeper than 1.5 m. In the dry summer months the level will be markedly lower. Much of the lake water disappears altogether in the dry season, but the central part of the Tuz Gölü contains a salt crust of about 40 cm thick with small quantities of water, that will not disappear not even in the most arid years. Salt minerals found are mainly halite and gypsum, with minor amounts of polyhalite and coelestine. Considerable annual fluctuations in water chemistry result from these seasonal changes in total water amount. Irion (1970) collected water samples (along with sediment samples) in the spring months of 1967 and during the summer of 1968 (Table III). Irion (1970) described, how the Mg/Ca ratio of the water of the salt lake fluctuates from about 10 (in spring) to values as high as 500 (during the summer months). Carbon-14 age determinations on the carbonate fraction of the sediment from the Tuz Gölü showed, that the carbonates were about 1800 years old. After leaching the calcium-containing carbonates from the sediment, an age determination was conducted on the dolomite itself: $C^{14}$ measurements indicated an age of about 6000 years.

The presence of modern dolomite in the sediments of Tuz Gölü has been confirmed by Camur & Mutlu (1996). The lake area can be divided into a "main zone", where water depth is about 70 cm in spring, but which dries completely during summer. Minimum water level occurs in September / October of each year; maximum water levels in March / April. In contrast the "deep zone" of the Tuz Gölü remains filled with water of at least 1 m deep. These two different zones are characterized by a distinct mineralogy (Irion, 1970). Modern dolomite (along with magnesite and huntite) is found only in the "main zone" (with its fluctuating water table).

In several other Turkish lakes (Aci Göl, Boluk Gölü, and Tuzla Krater Göl) dolomite of Recent age has been found by Müller et al. (1972). In addition Degens et al. (1984) reported on modern dolomite found in Lake Van (Van Gölü) in the eastern part of Turkey. Much like Müller et al. (1972), who had noted a distinct relation between the occurrence of dolomite and

fluctuations in water level, Degens et al. (1984, p.724) concluded: "Dolomite occurrence may be correlated with a low lake level stand, and subaerial exposure is indicated." Landmann et al. (1996) also confirmed the presence of dolomite in the Holocene sediments of Lake Van, and they stressed the cyclic nature of the sedimentation process since the last 14,570 years at this location. The presence of modern dolomite in the sediments of Lake Acigöl has been confirmed by Mutlu et al. (1999). The mineral dolomite is found only on the ephemeral mud flats around Lake Acigöl. The sediment at the centre of the lake consists of a black, organic-rich deposit. The carbonate there is mainly aragonite.

## UNITED KINGDOM

Hardy (1920, 1921) reported to have found dolomite in the Recent sediment (marine silt) of the salt marshes on the northwestern shores of The Wash (= tidal flat E. of Norwich, UK), immediately seaward of the village of Friskney. Details on the mineralogy of the silt have been published by Hardy (1920): "... dolomite ($MgCO_3.CaCO_3$) was definitely identified" (Hardy, 1920, p.543). Apart from this dolomite, carbonates such as calcite, aragonite (fragments of Pelecypoda, small pieces of ooids, and some foraminiferal tests), and ankerite were present. "The dolomite present occurs as typical "fresh"-looking crystals of rather large size and with well-marked rhombohedral cleavages" (Hardy, 1920, p.547). Concerning the possible origin of the dolomite Hardy (1920, p.547) remarked, that the appearance of the dolomite crystals suggested "... a secondary and comparatively recent origin of the mineral. Possibly the mineral was deposited from sea-water, and the crystals gradually built up during the successive wettings and dryings to which the modern Fenland salt-marsh silts are subjected."

Concretions dredged from the seafloor near the mouth of Loch Sunart (Scotland) at a depth of 50 to 70 m, were found to contain dolomite in addition to quartz, mica and calcite (with 1 mol % $MgCO_3$) (Brown & Farrow, 1978). Clasts of olivine from Tertiary igneous rocks nearby were included. All of the inorganic components making up the nodules were silt-sized or even smaller. A relatively large number of foraminifera were incorporated. Other marine life in evidence included bryozoa, barnacles, serpulids and hydroids. Borings by bivalves and polychaeta into the concretions could be observed. In the eyes of Brown & Farrow (1978) there could be no doubt, that these concretions had been formed around the burrows of mud-dwelling organisms such as crustaceans.[19]  Such burrows are often being stabilized with organic substances in the form of mucous coatings or faeces, in order to prevent caving in of the soft mud. Sulfate-reducing bacteria will use these organic substances. The resulting rise in alkalinity would cause the precipitation of calcium carbonate, which would then be changed into dolomite (Brown & Farrow, 1978).

Holocene dolomite from Caicos Island (British West Indies) has been described by Perkins et al. (1991, 1994). The Turks and Caicos Islands are located some 150 km north of Hispaniola, at the southeastern end of the Bahama Bank. The dolomite there was found in the Holocene sediments of the East Salina, a large (0.5 x 3 km) depression on the coast of Caicos Island. Evaporation rate averages 150 cm per year; the climate of Caicos Island is subtropical. The salina receives marine groundwater through barrier dunes, which separate the salina from the sea. Groundwater level in the salina rises and falls with the ocean tides; sea level rises to some 80 cm above the salina surface at maximum high tide. This height difference causes a hydrostatic gradient. Pore water has approximately the salinity of normal seawater, but becomes more and more saline towards the sedimentary interface. Evaporation near the top of the (at maximum) 2.4 m thick Holocene sequence leads to salinities as much as 7 times that of normal sea water. Occasional heavy rains inundate the surface of the salina to depths of several cm's.

Predominantly carbonates (aragonite, magnesium calcites, and dolomite) make up the Holocene sediments there. Near the top gypsum occurs, and an algal mat covered with gypsum and halite is present at the top of the sediment. Bacterial sulfate reduction had significantly modified the seawater present in the pores of the sediment. The dolomite of Caicos Island contains 52 to 60 mol % $CaCO_3$. Pyrite was found on the surface of some of the carbonates.


UNITED STATES


One of the first accounts on modern dolomite found in the United States is that by Sherman & Thiel (1939). In that paper the presence of dolomite in fine-grained lacustrine silts, that had been deposited on the floor of the former glacial Lake Agassiz, was described.[20]    At the time of its maximum extent Lake Agassiz measured some 400 x 1100 km, and covered large parts of the U.S. states Manitoba, North Dakota, Minnesota and South Dakota. The Pleistocene deposits left behind after the disappearance of Lake Agassiz, include ridges of sand and gravel washed up by beach waves, near-shore sand plains and offshore clays. The sand grades horizontally into silts and clays. From nearby limestones and dolomites amounts of the mineral dolomite will have been incorporated into the Lake Agassiz silt-sized deposits. Even so Sherman & Thiel (1939) maintained to have found authigenic dolomite in the form of an enriched zone, starting at a depth of about 30 cm, but with a total thickness that would greatly vary (at one locality it extended to a depth of 3 m). The horizontal distribution of the dolomite-containing zone was irregular; only a small fraction of the Lake Agassiz area was found to possess such a zone. "Dolomitization has taken place where the water table is near the surface or where the natural drainage is poor, but not typically swampy. There is some enrichment also under the gentle slopes around swampy areas but no dolomitization was observed where there is good natural drainage. In many localities the dolomite is associated with the offshore sands that dovetail with thin layers of silts and clays. In these sediments the water is under hydrostatic pressure, and thus the water table is near the surface": Sherman & Thiel (1939, pp.1545-1546). The dolomite in this zone could not have originated by way of a process of leaching by ground water, removing the calcium carbonate fraction of the silts: the dolomite zone occurred immediately below calcareous sands as well as under impervious clay layers. Nor was the dolomitic zone related to particular stratigraphic horizons of the Pleistocene deposits: its boundaries were seen to cut across bedding planes at various angles. Concerning the possible mode of formation of the modern dolomite Sherman & Thiel (1939) pointed out, that the ground water of Lake Agassiz is highly saline, and that therefore a parallel might exist with dolomite formation in the marine environment. The presence of magnesium chloride as well as magnesium sulfate would be instrumental in the low-temperature formation of dolomite. Local concentration of the saline groundwater, typically in poorly drained and shallow topographic basins, may have initiated the formation of dolomite. Especially there where the Pleistocene sediments were relatively more porous and finer grained than neighbouring sediments, dolomite would form. Thick beds of peat or heavy layers of humus underlie many of those dolomite-containing silts. The carbon dioxide generated by the decay of this organic matter would contribute to the formation of dolomite, in that it would hasten the dissolution of calcium carbonate.

