CHAPTER FIVE

ORGANIC OR INORGANIC ?

INTRODUCTION

Numerous geologists have noted the association between the mineral dolomite and organisms. In fact it was De Dolomieu himself, who stated, in his paper describing the large masses of the new carbonate in the mountains of Northern Italy, that he had observed "...some impressions of shells" in these rocks.[1] Similarly Tennant (1799) reported on the presence of fossils in dolomite strata, that consisted of dolomite instead of calcium carbonate ("In this quarry, the stone is frequently crystallised in a rhomboidal form; and petrified shells, not calcareous, but similar in composition to the stone itself, are sometimes, but very rarely, found in it": Tennant, 1799, p.311). Because for long the theory of the secondary formation of dolomite from pre-existing limestone postulated by Von Buch (1822 A) has dominated geological thought, emphasis has been placed on inorganic modes of formation. As mentioned before there were authors, who doubted this "dolomitization" theory of Von Buch. For example Wagner (1831) contested the observation of Von Buch (1822 A) concerning the alleged absence of fossils in dolomite rocks. Wagner (1831) had found numerous fossils in the Jurassic dolomites of southern Germany, much like Zeuschner (1829) before him. Wagner (1831) reported finding a dolomite rock, that contained an abundance of fossils.[2] Based on this observation, direct precipitation of dolomite from an aqueous solution was postulated by Wagner (1831).[3]

But not all geologists could agree with Wagner's (1831) theory of direct precipitation. For example Geikie (1882) stated, that although some dolomite might have been a primary precipitate, most of the fossil-containing dolomites must have originated by way of a process of conversion. ("Some dolomite appears to be an original chemical precipitate from the saline waters of inland seas ... But calcareous formations due to organic secretions are often weakly dolomitic at the time of their formation, and may have their proportion of magnesium carbonate increased by the action of permeating water, as is proved by the conversion into dolomite of shells and other organisms, consisting originally of calcite or aragonite and forming portions of what was no doubt originally a limestone, though now a continuous mass of dolomite": Geikie, 1882, p.304.)

A remarkable position in the considerations on "dolomitization" is undoubtedly being held by the paper of Högbom (1894), in that it seemed to contribute a theoretical basis for this process. In fact Högbom (1894) has proposed his "*Auslaugung*"(= leaching) theory on the basis of a rather curious observation. While analyzing the composition of Pleistocene clays from Southern Sweden, Högbom noted, how calcite dissolves more quickly than dolomite from a mixture containing both. This observation was brought into relation with the $MgCO_3$-content of calcareous organisms such as *Porites*, *Millepora*, *Oculina*, *Lithothamnium*, and various gastropoda. Especially the calcareous algae of the *Lithothamnium* genus appeared to be effective in concentrating magnesium carbonate: Högbom measured percentages $MgCO_3$ from 2 to 13 mol % . And after (partly) dissolving such a *Lithothamnium* sample in dilute acetic acid the percentage $MgCO_3$ had increased to about 20 mol %. On these two different observations Högbom (1894) based the following hypothesis: calcareous algae such as *Lithothamnium* would play an active role in the formation of dolomite, because the algae form an outer crust on reefs and atolls. Through leaching the calcareous algae would rapidly become enriched in magnesium carbonate, leading ultimately to the formation of dolomite.