The occurrence of dolomite in the Quaternary sediments of Lake Bonneville, Utah has been described by Graf et al. (1959). An organic-rich carbonate layer immediately above the dolomite-containing carbonate/clay laminations was analyzed with $C^{14}$ to be $11,300 \pm 250$ years old (Graf et al., 1961). More details on this particular deposit were published by Bissell & Chilingar (1962) and Pedone & Dickson (2000). The deposition of dolomite in the salt flats of
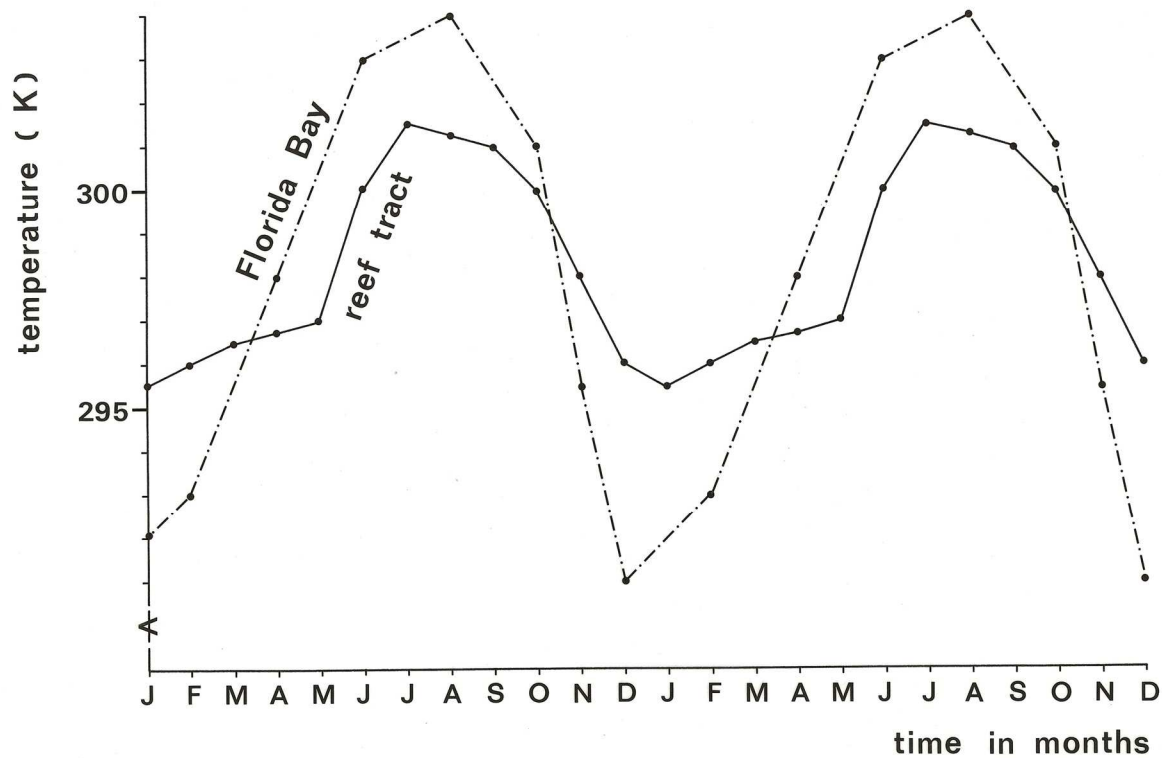
Fig.29 – Seasonal variation in water temperatures in Florida Bay (-.-) and in the Florida reef tract (---) (extrapolation of measurements by Lloyd, 1964).

western Utah took place at a time, when the Pleistocene Lake Bonneville desiccated to a considerable degree, because of a more arid climate, and the development of present-day Great Salt Lake. Graf et al. (1961) postulated, that dolomite formation took place in saline lakes more or less isolated from the present Great Salt Lake. The dolomite occurs together with aragonite and magnesite in mm-thick layers alternating with equally thin layers of clay. In the interpretation of Grim et al. (1960) and Bissell & Chilingar (1962) these alternating layers reflect the oscillations of the retreating Lake Bonneville, which caused fluctuations in pH, in alkalinity and in salinity of the water in it. The laminated sediments recorded numerous intervals of desiccation, alternating with episodes of lacustrine sedimentation, when the small lakes were flooded again. Detailed mapping in Utah and Nevada made it possible, to distinguish these oscillations of the retreating Lake Bonneville and the later, smaller lakes (Bissell, 1952). The multitude of oscillations affecting the size and the composition of the Pleistocene Lake Bonneville has been documented in geochemical studies by Eardley et al. (1973) and Spencer et al. (1984, 1985).

Dolomite has been found in soils at Foxhome (Wilkin County, Minnesota), Averill and Felton Clay County), Borup, Ada, and Lockhart (Norman County), Beltrami and Crookston (Polk County); all of which locations are situated in the Red River Valley, Minnesota. Sherman et al. (1962) described how dolomite in the Averill area is confined to the subsoil, which is alternately wetted and dried by a fluctuating water table. "In each instance, the dolomitic carbonates occurred on slopes of minor depressions and in that part of the profile that would be affected by the rise and fall of the fluctuating water table": Sherman et al., 1962, p.305). Both differential thermal analysis and X-ray diffraction showed, how in addition to quantities of magnesium calcite, dolomite was present in the carbonate fraction of these soils. Although the soils developed on the lacustrine sediments of the Pleistocene Lake Agassiz, Sherman et al. (1962) gave several reasons for their conclusion, that the dolomite had formed independent of sedimentation and had to be related to the process of soil formation. The horizontal distribution presented evidence, that dolomite formation was closely related to a fluctuating water table, rather than to any sediment property. In the sediments of Elk Lake, Grant County (west-central Minnesota) Dean & Gorham (1976) found dolomite of Recent age. "Elk Lake ... undoubtedly precipitates large quantities of calcium carbonate during summer, but dissolution of carbonate in the deeper waters of the lake has greatly reduced the amount of carbonate": Dean & Gorham (1976, p.264).

Authigenic dolomite from modern carbonate sediments occurring along the southern coast of Florida has been described by Taft (1961). Core samples from this location in Florida Bay (25$^o$ 05' 50" N / 80$^o$ 53' 58" W) showed, that the dolomite was being formed at the water-sediment interface within the Quaternary carbonate sediment, overlying the consolidated Miami Oolite (= Pleistocene). The environment here is intratidal: during phases of low water the sediment is exposed to the atmosphere. The dolomite crystals consist of euhedral rhombohedra; in several instances clusters of rhombohedra were found. The crystals and the crystal aggregates of dolomite did not show any trace of having been transported. Therefore Taft (1961) concluded that the dolomite crystals had to be authigenic. "The apparent concentration of dolomite near the top of the sediment cores suggests that dolomite is forming at the sediment-water interface rather than after burial in some diagenetic process": Taft (1961, p.562).

Florida Bay is subject to considerable seasonal variation in air temperature, amount of rainfall and evaporation rates. Data on these variations have been summarized by Lloyd (1964). The average annual rainfall in southern Florida is about 120 cm, but amounts of 50 to 175 cm have also been recorded for a single year. As a direct consequence of the changes in air temperature, the temperature of the water in the relatively shallow Florida Bay shows a distinctly seasonal variation (Fig.29). At the same time considerable fluctuations in the salinity of the seawater of Florida Bay exist. According to Lloyd (1964) this salinity may vary from as

low as 2 ‰ to values as high as 60 ‰ . Especially periods of high evaporation are responsible for a rise in salinity; periods of heavy rain dilute the water of Florida Bay to such a degree, that a very low salinity results. "Florida Bay undergoes a cyclic alternation of brackish to hypersaline water in response to variations in rainfall": Lloyd (1964, p.94). The annual variations in water chemistry also affect the pore water of the Florida Bay carbonate sediments.[21]   During phases of desiccation pore water salinities reach values of up to 5 to 6 times that of normal sea water; and the Mg/Ca ratio may reach a value as high as 40. The pore water of the sediment in the intratidal area is of normal salinity and possesses a Mg/Ca ratio of about 5 (Shinn, 1968 B). Taft's (1961) conclusion, that the dolomite crystals found at the sedimentary interface in Florida Bay would be authigenic, has been questioned by Deffeyes & Martin (1962). Using a sample of the same dolomite-containing carbonate sediment from Florida Bay as Taft (1961) had used, Deffeyes & Martin (1962) applied $C^{14}$ isotopic analysis. The dolomite crystal's carbon atoms showed no measurable $C^{14}$ activity, indicating that the sample was older than the limit of measurement of 35000 years. The rest of the carbonate sample from which the dolomite crystals had been separated, gave a radiometric age of 1750 ± 150 years B.P. for the bulk, and 1660 ± 130 years B.P. for the larger shell fragments contained in it. As a consequence Deffeyes & Martin (1962) had to conclude that the dolomite they had found had to be of detrital origin.

Dolomite from a supratidal mud flat on Sugarloaf Key, Florida has been described by Shinn & Ginsburg (1964) and Shinn (1968 B). The well-bedded carbonate sediment making up most of the Holocene deposits on Sugarloaf Key, is interlaminated with dolomite. The dolomite-containing pelleted mud of the supratidal zone has been cemented into a crust of 2.5 to 10 cm thick. The crust contains mudcracks, algal mats and abundant birdseye structures: all of these are indications of periodic alternations between dry phases and phases of inundation by sea water or exposure to rain. At this location, where the supratidal environment predominates, long phases of desiccation are interrupted only on rare occasions by flooding of seawater. "Numerous observations over a period of several years showed that the area is flooded only by high spring and storm tides": Shinn (1968 B, p.613). Objections against Shinn's (1968 B) claim, that the dolomite crystals found here are of Holocene age, are virtually untenable: radiocarbon measurements showed, that the crystals are only 300 to 900 years old.

Since Shinn's first visit to Sugarloaf Key, several other geologists have studied the island's sediments. The observation made by Shinn & Ginsburg (1964) and Shinn (1968 B), that the Recent dolomite occurs in a crust at or near the sedimentary interface of the tidal deposits, has been confirmed by Atwood & Bubb (1970). In addition it was noted, that dolomite formed especially near the shoreline and that the percentage of dolomite decreased towards the higher parts of the tidal flats. No dolomite was found in the carbonate sediments of the adjacent bays. In this respect Atwood & Bubb (1970) suggested, that apparently dolomite forms only in those parts of the sediment, in which a maximum contrast exists between wet and dry conditions. A conclusion that has been repeated by Carballo & Land (1984): the highest concentrations of modern dolomite are found in Sugarloaf Key there, where the sediment layer is at its thinnest.

A comprehensive survey of the occurrence of Holocene dolomite on Sugarloaf Key has been published by Carballo et al. (1987). There the relation between local hydrology and dolomite formation was emphasized: the comparatively high mean tidal range of Sugarloaf Key affects almost all of the Holocene sediments. In addition there is a marked difference in permeability in the three stratigraphic units recognized by Carballo et al. (1987): the Pleistocene Miami oolite is highly porous and permeable; the overlying Holocene carbonates are several orders of magnitude lower in measured permeability, and the topmost algal laminates form a layer of considerably decreased permeability. Even so the tidal fluctuations affect the whole of the supratidal sequence: a rising spring tide causes first the expulsion of entrapped air from the sediment (the "breathing" of the sediment described by Shinn et al., 1965), after which small wet areas appear on the surface of the supratidal flats. Ultimately the supratidal flats are covered

by large, coalescing puddles, "... that are in no way connected over the surface to any of the adjacent water bodies such as the pond, lagoon, or Florida Bay" (Carballo et al., 1987, p.161). In the final stages of these spring tides the supratidal areas will be completely flooded by a layer of about 0.5 m of seawater, slowly flowing in from the open sea. After digging a number of wells into the sediments of the supratidal flats, Carballo et al. (1987) observed, how the withdrawal of the sea water masses after spring tide flooding does not only take place by a gradual return to the sea, but the more so by infiltration into the sediment. The highly permeable Pleistocene oolite plays a crucial role in creating the phenomenon. In areas where the oolite is exposed, surface water can be seen to spiral into holes in the bedrock after spring tide flooding (much like water down a drain).