Because of the rather low percentages of $MgCO_3$ present in most of the living calcareous organisms, extensive dissolution and removal of the calcium carbonate for example making up a reef, would be required. Such a large-scale removal of calcium carbonate might well destroy any calcareous remains of the fossils. This observation seems to be incompatible with the frequent good state of preservation of the fossils in a dolomite rock. From this apparent contradiction Skeats (1905, p.133) drew the following conclusion: "The rock was without doubt originally a limestone, composed entirely of organisms, and was subsequently converted into dolomite. There can be no question that the magnesium was obtained from the seawater. Chief interest is centered in the conditions under which this partial replacement of calcium-carbonate by magnesium-carbonate took place." In the view of Skeats (1905) not only water depth, rate of subsidence, porosity and time of exposure to "... the conditions producing dolomitization", would control the conversion of a fossiliferous limestone into a dolomite, but also "the power of sea-water to dissolve limestones".[4] But the effects of the conversion could work out differently on different kinds of organisms. "Unstable forms like the corals" would be the first to undergo the change into dolomite, because corals already contain noticeable amounts of magnesium. Next would come those organisms, which consist of calcite with much organic matter incorporated. Because, as Skeats (1905) put it, organisms made up from aragonite also contain much organic matter, these would also be particularly prone to "dolomitization". The calcareous algae of the genera *Halimeda*, *Lithothamnion* and *Lithophyllum* would offer a good case in point. Organisms with skeletons consisting of pure calcite, such as the foraminifera and the spines of the echinodermata, would resist "disintegration and dolomitization" longer.

DOLOMITE IN REEFS

In his book on the dolomite rocks of Southern Tyrol Von Richthofen (1860) had merely suggested a genetic relation between corals and dolomite, but in a later paper Von Richhofen (1874) gave a number of arguments in favor of his suggestion.[5] The Schlern dolomite of Southern Tyrol showed considerable differences in thickness amongst neighbouring reef structures. But no traces of large-scale denudation of a dolomite formation of more or less uniform thickness, that once must have covered the whole area, could be found. Furthermore fossils had been found at locations high above sea level (present sea level that is). Geological evidence indicated, that the contacting tuffs and porphyry had been formed side by side with the dolomite. As a fifth argument Von Richthofen (1874) mentioned, that the contacting tuffs had been found to include pieces of dolomite rock. Only two arguments could be raised against the coral reef theory: in the first place the fact, that a large part of the dolomite showed bedding planes. But, as Von Richthofen explained, even a coral reef could show associated carbonate deposits, which had been formed from particles settling from suspension and thus showing bedding. A second argument against the interpretation of the Schlern dolomite as a coral reef concerned the scarceness of fossils, especially corals.

As a major argument in favor of his theory on the inorganic formation of dolomite in the mountains of Southern Tyrol Von Buch (1822 A) had mentioned the absence of fossils. Von Mojsisovics von Mojsvár (1879) advanced the view, that these dolomite masses had originated as giant reefs and used the absence of (macro-) fossils as evidence supporting the reef theory. In this respect Von Mojsisovics von Mojsvár (1879) drew a parallel with the observation made by Dana (1872) as well as Darwin (1874), concerning the absence of any (macro-) fossils in the limestone formations of the modern atolls and reef islands in the Pacific Ocean. Dana (1872, p.352) had even stated: "Absence of fossils has been mentioned as a frequent characteristic of the fine compact coral reef-rock...". This absence of fossils had to be attributed to two different processes. In the first place a process of mechanical degradation, of abrasion caused by the waves, would change all larger pieces of calcium carbonate into fine grained carbonate sand. In addition the activities of various boring organisms would enhance this process of diminution. In the second place cementation would take place, changing the loose carbonate sand into a limestone formation. This cement would be formed through the partial dissolution of some of the carbonate sand, followed by precipitation upon the escape of the carbon dioxide that had kept the carbonate in solution. Dissolution would take place, there where high amounts of carbon dioxide would be produced during the decomposition of organic compounds. Notably that layer of the reef, where the reef building organisms would die and be decomposed by bacteria, would be the site of dissolution of carbonate. There where the excess carbon dioxide could escape from the bicarbonate solution, such as in the surf zone, cementation would take place. The interactions between mechanical abrasion, chemical dissolution and re-precipitation led to the removal of all of the traces of (macro-) fossils; a process that Dana (1872) coined "obliteration". Von Mojsisovics von Mojsvár (1879) considered this mechanism to be the very cause of the general scarcity of fossils in the dolomite rocks of Southern Tyrol. At the same time it was used to explain the marked differences between the dolomite reefs of Southern Tyrol and the well-known Palaeozoic reefs of Europe with a wealth of corals, crinoids, foraminifera, and the like.