Holocene dolomite, together with aragonite and magnesium calcite, has been found by Swart et al. (1989) and Andrews (1991) in various subtidal mud banks and smaller islands of Florida Bay.

In the sea bed off the West Florida coast some 45 km SSW of Fort Meyers six different warm water springs have been discovered by Fanning et al. (1981). Earlier Kohout (1960, 1967) had revealed the existence of geothermal heating of the percolating ground water of the Florida aquifer. Water streams at rates of about 25 cm/s from these warm springs onto the continental shelf of western Florida. This warm spring water (average temperature 313 K) is in fact seawater impoverished in oxygen, phosphate, and nitrate. At the same time it is enriched in ammonia and hydrogen sulfide. In other words bacterial sulfate reduction must have affected the spring water. Because of the measured increase (of about 35 %) in the amount of dissolved calcium and a decrease (of about 5 %) of magnesium, Fanning et al. (1981) surmised dolomite to be forming in the Floridan aquifer (much like Hanshaw et al., 1971).

Khoury et al. (1982) found dolomite, apparently of Quaternary age, in playa deposits of the Amargosa Desert, Nye County, Southern Nevada. (Earlier Papke, 1972 had reported dolomite from the same playa deposits.) The area must have been a large lake during Late Pliocene and Pleistocene times. Due to changes in the climate the level of the lake fluctuated, and from time to time the lake must have become subdivided into a number of smaller lakes. The Amargosa Flat is now a playa covered by a thin salt crust, and conditions are still dynamic. Although the warm and dry climate that prevails in the region (mean annual temperature of 291 K; precipitation = 8 to 10 cm per year), leads to high evaporation rates (of some 250 cm/year), occasionally heavy rains do occur. Authigenic dolomite was found especially in smectite-sepiolite clay deposits. A distinction could be made by Khoury et al. (1982) between the authigenic form of dolomite and detrital grains of dolomite. Scanning electron photomicrographs showed crystals of this dolomite to be distinctly euhedral. Size of the crystals was given as ranging from 2 to 10 micrometer. The dolomite crystals were mixed with and embedded in a matrix of authigenic magnesium clay minerals: indication of the *in situ* mode of formation. Additional evidence was found in isotope ($O^{18}$ and $C^{13}$) analyses of samples of the authigenic dolomite. From the isotope analyses it can be concluded, that the dolomite had been precipitated from solutions not subjected to extensive evaporation. This conclusion is contradicted by the mineral paragenesis itself, because the precipitation of sepiolite requires relatively high salinities. The clay minerals kerolite and stevensite require the pH to be in the 8.5 to 9.0 range.

Dolomite of only 3500 years old has been found in the "Overburden Mud" of Late Quaternary deposits in Searles Lake, California (Haines, 1959; Smith & Haines, 1964; Smith, 1979). This lake, covering an area of about 100 km$^2$, is in fact a dry salt pan in the desert of southeastern California. The climate of the region is hot and arid; rainfall averages some 96 mm per year. The mean temperature is 292 K, with maxima around 321 K and minima near 261 K. During winter rainfall creates a water layer of several cm's thick, standing on Searles Lake for a few weeks or months. Most of the year Searles Lake is dry. The salt flat contains essentially

sodium- and potassium carbonate, sulfates, chlorides and borates, intercalated with mud layers. There is no plant growth on the salt flat, but the surrounding alluvial fans and mountains are covered by sparse vegetation. Eugster & Smith (1965) stressed the possible importance of fluctuations in the amounts of dissolved carbon dioxide (as influenced by the actions of plants and bacteria) and of seasonal changes in the concentration of the solution (as controlled by dilution from rainfall) on the mineral parageneses of Searles Lake. According to Smith (1979) the salts and muds of Searles Lake have been formed during Pleistocene and Holocene times in a series of interconnected lakes, that were once quite large and deep and that fluctuated in response to climatic changes. Using $O^{18}$ isotopes on core samples from Searles Lake, Phillips et al. (1989) found evidence of large-scale lake level fluctuations with a cyclic character.

Dolomite crystals have been found in Deep Springs Lake, California by Peterson et al. (1963) and by Jones (1965). This small, spring-fed lake lies at the centre of an intramontane basin east of Inyo and White Mountains, California. The climate in this part of the United States is arid, with hot and dry summer months. The lake itself has distinct playa characteristics; its volume fluctuates markedly with the seasons. Maximum water depth (of only 30 cm) is reached every winter or spring, and during the rest of each year the lake's water level gradually declines. But even in the midst of a dry summer a small quantity of brine fills the centre of the lake. Smith (1979, p.81) added the observation, that "In Deep Spring Lake, dolomite is abundant in the area flooded seasonally as the lake rises and falls, and along the side where lake waters mix with perennial, nearly fresh springs (Jones, 1965; Clayton et al., 1968)". The water of Deep Spring Lake contains especially dissolved carbonates and sulfates. The pH of the lake is, according to Peterson et al. (1963), about 9.5 to 10. Part of the dolomite found in Deep Spring Lake may be detrital contamination from dolomite formations in the nearby White Mountains, but much of the dolomite must be authigenic. Dating with radioactive isotopes showed the dolomite to be virtually Recent, and that it "... is still forming today" (Peterson et al., 1963, p.6498). And Jones (1965, p.44) concluded: "Precipitation of dolomite directly from solution is suggested by the occurrence of euhedral grains and the distribution of the dolomite; muds within areas of relatively frequent flooding by lake waters contain the highest percentage of dolomite." In more detail Jones (1965) observed how dolomite forms the dominant mineral of the gray-green and black muds of the lake area itself. But the distribution of dolomite here is related to the microrelief of the playa. Especially near the highest shoreline reached by the ephemeral lake, the percentage of dolomite is at maximum. The minerals deposited in Deep Springs Lake form a sequence going from playa margin to its centre of calcite and/or aragonite, dolomite, gaylussite, thenardite and burkeite (Jones, 1965).

Although Hardie (1968) doubted, whether he had found authigenic dolomite in Saline Valley, California and tended to believe, that he was describing a detrital dolomite washed into the playa-lake sediments, his findings will also be reviewed here. Saline Valley is a small, intramontane basin in Inyo County, California. The lowest part of Saline Valley is covered by a salt-encrusted playa of about circular form, with an approximate area of 40 km$^2$. Only part of the playa contains a very shallow layer of water, or rather a saturated solution of sodium chloride. The brine permeates much of the Pleistocene / Holocene lake sediments of Saline Valley to a depth of 0.3 to 4.5 m. The climate and rainfall of Saline Valley are not on record, but such records do exist for the nearby Death Valley. Data collected by Hunt et al. (1966) show, that here too a pronounced seasonal variation in amount of rainfall exists.

Barnes & O'Neil (1971) described dolomite from the Holocene travertines and conglomerate cements in perennial streams in the central and northern Coast Ranges of California (New Idria Creek, Adobe Creek and Big Austin Creek). The water of these streams consists of a magnesium bicarbonate solution (the Mg/Ca ratio of the water of New Idria Creek is 24.4 ; the Mg/Ca of the water of Adobe Creek is 31.2 ; and the water of Big Austin Creek had at the time of measurement Mg/Ca = 13.8 ). The relatively high concentrations of magnesium

cations are the result of the weathering of ultramafic rocks (serpentinites) in the source area. Water samples taken, yielded after desiccation in the laboratory only nesquehonite. There is a marked day/night periodicity introduced by the photosynthetic activity of freshwater algae in these creeks. In addition an annual fluctuation in water chemistry exists, which is caused by a seasonal supply of rainwater ("In the Mediterranean-type climate of the California Coast Ranges, stream discharge fluctuates seasonally": Barnes & O'Neil, 1971, p.704). The occurrence of Holocene dolomite in freshwater cements from the Coast Range of California has been confirmed by Blake & Peacor (1985). Although many of the fluviatile cements were found to consist of magnesium calcite, Blake & Peacor (1985) did find a number of samples consisting of dolomite *sensu stricto* with superstructure reflections.

Recent dolomite from six different pluvial lakes (Muleshoe Lake, Silver Lake, Rich Lake, Mound Lake, T-Bar Lake, and Guthrie Lake) from southern Llano Estacado, Texas has been described by Reeves & Parry (1965). Radiocarbon isotope measurements showed, that the dolomite is about 17,400 ± 600 to more than 37,000 years old. Reeves & Parry (1965) pointed out, that these seasonal lakes undergo drastic changes over relatively short intervals of time, due to climatic reversals. The carbonate precipitation in these lakes would be caused by 1) desiccation, 2) a rise in temperature, 3) a rise in pH; or 4) a combination of the preceding three factors.

Dolomite crystals with an age of 20,300 ± 825 years B.P. (collected at a depth of 87.5 cm below the surface of the sediment) from the Salt Flat Graben, western Texas were reported by Friedman (1966). The intramontane basin that constitutes the Salt Flat, is filled with laminated sediments. The laminae of these sediments are made up of light-colored seams containing gypsum and halite and black seams with calcite, aragonite, and dolomite. The black layers contain iron sulfide, hydrogen sulfide and native sulfur; all of which are indications of the activities of sulfate reducing bacteria. According to Friedman (1966) the laminations represent fluctuations of water level. The laminated deposits of the Salt Flat Graben show a definite relation between dolomite content and a decrease in halite/gypsum content: "Apparently what gypsum was formed during the deposition of dolomite was transformed to sulfide and native sulfur": Friedman (1966, p.265). In the explanation of Friedman (1966) dolomite formation must have taken place, when the lake was deep and bacterial sulfate reduction could flourish. When the water table was lower, deposition of halite and gypsum must have taken place. Subsequently the lake was filled again with water and another layer of dolomite was deposited.

Holocene dolomite from the subtidal deposits of Baffin Bay, Texas has been described by Behrens & Land (1972). Carbon isotope measurements gave an age of some 2300 to 4300 years to the dolomite samples. According to Behrens & Land (1972) this dolomite could have been formed only in the intratidal environment. From a series of carbonate isotope measurements from one core it could be concluded, that the same depositional environment must have existed for the last 4000 years. Beds of dolomite were found in cores from about 7 m below the present sea level to a maximum depth of 11.6 m. Structures typical of the supratidal environment (such as mudcracks, birdseye structures and root casts) were not found. Therefore the reducing muds under Baffin Bay must have been deposited in the intratidal zone only (Behrens & Land, 1972). Baffin Bay is part of a small and restricted drainage basin, and is located in a semi-arid climate. Salinity of the water is usually higher than that of normal seawater, but rarely exceeds 85 ‰. In addition this salinity clearly fluctuates: Folk & Siedlecka (1974) described Baffin Bay as an example of the "schizohaline environment", because the salinity varies here from as much as 75 ‰ during drought years to as low as 1.4 ‰ during storm floods and local deluges.

Authigenic dolomite from the Holocene sediments of Laguna Madre, Texas has been described by Miller (1975). The semi-arid climate of western Texas (where evaporation exceeds precipitation by some 500 mm per year) is the main cause for the high salinity of the water in

the lagoon. During dry summer months salinities of more than 50 ‰ can be measured in the Laguna Madre. The extensive tidal flats associated with the ephemeral Laguna Madre contain numerous small depressions, which will be flooded as soon as the area is inundated by high tides of the sea or by heavy rains. Most of these ponds are less than 25 cm deep, and algal mats flourish shortly after such flooding. At the same time clay taken into suspension during the flooding will settle again and will so be incorporated into the algal mats. After each flooding the water of the small basins starts to evaporate, and small salt pans are formed, where mainly halite precipitates. In these small ponds the halite is not preserved in the sediment itself. The only evidence of the former existence of the small ponds in the sediment are thin layers (2 to 8 cm thick) of black clay, with a high percentage organics and a carbonate content of some 5 % (Miller, 1975). Authigenous dolomite from the Holocene sediments of the Salt Flat, Western Texas, has been documented by Warren & Hussain (1984). "The lake sediments show well defined varve-like lamination of alternating dark and light layers" (Warren & Hussain, 1984, p.117). Two different sorts of modern dolomite were found: one of the two is well crystallized with superstructure reflections.

On Elmer's Island, Louisiana modern dolomite has been found by Kocurko (1986) in the form of a surface crust cement. Hypersaline conditions in combination with algal growth were thought to be responsible for crust development and the nucleation of high-magnesium calcite and dolomite. "Samples of surface crusts collected ... range from a combination of aragonite, dolomite and high magnesium calcite, to samples cemented entirely by high magnesium calcite. This probably indicates periodic changes in the precipitating environment": Kocurko (1986, p.14). Distinct seasonal fluctuations in groundwater chemistry were measured. Samples taken in one particular area in January 1984 gave an average salinity of 38.8 % at 285 K and pH = 6.7 . But analyses in August 1983 of samples from the very same area had given a salinity of 45.2 % at a temperature of 303 K and pH = 8.2 .

Chemical analyses of soil samples from the Lualuaei Valley, Waianae Valley and Makaha Valley, all situated on the Island of Oahu (Hawaian Islands) revealed the presence of high percentages of authigenic dolomite (Sherman et al., 1947). The formation of dolomite in the soils could only have been authigenic, because the alluvial parent material did not contain any dolomite. The magnesium content of the soils is high (from 20 to 45 % of the exchangeable cations are magnesium cations), and appeared to be related to the high content of magnesium silicate in the parent rock. In certain horizons the percentage authigenic dolomite was as high as 94 %. The dolomite was found especially in the upper parts of the soil profile (0 to 50 cm); below this level crystals of gypsum were often found. Sherman et al. (1947) noted, that the presence of dolomite was directly related to the presence of gypsum in the deeper layers of the soil profile. When gypsum crystals were found, the upper layers of the soil invariably contained dolomite. With regard to the mode of formation of the dolomite Sherman et al. (1947) concluded, that the presence of soluble salts of magnesium (in this case magnesium sulfate) was essential. The soils containing dolomite all go through a pronounced annual cycle of wetting and drying.[22]      The desiccation of the soil during the dry season leads to high concentrations of magnesium, the Mg/Ca ratio will be raised to values far greater than unity, and thus conditions "... favorable to the formation of dolomite" are created (Sherman et al., 1947, p.43).

Dolomite *sensu stricto* has been found by Capo et al. (2000) in a soil on the Kohala peninsula, northwestern Hawaii. The soil developed on basaltic lava flows on the semi-arid northwestern slope of the Mauna Kea and Kohala volcanoes. The weathered part (about 1 m thick) of this soil is fine-grained (< 2 mm) and is composed mainly of gibbsite, hematite and halloysite. Between 1 and 3 m depth the unweathered lava contains carbonate, which acts as a cement in between rock fragments. X-Ray diffraction showed the carbonate to consist of dolomite (including superstructure reflections). The dolomite in this soil must have developed in an oxidizing environment under the influence of rain water only. The source of magnesium

cations here is most probably the weathering of olivine or high-Mg glass present in the volcanic lava. Léveillé et al. (2000) found modern dolomite (together with aragonite, Mg-calcite, monohydrocalcite, magnesium hydroxide carbonate, and magnesite) in caves on the island of Kauai, Hawaii. The parent rock at this location consists of basalt. In microprobe analyses the dolomite from Kauai was measured to contain 46 to 58 (mol) % $MgCO_3$.

Dolomite has been reported by Gill et al. (1995) from St. Croix, U.S. Virgin Islands (Antilles). Pliocene carbonates were seen to contain dolomite only in the Krause Lagoon, an embayment on the coast of St. Croix. The unconsolidated sediments of this lagoon are made up from a mix of carbonate sand plus siliclastics, with indications of its origin as mangrove-lagoon carbonates and alluvium eroded from nearby eroded strata. Dolomite was not found elsewhere on the island of St. Croix.

## DOLOMITE IN DEEP-SEA SEDIMENTS

Although dolomite is mentioned to occur in the sediment samples collected during the voyage of H.M.S. *Challenger* (1873-1876), Murray & Renard (1891) did not want to consider it as an authigenous mineral: "Dolomite ... occurs in the deposits as fragments of dolomitic rocks associated with blocks or gravel of older crystalline and sedimentary rocks transported by icebergs" (Murray & Renard, 1891, p.20). One of the earliest accounts on Recent dolomite dredged or cored from deep-sea sediments is that of Phillipi (1907), describing carbonate nodules, that had been dredged by the German research vessel *Valdivia* from a depth of about 150 m from the Seine Bank near Madeira ($33^o$ 47' N / $14^o$ 20' W). The nodules were studied by chemical analyses as well as in thin section. Microscopic examination revealed the hard nodules to consist of the calcareous parts of molluscs, gastropoda and calcareous algae. In addition foraminifera (*Globigerina*), echinodermata, bryozoa, and coral remains could be recognized. The hard parts had been cemented by very fine-grained cement, with a dark colour probably caused by organic matter. Overall chemical analyses gave compositions of about 80 wt.% $CaCO_3$ , 14 wt.% $MgCO_3$ and small amounts of $SiO_2$ and $Ca_3(PO_4)_2$ . After colouring the thin sections with a hot solution of aluminium chloride, amounts of dolomite were recognized by Philippi (1907): the fine-grained cement consisted for about 90 % of dolomite (indicating its authigenous origin). Especially the calcareous algae had been changed into dolomite, as could be seen in thin sections. Morphological details of the conversion of the calcareous algae into dolomite could be recognized.[23]

Bøggild (1916) reported finding dolomite concretions in three different samples from the Siboga Expedition held in 1899-1900 in the sea off the Dutch East Indies (= Indonesia).

In rock samples dredged from the Mid-Atlantic Ridge near St. Paul's Rock ($01^o$ 23' S / $29^o$ 49' W) fragments of serpentinite together with amounts of sepiolite, montmorillonite, zeolite and some dolomite crystals have been found by Hathaway & Sachs (1965). Up to that moment no sepiolite from the deep-sea environment had been known. The mineral sepiolite had been reported earlier to occur in association with dolomite for example by Rogers et al. (1956).[24]   In one of the pieces of (Pleistocene) lithified carbonate sediments dredged from equatorial Atlantic Ocean in the vicinity of St.Paul's Rock, Thompson et al. (1968) found dolomite in a loosely knit framework. Individual grains measured from 0.03 to 0.08 mm. Mixed with the dolomite were serpentine and chlorite. Larger fragments were identified as pieces of ultrabasic rocks, especially serpentinite.

A large boulder dredged from a depth of 1719 m off the coast of southern California ($33^o$ 44' N / $120^o$ 45' W), was found to consist almost entirely of dolomite. Perhaps this particular sample was but a stray boulder from the nearby Point Fermin dolomitic sandstone, but

Pierce & Melson (1967) left the possibility open, that the boulder was a piece of lithified deep-sea ooze.

Fischer & Garrison (1967) described a sample of indurated *Globigerina* ooze from the eastern Mediterranean Sea (from the 1891 Austrian *Pola* expedition; more in detail it was sample 85 collected from a depth of 2055 m at $31^o\,38'\,37''$ N / $28^o\,51'\,19''$ E) and from a locality off the coast of Barbados ($12^o\,52'$ N / $59^o\,32'$ W) (collected in 1964), which contained dolomite.

Dolomite of Pleistocene to Holocene age was found at depths of 185 to 455 m on the Aves Swell, a sea mount in the Caribbean Sea ($13^o\,30'$ N / $63^o\,10'$ W) and described by Marlowe (1971 B). The host rock consists of a carbonate conglomerate, made up predominantly by fragments of algae and molluscs, with clasts measuring ± 3 cm. Its color was reddish-brown, mottled with patches of grey and tan. Apart from dolomite, minerals such as apatite, calcite and oxides of iron and manganese were identified in X-ray diffraction. Dolomite occurred in general as isolated rhombs in a black colored matrix. Concentrations of dolomite crystals were found surrounding tests of foraminifera. The highest concentrations of dolomite were found there, where replacement and discoloration by iron and manganese were at maximum (Marlowe, 1971 B). Botz et al. (1988) described core samples from the Green Canyon Block 183 in the Gulf of Mexico as containing well-ordered dolomite ($Ca_{51}Mg_{49}$ on average).