Arguments against the suggested coral reef origin of the Schlern dolomite of Southern Tyrol were published by Von Gümbel (1873). Although not many fossils had been found up to that time in this dolomite formation, Von Gümbel (1873) reported finding "astonishing amounts" of foraminifera, ostracods and even gastropoda in the black dolomite of the Puster Valley. A second argument used by others to prove a possible origin as a coral reef, the absence of bedding, was also refuted. Von Gümbel (1873) cited a location, where clear bedding planes could be discerned.[6] In fossil-rich parts of the Schlern dolomite the fossils could be seen arranged in distinct horizons. At places marly intercalations in the dolomite gave rise to bedding planes of 1 to 3 m thickness. But the most convincing argument against the coral reef theory was of course the absence of any traces of corals in thin-sections of the Schlern dolomite. Although Von Gümbel (1873) noted in his microscopic analyses the presence of numerous remains of other organisms, no coral could be discerned by him. What's more Von Gümbel (1873) added, that previously no other author had claimed finding traces of corals in the Schlern dolomite. Lepsius (1878) did not find any indications for the supposed formation as a reef for the Schlern dolomite. In the absence of any convincing arguments in favor of the reef theory a normal and uninterrupted process of sedimentation had to be assumed according to Lepsius (1878). Earlier Daubeny (1841) had pointed out, how the impressive topography of the dolomite masses of Tyrol had to be attributed to the resistance of the dolomite rock to weathering: topography alone is not an argument in favor of the reef theory. After acknowledging the fact, that little or no corals had been found in the massive deposits of dolomite such as the Schlern, Ogilvie (1894) called attention to coral growth in the form of the "Cipit blocks" and "Cipit limestones": "They, and not the mountains of Schlern dolomite, deserve the name "Coral Reefs" in South Tyrol" (Ogilvie, 1894, p.7).[7]

Concerning the change of the initially deposited calcium carbonate of the coral reefs into dolomite various theories have been proposed. That the initial precipitate had been calcium carbonate, whether calcite or aragonite, was not doubted at all: fossils known from numerous other locations as consisting of calcium carbonate had been found in dolomite formations in the form of dolomite. But the nature of the possible conversion remained problematical. Scheerer (1866) did not hesitate to draw a parallel between dolomite formation and modern coral islands and atolls. According to Scheerer (1866) it was especially the large-scale porosity of the coralline structures, that had to be responsible for dolomite formation by way of exposing the pre-existing limestone to the "dolomitizing agencies".

First mention of dolomite in the coral reefs of the atolls of the Pacific Ocean must have been made by Dana (1872), who had studied the limestone from the upraised coral island of Makatea. Dana (1872) delineated the surrounding sea water as the source of the magnesium required for the conversion of coral limestone into dolomite. Skeats (1905) followed the suggestion of Dana, that "differential leaching" of the pre-deposited limestone would initiate the change into dolomite, but added, that he had not encountered any evidence of such a process of leaching in the cores from Christmas Island and Niue. Even the contrary was true: Skeats (1905) had noted secondary calcite and secondary aragonite deposited in these limestone samples. Therefore Skeats (1905) could only conclude, that dolomite formation on such coral islands would take place in shallow water, aided by the percolation of sea water through a relatively porous limestone and requiring so much time, that the coral island as a whole should have a slow rate of subsidence. The conversion would involve a process of dissolution, initiated by the production of carbon dioxide upon the decay of organic matter from plants and animals. Because aragonite was known to be more soluble than calcite, the aragonite skeletons of corals and that of the calcareous algae such as *Halimeda* would be much more susceptible to dolomitization than foraminifera or the spines of echinodermata. But then the latter contained markedly less organic material than the much larger corals.