The worldwide drilling activities in connection with the Deep Sea Drilling Project (which started in 1968) have revealed a relatively large number of new occurrences of modern dolomite in marine sediments. (Because Holocene marine sediments are somewhat rare, the term "modern" will be used in this section to include the whole of the Quaternary era.) Dolomite probably of Miocene age has been found by Zemmels et al. (1972) in cores 6 and 7 of DSDP site 98 ($25^o\,22.95'$ N / $77^o\,18.68'$ W), north-east Providence Channel; at various depth intervals at site 101 A ($25^o\,11.93'$ N / $74^o\,26.31'$ W), southern end of the Blake-Bahama outer ridge, dolomite occurred together with siderite, manganosiderite and rhodochrosite. At the very top of the core drilled at site 104 ($30^o\,49.65'$ N / $74^o\,19.64'$ W), northern end of the Blake-Bahama outer ridge, modern dolomite was found in a hard, burrowed calcareous crust consisting mainly of calcite.

Davies & Supko (1973), after evaluating samples drilled up to that time during the Deep Sea Drilling Project, attributed most of the dolomite found in deep-sea sediments to magnesium enrichment from igneous or volcanic activity, but added, that dolomite formation might be related in some instances to the predominance of reducing conditions. Sediments collected at DSDP site 147 ($10^o\,42.48'$ N / $65^o\,10.48'$ W), which is located in the Cariaco Basin on the continental shelf of Venezuela, contain several thin layers of almost pure dolomite at a depth of around 100 m (Edgar et al., 1973; Fan et al., 1973). Pyrite was found throughout the entire core. High intensity bacterial sulfate reduction led to the depletion of dissolved sulfate anions at depths exceeding 5 m below the top of the core (Gieskes, 1973; Sayles et al., 1973). Only trace quantities of dolomite were found in the top 20 m of this core. Gieskes (1973) analyzed a multitude of pore water samples from DSDP sites 147, 148 and 149, and found in the core from site 147 a sharp increase in $NH_4$ content and in alkalinity below a depth of 60 m "... which is clearly due to the process of fermentation as suggested by the high $CH_4$ and $CO_2$ contents in the gas pockets of these sediments" (Gieskes, 1973, p.818). In the lower part of the core from site 147   pH = 6.6 was predominant. In the pore water samples from site 148 comparable large changes in sulfate content, in alkalinity, in ammonia-, in calcium- and magnesium content with depth were measured. Below 100 m in the core from site 148 siderite was found by Gieskes (1973). In contrast the samples from core 149, which have in general a different mineralogy, did not show a correlation between changes in alkalinity and the process of bacterial sulfate reduction.

Dolomite layers of 20 to 30 cm thick alternating with sapropel layers, both containing pyrite, were found in a core at DSDP site 138 ($25^o\,55.37'$ N / $25^o\,33.79'$ W), some 1000 km west

of Cap Blanc, Africa. Berger & Von Rad (1972) were convinced, that the dolomite found at DSDP sites 135 to 144 had originated by way of enrichment through "differential dissolution", and part of it must have been re-deposited. But Davies & Supko (1973) considered the perfectly planar crystal surfaces they had observed with the scanning electron microscope, to be evidence of an authigenic origin.

Hein et al. (1979) described authigenic dolomite from DSDP sites 184 ($53^o$ 42.64' N / $170^o$ 55.39' W), 185 ($54^o$ 25.73' N / $169^o$ 14.59' W), 186 ($51^o$ 07.81' N / $174^o$ 00.34' W), 188 ($54^o$ 45.21' N / $178^o$ 39.56' W), 189 ($54^o$ 02.14' N / $170^o$ 13.38' E), 190 ($55^o$ 33.55' N / $171^o$ 38.42' E), 191 ($56^o$ 56.70' N / $168^o$ 10.72' E) and 192 ($53^o$ 00.57' N / $164^o$ 42.81' E) (Bering Sea, near the Aleutian Islands) in association with rhodochrosite, siderite, manganosiderite and pyrite. From the paragenesis with partly to completely siliceous microfossils Hein et al. (1979) concluded a replacement origin for the carbonates (including dolomite). Not only siliceous sediments had been replaced by carbonates: the same had happened in several instances to layers of ash and bentonite. "Sedimentary sections in the Bering Sea contain at least forty authigenic carbonate beds or replacement zones that are as much as 60 cm thick": Hein et al. (1979, p.696). That this dolomite must have been a primary precipitate, was concluded by Hein et al. (1979) on the basis of textural evidence; the conditions favouring its deposition must have been caused by bacterial sulfate reduction. After completion of sulfate reduction ongoing bacterial fermentation led to the generation of methane; the resulting high pH of the pore water led to the precipitation of carbonates. At this stage, or possibly even later, the dissolution of silica must have taken place (Hein et al., 1979).

Dolomite of Miocene to Pliocene age has been found by Supko et al. (1974) in the cores from the central Red Sea Main Trough, DSDP sites 225 ($21^o$ 18.58' N / $38^o$ 15.11' E), 227 ($21^o$ 19.86' N / $38^o$ 07.97' E), and 228 ($19^o$ 05.16' N / $39^o$ 00.20' E). "In both the Mediterranean and Red Sea, the dolomites are associated with organic matter and pyrite": Supko et al. (1974, p.876). In several instances the amount of organic matter mixed with the dolomite in these core samples was such, that Stoffers & Kühn (1974) described it in terms of stromatolites and oncolites.

In several cores from the Deep Sea Drilling Project taken off the coast of Peru and Chile, as well as in gravity cores, Burnett (1977) found Holocene deposits of phosphorite together with modern dolomite. In all cases the dolomite-containing sediments are anoxic with indications of active bacterial sulfate reduction. Similarly Glenn & Arthur (1988) reported finding modern dolomite (together with phosphorite, pyrite and glauconite) in the organic-rich sediments off the coast of Peru. According to Glenn & Arthur (1988) the aforementioned authigenic minerals must have formed within a few centimeters or within a few tens of centimeters below the interface sediment-water. Notably in the core from their station 4 ($12^o$ 05.1' / $77^o$ 40.0' W) large amounts of dolomite, with 47.8 to 49.0 mol % $MgCO_3$ , which according to Glenn & Arthur (1988) may have precipitated in association with bacterial sulfate reduction and/or methane formation. The zoning of the accompanying pyrite concretions has been attributed to "…the delicate chemical fluctuations that must occur during the precipitation of each of these species": Glenn & Arthur (1988, p.257).

Carbonate nodules from site 434 of the Deep Sea Drilling Project ($39^o$ 44.76' N / $144^o$ 06.12' E; i.e., the lower slope of the land ward wall of the Japan Trench) containing dolomite, siderite and manganese carbonate have been described by Okada (1980). In the Plio-Pleistocene muds off the southern coast of California at DSPD site 467 ($33^o$ 50.97' N / $120^o$ 45.47' W) dolomitic beds were found in ten different horizons from depths of 148 m and more from the top of the core (Yeats et al., 1981). Dolomite in a variety of forms (dispersed rhombs, dolomite nodules and beds of almost pure dolomite) was reported by Kelts & McKenzie (1982, 1984) from the cores collected at DSDP site 479 ($27^o$ 50.67' N / $111^o$ 37.49' W), on the Guayamas Slope in the Gulf of California. Dredged samples from the same locality consisted of almost

pure dolomite. In the core samples bacterial sulfate reduction was found to be complete below a depth of 2 m from the top of the core. Pyrite was an abundant accessory in the samples.

From the Pliocene and Pleistocene sediments on Walvis Ridge off the southwestern coast of Africa at DSPD sites 362 ($19^o$ 45.45' S / $10^o$ 31.95' E) and 532 ($19^o$ 44.61' S / $10^o$ 31.13' E) dolomite has become known (Gardner et al., 1984). Only small amounts of dolomite were found in the Pleistocene deposits, but as much as 30 to 40 wt. % were found in the upper Pliocene muds. The dolomite found there, shows superstructure reflections. Throughout the whole of section 362 authigenic pyrite was found. Bacterial sulfate reduction was taking place in the core of site 532 up to a depth of as much as 120 m below the sedimentary interface; below 120 m the first methane gas was measured. Gardner et al. (1984) reported to have found a distinct large-scale periodicity in percentage carbonate, in color and percentage organic carbon in the Quaternary sediments of DSDP site 532 on Walvis Ridge. The three different cycles did not coincide in frequency: the average of the carbonate cycle was about 36,000 years. Even so minima in calcium carbonate usually coincided with the darkest parts of the core: the carbonate-rich were usually light coloured. The origin of the periodicity as such has to be found, in the view of Gardner et al. (1984), in productivity changes associated with changes in the global sea level. Because of the similarity of the $CaCO_3$-cycles to those measured in cores from the western Caribbean and eastern equatorial Pacific (Gardner, 1982), the cause of the periodicity had to be related to a global rather than a local event. The oceanic sediments off the coast of the Southern Cape Basin (Southwest Africa) undergo intense chemical reactions (caused by transformations of the high percentage of organic matter) involving dissolution and precipitation of minerals. According to Wefer et al. (1998) the reactions taking place in these sediments include the dissolution of biogenic (Mg-) carbonate and the formation of dolomite.

Quaternary sediments from cores from DSDP site 102 (on the outer ridge of the Blake Plateau, east of Florida) as well as those collected from the nearby DSPD site 533 ($31^o$ 15.6' N / $74^o$ 52.5' W) contain dolomite: Hollister et al. (1972), Matsumoto (1983). Active bacterial sulfate reduction takes place in the upper 15 m of the core from DSDP site 533; dissolved oxygen is absent from the pore water even at very shallow depths of less than 1 m (Claypool & Threlkeld, 1983). The rapid increase in alkalinity with depth of this core leads to the precipitation of carbonate minerals including dolomite. According to Matsumoto (1983) the main part of the carbonate fraction from the core taken at site 533 consists of calcite: it is pure calcite from coccoliths and foraminiferal tests. Dolomite was found in the upper 192 m of the core; but it usually makes up only 5 to 10 % of the sediment. The main diffraction peak of the dolomites ranged from 28.87 to 29.06 nm. In scanning electron microscopy Matsumoto (1983) found two different fabrics of dolomite: the first one consists of isolated rhombs and the second one of interlocking polyhedral crystallites. The latter type of fabric was found in the few dolomitic lenses of this core. Sediments cored at site 533 were found to be rich in organic compounds: some 0.5 to 1 % organic carbon was measured. The entire core contains siderite in amounts approximately equivalent to the amounts of dolomite, but dolomite is more abundant in the upper part. Lower Eh values at greater depths of the core made it possible for siderite to precipitate, but only after ferroan dolomite had formed first (Matsumoto, 1983). Dolomite formation was, according to Matsumoto (1983), favored by the high alkalinity due to sulfate reduction, by a high pH caused by nitrate reduction, and by high Mg/Ca ratio's in the pore water of the sediments at site 533.

From the descriptions of the cores from DSPD sites 102, 147, 362, 467, 479, 532, and 533 Baker & Burns (1985) concluded, that modern dolomite forms only there, where sedimentation rates are less than 500 m/million years, and where the content of organic carbon is greater than 0.5 wt.% . Most likely all of this dolomite formed, or is still being formed, in the upper 10 to 20 m of the sediment, in the zone of active bacterial sulfate reduction. Typically the pore water chemistry at a site of active dolomite formation shows a depletion of dissolved

sulfate anions within the upper 10 to 15 m of the sediment column. At the same time the alkalinity of the pore water samples increases over the same trajectory: an indication for the possible precipitation of carbonate minerals. "It is not known whether the first shallow precipitate is calcite or dolomite": Baker & Burns (1985, p.1918). The precipitation of carbonate can also be concluded from the curve which denotes the calcium concentration as a function of depth of the core. The decrease in calcium is as abrupt as the decrease in sulfate anion groups. But in general Baker & Burns (1985) found the magnesium content of the cores not to decrease as abruptly as that of calcium. From this observation the conclusion was drawn, that dolomite would be precipitating at "somewhat greater depths". Methane production invariably takes place below the zone of active bacterial sulfate reduction and carbonate precipitation. Some of the DSPD cores showed bacterial sulfate reduction only in the topmost 5 m of the section. In other cores bacterial sulfate reduction was evident in the upper 120 m. Methane production would start only after bacterial sulfate reduction had ceased, whether after 5 m or after 120 m.

The dolomite (plus magnesium calcite and aragonite) found as an authigenic carbonate in hardgrounds and mounds on the Louisiana continental slope, was explained by Roberts et al. (1993) to be the result of bacterial activity in combination with hydrocarbon seepage. Stakes et al. (1999) attributed the formation of magnesium calcite and dolomite in the form of pavements of shallow cemented marine sediments to the escape of methane gas. Often the authigenic carbonate minerals were accompagnied by pyrite, illustrative of active bacterial sulfate reduction. Stoichiometric dolomite was found in the form of aggregates of idiomorphic crystals, often as overgrowths on detrital quartz grains. In addition the dolomite-rich samples contained more organic debris, more apatite and glauconite, than dolomite-free samples. All of the authigenic carbonate samples (whether slabs, knobs, crusts, chimneys, pavements or concretions) were pitted with worm and/or clam borings and showed dissolution pits.

After reviewing data from DSDP sites 147, 467, 479, and 533, Compton's (1988) calculations on the degree of dolomite and calcite saturation showed the interstitial waters at these sites to be highly supersaturated with dolomite. "The calculated values range from 4 to 1950 times supersaturation; most interstitial water is 60 to 250 times supersaturated... The degree of dolomite saturation increases rapidly and then gradually decreases with sediment depth": Compton (1988, p.319). The most comprehensive survey of all of the dolomite found in the cores of the Deep Sea Drilling Project up to that time (7,167 X-ray files from legs 1 to 37 and 55,886 smear slides from all 96 legs) has been published by Lumsden (1988). The following observations were made by Lumsden(1988): - dolomite rhombs occur mainly in interstices of the sediment and the smaller crystallites (4 to 8 micrometer) did not show evidence of mechanical wear; - few indications pointing towards a replacement origin were found ["Only one sample showed definite replacement (where dolomite cuts across calcite textures); forams were partially replaced by dolomite crystals": Lumsden, 1988, p.1026]; - only 96 out of the 55,886 smear slide samples showed a relation between organic material and dolomite; - dolomite does not increase in crystal size or in degree of stoichiometry with increasing burial depth (age); and - dolomite occurs in deep-sea sediments in almost all cores of the Deep Sea Drilling Project, but more so in those from the Atlantic Ocean, especially from small basins and near continental shelves.

Von Rad et al. (1996) described modern dolomite (together with calcite and Mg-calcite) from crusts of authigenic carbonates at the sedimentary interface in the Arabian Sea off the coast of Pakistan. Seepage of methane and hydrogen sulphide from the zone of active microbial sulphate reduction, followed by (partial) oxidation of methane to carbon dioxide, was thought to be the main mechanism involved (comparable to the processes taking place in North Sea sediments studied by Iversen & Jørgensen, 1985). According to Roberts & Carney (1997) the escape of hydrocarbons (fluids or gases such as methane) from sediments accumulating on the continental slope rarely is a continuous process. Slow escape would be responsible for the

(submarine) formation of carbonate hardgrounds, whereas more vigorous escape gives rise to chimneys and cones. But all venting and seeping phenomena show an episodic, periodically interrupted, pattern (Roberts & Carney, 1997).


DOLOMITE IN CAVES


Elschner (1913) reported on finding large caves with dolomite stalactites in the (Holocene ?) limestones of the Nauru atoll.[25]    Pobeguin (1960) found dolomite in a cave near Saint-Cézaire (Alpes maritimes, France). In addition to the dolomite, aragonite, magnesite and huntite were found. Infrared spectroscopy was used in the mineralogical analysis, and therefore no information on the presence or absence of superstructure reflections has become available. The caves in this region of France occur in Jurassic limestones and dolomites. Dolomite has been found in the Lehman Caves (Nevada, USA) and in the Titus Canyon Cave (California, USA) by Moore (1961 A,B). The dolomite of the Lehman Cave occurred as "... an outer milky layer" on aragonite crystals. From the paragenesis it was concluded, that the mineral dolomite had been formed "... by an alternation of aragonite on the surface of the speleothems by contact with a solution rich in magnesium ions" (Moore, 1961 A, p.82). In certain places the dolomite formed a coating over deposits of huntite; at other locations dolomite was found mixed with calcite. Dolomite occurring on a "... bizarre, irregularly curved, crust-like speleothem" from Tecoma Crystal Cave (Utah, USA) has been described by Halliday (1961). Thrailkill (1968) found dolomite in the "Big Room" of the Carlsbad Cavern (New Mexico, USA); the occurrence of dolomite in this cave has been confirmed by Gonzalez & Lohmann (1988) as well as Polyak & Güven (2000). In the view of Thrailkill (1968) the dolomite had to be authigenic: the bedrock of this part of the cave does not contain any dolomite (but the Yates Formation that crops out in other parts of the cave, consists of pure dolomite: Thrailkill, 1971). The temperature in the Carlsbad Cavern is constant throughout the year. A temperature of 287.5 K is maintained within $0.5^o$ in the area of collecting (Thrailkill, 1968). Fischbeck & Müller (1971) reported on the occurrence of dolomite, together with calcite, aragonite, magnesium hydroxide carbonate and nesquehonite, in a small cave (Eibengrotte) near Wiesenttal (SE of Bamberg, Germany). Although this cave is situated in dolomitic rocks of Jurassic age, the authigenic dolomite of modern age could be distinguished from the quartz-containing detrital dolomite on the basis of petrographic analysis. In the Sumidero Tenejapa, a large cave in central Chiapas State (Mexico), Broughton (1974) has found (proto-) dolomite. In addition magnesium hydroxide carbonate, calcite and magnesite were found by Broughton (1974) in this Mexican cave. Ward & Halley (1985) reported on a core sample reaching into a limestone cave of the Yucatán Peninsula, Mexico. The travertine samples recovered contained zoned dolomite crystals, in which dolomite alternating with calcite and aragonite was detected. Recent dolomite has been found by Fischbeck (1976) in the Križna Jama Cave, near Postojna (the former Yugoslavia). Doubt might arise concerning the observation that this dolomite really is of authigenic origin, because like in the case of the Eibengrotte the host rock contains dolomite. At least in the case of the Eibengrotte Fischbeck (1976) was able to demonstrate, that the samples collected were of Holocene age (in clear contrast to the host rock, which is of Jurassic age). Radiocarbon measurements gave age determinations of 1815 ± 165 and 795 ± 145 years. From the *Montmilch* deposits in the Haitón de Sabana Grande and the Segunda Cascada caves (Venezuela) Urbani (1977) has described dolomite. In several caves of the Transvaal region (South Africa) Martini & Kavalieris (1978) found authigenic dolomite in the form of cave popcorn, as a loose powder on the ground of the caves or as *Montmilch*.

Although caves are in fact large dissolution features, local precipitation of previously

dissolved carbonates may well take place. The large-scale change from dissolution to precipitation finds its origin in seasonal changes in the amounts of groundwater and/or the amount of dissolved carbon dioxide. Enrichment in dissolved carbon dioxide takes place through the carbon dioxide release of plant roots and carbon dioxide production of soil microorganisms. In this respect it is important to note the observation made by Holland et al. (1964), who have measured $pCO_2$ values 24 times as high as the atmospheric $pCO_2$ in the drips from stalactites and the water from pools in the Indian Echo Cave (Pennsylvania, USA) and the Lurray Caverns (Virginia, USA). The resulting high bicarbonate concentrations are responsible for the dissolution of calcium carbonate, magnesium carbonate or dolomite of the host rock. The amounts of groundwater and the quantity of dissolved carbon dioxide vary with the seasons of the year (Todd, 1959; Davis & DeWiest, 1966). In addition fluctuations in amounts of rainfall between summer and winter there are secular variations between wet and dry years, when marked changes in the long term average takes place (Todd, 1959).

Small amounts of modern dolomite were identified by Léveillé et al. (2000 A) in cave deposits from the island of Kauai, Hawaii. This dolomite must have an authigenic origin, because the basalt in which the caves occur, nor the soils on top of the caves, do not contain any dolomite. According to Alonso-Zarza & Martín-Pérez (2008) the modern dolomite found in the Castañar Cave, near Cáceres (Extremadura), Spain, proves that not all dolomite is the result of bacterial sulfate reduction in anaerobic environments. Dolomite, along with huntite and magnesite, was reported by Pogson et al. (2001) from the Jenolan Caves, Australia.

A relatively large number of occurrences of dolomite in caves has been compiled by Hill & Forti (1997); for example in the Cango Cave, South Africa; Bethelem Cave, USA; the Dachstein Mammuthöhle, Austria; Mungyeong caves, South Korea; Beremend Crystal Cave, Hungary; caves of the Malguzar Mountains, Uzbekistan; Valea Rea Cave, Romania; and the Santa Barbara mine cave of Sardinia, Italy.


DISCUSSION


In the introduction to this chapter the suggestion was made, that perhaps a listing of local parageneses might provide a clue to solve the dolomite problem. Now the contrary seems to have come true: a bewildering mass of details has resulted, apparently without any factor or factors in common. Not only conditions seem to vary from country to country, even within one country the conditions appear to diverge. It really seems hard to draw any conclusion at all.

At least one conclusion can be drawn at this moment: the general idea, that dolomite would form only in the marine environment is not based on facts. As early as 1834 Le Play recognized, that dolomite of Quaternary age in the Badajoz area (Spain) had to be of limnic origin. Similarly Leube (1839) described the occurrence of a non-marine dolomite.

Another conclusion concerns the possible significance of specific factors present in an environment, where modern dolomite has been found. According to Patterson & Kinsman (1982) the low-temperature formation of dolomite would take place under the following conditions: a) chloride concentrations between 3.25 and 3.75 $mCl^-/kg$; b) Mg/Ca ratio of more than 6; c) pH between 6.3 and 6.9; d) minimum $pCO_2$ between $10^{-2}$ and $10^{-3}$ bar; e) temperature between 298 and 313 K; f) saturation with respect to gypsum; and g) reducing conditions as caused by the presence of hydrogen sulfide. Earlier Folk & Land (1975) had suggested, that dolomite would form in a hypersaline environment at Mg/Ca ratio's between 5 and 10. When studying the spread amongst the values for the Mg/Ca ratio's (Table IV), the different salinities (Table V), and the pH values (Table VI) measured in various locations where modern dolomite has been found, little if anything can be concluded, let alone be predicted.

However, one factor really seems to be of significance with regard to the low-temperature formation of dolomite: fluctuations. The multitude of regional occurrences of Recent (at least Quaternary) dolomite presented here, together with evidence of the presence of fluctuations in pressure (p), temperature (T), or concentration (x), may have amazed some, but will certainly have raised scepticism in others. It will go without too many words, that in virtually every ecosystem fluctuating parameters can be discerned, hence also in those environments, where Recent dolomite is being formed. Such fluctuations in p, T, or x are virtually omnipresent. Even in deep-sea carbonates the effects of (very low frequency) fluctuations has been recognized (see for example Gardner et al., 1984). Fluctuations with different frequency and amplitude are known to occur in nature. To mention only a few: 1) day & night changes in temperature; 2) day & night changes in $pCO_2$ as the result of alternations between photosynthesis and respiration; 3) (diurnal) tides of the sea; 4) seasonal storms, which flood the supratidal flats; 5) the seasonal changes in temperature, in rainfall and desiccation; 6) seasonal changes in accumulated water mass of lakes or playa's; 7) seasonal changes in pore water level and pore water chemistry of soils, et cetera. Very few authors have taken up the example of Camur et al. (1996) and quantified the seasonal changes taking place in water chemistry of environments where dolomite or magnesite were found. (But those changes cannot be overlooked. In the Tuz Gölü salt sea, Turkey, the concentration of potassium changed seasonally from 800 to 10,000 mg/dm$^3$; the Mg/Ca ratio from 2 to 190; alkalinity from 2.10 to 14.43 meq/dm$^3$; and sulfate ion concentration from 6.6 to 67 gr/dm$^3$.) Even living organisms contribute to the occurrence of fluctuations. There is at least one observation, indicating, that possibly living trees have something to do with dolomite formation: Baltzer et al. (1982) found more dolomite, there where mangrove trees were growing on the sediments of the delta of the Mehran River (Iran), than there where no trees grew. From studies on the hydrology of forests and soils it is known, that because of their vast capacity for evaporation living trees will influence the position of the water table.

The causal relation between the low-temperature nucleation of dolomite and fluctuations proposed by me (Deelman, 1999) appears to receive support from "static controls" found in nature, that is carbonate-precipitating environments without marked fluctuations. A number of those environments will be discussed.

Skinner (1963) expressed her astonishment over the fact, that in contrast to most of the ephemeral lakes associated with the Coorong Lagoon, the Quaternary sediments of the Magrath Flat (part of the Coorong Lagoon itself) did not contain any dolomite. The prevailing temperature (of around 297 K), the pH (of 9.2) and the salinity of the water (of 26.7 ‰), as well the occurrence of plants, were all factors the two environments had in common. The only difference was, that the ephemeral lakes went through a pronounced annual cycle of desiccation and flooding, whereas the Magrath Flat is *"... not subject to the same periodic wet-dry cycle as the southern end of the Coorong and its lagoons*": Skinner (1963, p.462).

Angino et al. (1964) described carbonate precipitation in Lake Bonney, Antartica. The salinity of the water of this lake exceeds 400 ‰, the Mg/Ca ratio of the water varies between 0.7 and 16.9, but the only carbonate precipitated is aragonite (together with gypsum and sodium sulfate). A large number of "static controls" has been described by Müller et al. (1972): Lake Ngorongoro (Tanzania), Lake Natron (Tanzania), Lake Shala (Ethiopia), Lake Constance (Germany/Switzerland), Plitvičkih jezera (the former Yugoslavia), Band-e-Amir (Afghanistan), Lake Manyara (Tanzania), Lake Nakuru (Kenya), Lake Balaton (Hungary) all precipitate calcite or magnesium calcite, but not dolomite. In contrast the "dynamic lakes" (i.e., lakes with pronounced fluctuations) Neusiedler See (Austria/Hungary), Dasht-i-Nawar (Afghanistan), Tuz Gölü (Turkey), Aci Göl (Turkey), Boluk Gölü (Turkey) and Tuzla Krater Gölü (Turkey) all precipitate dolomite (in addition to magnesium calcite, aragonite, huntite, and/or magnesite).

It might be argued, that the marked differences in chemistry between the "static" and the

"dynamic" lakes would be responsible for the formation of modern dolomite. In fact the chemistry of the series of "static" lakes (with salinities ranging from 0.3 to 75 ‰, with its pH between 7.0 and 9.0 , and with Mg/Ca ratio's between 4.5 and 500 ) matches that of the "dynamic lakes". However there is a third category of carbonate precipitating lakes, which contradicts any suggested relation between salinity and dolomite, between pH and dolomite, or between dolomite and Mg/Ca ratio. The waters of the Krater Aci Göl (Turkey), Ob-i-Istada (Afghanistan), Burdur Gölü, Van Gölü, Ercek Gölü and Arin Gölü (all four in Turkey) have salinities ranging from 13 to 67 ‰, pH values ranging from 7.6 to 9.9 , and Mg/Ca ratio's between 25 and 181 , but in these lakes only aragonite precipitates (Müller et al., 1972). This third group of lakes is of the "static" kind.

| author(s) | location | Mg/Ca |
|---|---|---|
| Aharon et al. (1977) | Solar Lake, Israel | 8.2 – 10.5 |
| Alderman (1965) | Coorong Lagoon, Australia | 3 – 100 |
| Alderman & Skinner (1957) | Coorong Lagoon, Australia | 2.9 – 6.5 |
| Atwood & Bubb (1970) | Sugarloaf Key, Florida | 2.9 – 6.8 |
| Azzaro et al. (1983) | Lake Specchio, Italy | 31 – 48.5 |
| Baker & Burns (1985) | deep-sea sediments | 1 – 5 |
| Barnes & O'Neil (1971) | rivers, California | 13.8 – 31.2 |
| Von der Borch (1965) | Coorong area, Australia | 8 - 20 |
| Von der Borch (1976) | Coorong area, Australia | 0.1 – 3 |
| Von der Borch et al. (1975) | Coorong Lagoon | 0.58 – 2.6 |
| Burns & Swart (1992) | Jimmy Key, Florida | 4.8 – 10.9 |
| Bush (1973) | sabkha, Abu Dhabi | 5.1 - 235 |
| Butler (1969) | sabkha, Trucial Coast | 5.3 – 35 |
| Camur et al. (1996) | Tuz Gölü, Turkey | 0.1 – 2.5 |
| Comin et al. (1990) | Lake Gallocanta, Spain | 7 – 50 |
| Cook (1973) | Broad Sound, Australia | 2.3 – 10.7 |
| DeDeckker & Last (1989) | lakes, Australia | 6 - 94 |
| Deffeyes et al. (1964) | Pekelmeer, Bonaire | 3.14 |
| Eugster & Hardie (1978) | Basque Lake 2, Canada | 78 |
| Friedman et al. (1985) | Ras Muhammed Pool, Israel | 2.4 – 19.8 |
| Glenns & Evans (1976) | Ranns of Kuch, India | 3 - 240 |
| Gunatilaka (1991) | Al-Khiran, Kuwait | 3.6 – 14 |
| Gunatiliaka et al. (1984) | lagoon, Kuwait | 5.2 – 6.3 |
| Hardie (1968) | Saline Valley, USA | 0.03 - 30 |
| Irion (1970) | Tuz Gölü, Turkey | 8.6 – 514 |
| Jakher et al. (1990) | Sambhar Lake, India | 0.4 – 2.9 |
| Kelts & Shahrabi (1986) | Lake Urmia, Iran | 0.3 - 72 |
| Kohut et al. (1995) | soil, Canada | 37 - 72 |
| Koppenol et al. (1977) | Naxos, Greece | 0.3 – 5.5 |
| Last (1990) | lakes, Canada | 2 - 81 |
| Mann & Deutscher (1978) | lakes, Australia | 0.62 – 6.41 |
| Marfil et al. (1975) | lakes, Spain | 1.31 – 47.1 |
| Mazzullo et al. (1995) | Cangrejo shoals, Belize | 8 - 12 |
| McKenzie et al. (1980) | sabkha, Abu Dhabi | 2.5 – 27 |
| Medhioub & Perthuisot (1981) | Sabkha, Tunisia | 3.14 – 3.98 |
| Molnár (1980) | lake, Hungary | 2 – 50 |
| Müller et al. (1972) | various lakes | 4.5 – 500 |
| Müller et al. (1990) | sabkha, Abu Dhabi | 1.50 – 9.76 |
| Mutlu et al. (1999) | Lake Acigöl, Turkey | 0.84 – 10.1 |
| Nesbitt (1990) | Basque Lake, Canada | 12.68 – 78.20 |
| Nissenbaum (1980) | sabkha, northern Sinai | 3.5 - 118 |
| Patterson & Kinsman (1982) | sabkha, Arabian Gulf | 5 - 35 |
| Perthuisot (1971) | sabkha, Tunesia | ± 100 |
| Pierre et al. (1984) | lagoon, Mexico | 1.7 – 19.8 |
| Renaut (1990) | saline lakes, Canada | 3 – 350 |
| Rosen et al. (1992) | Lake Hayward, Australia | 7 - 10 |

| | | |
|---|---|---|
| Rostad (1975) | Debden, Canada | 6.2 – 12.2 |
| Sherman et al. (1947) | soils, Hawaii | 0.14 – 0.7 |
| Sinha & Raymahashay (2000) | Sambhar Lake, India | 0.12 |
| Skinner (1963) | lakes, Australia | 2.4 – 19.0 |
| Soriano et al. (1977) | Laguna de Salicor, Spain | 7.4 – 66.8 |
| Taylor & Illing (1969) | Qatar | 3.0 – 6.0 |
| Thrailkill (1968) | Carlsbad Cavern, USA | 1.69 - 146 |
| Vasconcelos & McKenzie (1997) | Lagoa Vermelha, Brazil | 1.66 – 3.17 |
| Whipkey et al. (2002) | Hawaii | 0.7 – 1.0 |
| Wright & Wacey (2005) | Coorong area, Australia | 9 - 329 |

**Table IV – Variability in Mg/Ca ratio's measured at locations, where Recent dolomite has been found.**

| author(s) | location | salinity ‰ |
|---|---|---|
| Aharon et al. (1977) | Solar Lake, Israel | 76 – 147 |
| Alderman & Von der Borch (1965) | Salt Creek, Australia | 32 |
| Alderman & Skinner (1957) | Coorong Lagoon, Australia | 88 – 101 |
| Atwood & Bubb (1970) | Sugarloaf Key, Florida | 38.5 – 79.0* |
| Von der Borch et al. (1975) | Coorong area, Australia | 1.4 – 8.2 |
| Bourrouilh-Le Jan (1973 A) | Clipperton | 10 – 15 |
| Bowler (1981) | Lake Keilambete, Australia | > 60 |
| Buddemeier & Oberdorfer (1986) | Enewetak Atoll | 0.23 – 35.6* |
| Butler (1969) | sabkha, Trucial Coast | 44 - 155 |
| Camur et al. (1996) | Tuz Gölü, Turkey | 16 - 466 |
| Comin et al. (1990) | Gallocanta Lake, Spain | 15 – 100* |
| Cook (1973) | Broad Sound, Australia | 35.5 – 36.5 |
| De Decker et al. (1982) | Pillie Lake, Australia | 33.6 |
| Durgasprasada Rao et al. (1978) | Lawson's Bay, India | 17.4 – 34.96 |
| Ebanks (1975) | Ambergris Cay, Belize | 25 - 123 |
| Gac et al. (1977) | Lake Yao, Chad | 0.69 – 104.9 |
| Gonzalez Lopez et al. (1983) | Gallocanta Lake, Spain | 15.5 – 34.4* |
| Gunatilaka (1991) | Al-Khiran, Kuwait | 44 – 240 |
| Hardie (1968) | Saline Valley, California | 1.6 – 280* |
| Jakher et al. (1990) | Sambhar Lake, India | 2 - 267 |
| Kelts & Shahrabi (1986) | Lake Urmia, Iran | 1 - 300 |
| Kocurko (1986) | Elmer's Island | 452 |
| Last (1990) | lakes, Canada | 1 - 300 |
| Mazzullo et al. (1995) | Cangrejo shoals, Belize | 38 |
| Medhioub & Perthuisot (1981) | sabkha, Tunisia | 40 - 51 |
| Müller et al. (1972) | various lakes | 1 – 450 |
| Patterson & Kinsman (1982) | sabkha, Persian Gulf | 5.83 – 7.26* |
| Perthuisot (1971) | sabkha, Tunisia | 200 – 250 |
| Pierre et al. (1984) | lagoon, Mexico | 150 – 408* |
| Rosen & Coshell (1992) | Lake Hayward, Australia | 64 - 214 |
| Skinner (1963) | ephemeral lakes, Australia | 16 – 274 |
| Talbot & Kelts (1986) | Lake Bosumtwi, Ghana | 0.725 |
| Taylor & Illing (1969) | Qatar | 35.9 – 129.5 |

**Table V – Variability among salinities measured at locations, where Recent dolomite has been found. (\* = calculated from chlorinity data using the equation of Kundsen et al., 1902: salinity = 1,811 x Cl + 0.07 g/kg)**

| author(s) | location | pH |
|---|---|---|
| Aharon et al. (1977) | Solar Lake, Israel | 7.17 – 8.18 |
| Alderman (1965) | Coorong Lagoon, Australia | 8.4 – 10.2 |
| Alderman & Skinner (1957) | Coorong Lagoon, Australia | 8.2 – 9.2 |
| Atwood & Bubb (1970) | Sugarloaf Key, Florida | 7.3 – 8.25 |
| Azzaro et al. (1983) | Lake Specchio, Italy | 6.3 – 9.0 |
| Von der Borch (1965) | Coorong area, Australia | 8.9 – 10.2 |
| Bourrouilh-Le Jan (1973 A) | Clipperton | 7 – 11 |
| Buddemeier & Oberdorfer (1986) | Enewetak Atoll | 7.1 – 8.5 |
| Burton et al. (1992) | Basque Lakes, Canada | 7.2 – 8.4 |
| Calvo Betes et al. (1978) | Laguna de Gallocanta, Spain | 7.5 – 9.3 |
| Camur (1996) | Tuz Gölü, Turkey | 7.1 – 8.5 |
| Compton (1988) | various DSDP sites | 6.8 – 8.1 |
| Cook (1973) | Broad Sound, Australia | 3.5 – 8.5 |
| Curtis et al. (1963) | sabkha, Abu Dhabi | 6.0 – 6.2 |
| De Decker & Last (1989) | lakes, Australia | 8.14 – 9.58 |
| Gac et al. (1977) | Lake Yao, Chad | 7.9 – 10.3 |
| Gonzalez Lopez et al. (1983) | Gallocanta Lake, Spain | 7.2 – 7.8 |
| Gunatilaka (1991) | Al-Khiran, Kuwait | 6.4 – 8.4 |
| Hardie (1968) | Saline Valley, California | 7.3 – 9.8 |
| Jakher et al. (1990) | Sambhar Lake, India | 8.8 – 9.6 |
| Kelts & Shahrabi (1986) | Lake Urmia, Iran | 6.5 – 8.9 |
| Khoury et al. (1982) | Ash Meadows Lake, USA | 7.4 |
| Kocurko (1979) | San Andres, Columbia | 8 – 10 |
| Kocurko (1986) | Elmer's Island, USA | 6.7 – 8.2 |
| Kohut et al. (1995) | soil, Canada | 7.5 – 8.1 |
| Koppenol et al. (1977) | Naxos, Greece | 7 – 8 |
| Last (1990) | lakes, Canada | 6.9 – 10.5 |
| Mann & Deutscher (1978) | lakes, Australia | 6.35 – 8.20 |
| Marfil et al. (1975) | lakes, Spain | 7.60 – 8.80 |
| Mazzullo et al. (1995) | Cangrejo shoals, Belize | 7.8 – 8.0 |
| Müller et al. (1972) | various lakes | 7.5 – 9.0 |
| Mutlu et al. (1999) | Lake Acigöl, Turkey | 7.10 – 8.80 |
| Nesbitt (1990) | Basque Lake, Canada | 6.86 – 8.10 |
| Ordóñez et al. (1973) | Laguna de Pétrola, Spain | 6.70 – 9.20 |
| Patterson & Kinsman (1982) | sabkha, Persian Gulf | 6.32 – 7.26 |
| Perthuisot (1971) | sabkha, Tunisia | 6 – 6.5 |
| Pierre et al. (1984) | lagoon, Mexico | 6.1 – 7.1 |
| Rodgers et al. (1982) | Niue Island | 7.3 – 7.6 |
| Rostad (1975) | Debden, Canada | 7.8 – 8.5 |
| Sinha & Raymahashay (2000) | Sambhar Lake, India | 8.4 |
| Skinner (1963) | ephemeral lakes, Australia | 8.4 – 9.2 |
| Soriano et al. (1977) | Laguna de Salicor, Spain | 7.7 – 8.0 |
| Talbot & Kelts (1986) | Lake Bosumtwi, Ghana | 8.1 – 9.6 |
| Taylor & Illing (1969) | Qatar | 6.2 – 8.33 |
| Wright & Wacey (2005) | Coorong area, Australia | 6.62 – 9.11 |

**Table VI – Variability among pH values measured at locations, where Recent dolomite has been found.**