Branner (1904) confirmed the observation made by Silliman Jr.(1846) and Dana (1852), that living corals contain very little or no $MgCO_3$, and that dead corals were known to accumulate considerable amounts of magnesium carbonate. In this respect Dana's theory contrasted with that of Forchhammer (1852), who had postulated, that all of the magnesium carbonate found in fossils such as corals had to have been deposited by the living organisms themselves. Forchhammer (1852) excluded at beforehand any later process of incorporation of magnesium from the sea water into the calcium carbonate. (The observations of Dana, 1852 and Branner, 1904 have been confirmed by Baas-Becking & Galliher, 1931. The latter two authors stated: "... the only mineral that is deposited by the living coralline is calcite" and therefore "... the deposition of magnesium in the coralline is a secondary phenomenon": Baas-Becking & Galliher, 1931, p.479.) Judd (1904) thought, that selective leaching of $CaCO_3$ by way of CO_2-rich water had enriched the limestone in the topmost part of the Funafuti cores from an initial 2 to 3 % $MgCO_3$ to values of some 16 % at a depth of 5 m and more.

Land (1967), Richter (1974 A,B), Davies et al. (1975), Lohmann & Meyers (1977) and Richter & Füchtbauer (1978) discussed the formation of dolomite in terms of magnesium cations being relocated during the recrystallization of biogenic magnesium calcites, thereby following the example of Schlanger (1957). Buddemeier & Oberdorfer (1986) observed how the chemistry of the pore water in the Davies Reef (in the central part of the Great Barrier Reef) was notably different from the water of the surrounding sea. Concentrations of nitrogen and phosphorus were about two times as high in the pore water; the pH was lower than that of sea water, and the concentration of dissolved carbon dioxide was notably higher than that measured in the sea water. The marked differences between the seawater and the pore water were explained to result from the decomposition of organic matter in the carbonate sediment, leading to anoxic conditions with concomitant formation of sulfides.

DOLOMITE IN PEAT AND COAL

In 1855 Hooker & Binney described the occurrence of calcareous concretions in coal seams of Lancashire and Yorkshire, and observed how well in general plant remains had been preserved in these "coal balls" (or seam nodules, bullions or plant bullions as these were known to the miners). Such calcareous concretions were invariably correlated with the occurrence of marine fossils in the layers above that coal seam.[8]

Weiss (1884) found concretions consisting of dolomite mixed with numerous fragments of plants, but these concretions came from dumps of a coal mine near Langendreer in Westphalia (Germany) and were obviously not *in situ*. Coal balls from the Hansa coal mine near Dortmund have been described by Nasse (1887) and Piedboeuf (1888); coal balls from the British Coal Measures were described by Binney (1868-1875). Chemical analyses showed these concretions to consist of calcium magnesium carbonate, pyrite and iron carbonate. In polished sections an abundance of plant remains could be seen, and in microscopic thin sections details up to individual plant cells could be discerned ("All observers have been struck with the wonderful perfection of the process by which the most microscopic parts of minute vessels and cells have been preserved in form...": Binney, 1868-1875, p.15). The coal seam containing the dolomite coal balls was directly overlain by a layer of bituminous shale, containing a wealth of (pyritized) fossils such as *Aviculapecten*.

Strahan (1901) described the relations between a coal seam and a layer consisting mainly dolomite, occurring in the English Coal Measures near Neston, Cheshire. The dolomite layer is black colored, and part of it consists of pisolites. "When cut across they show a radiate crystalline structure, with less clear concentric rings. Coaly matter occurs in them, and crystallization has obviously taken place in water containing coaly matter in suspension": Strahan (1901, p.300). Chemical analyses showed the rock to be composed of a virtually pure dolomite along with some coal, iron and "... a not inconsiderable residue chiefly made up of silica and alumina." In addition dolomite was found in recognizable plant tissue in the coal layer. From his microscopic examinations Strahan (1901, p.301) drew the conclusion, that "... crystallization has evidently taken place in the presence of coaly matter." No indications were found for turbulent water; the deposit must have originated in "...almost motionless water". Strahan (1901) wondered what exactly the role of the plant remains would have been in the formation of the dolomite. Algae might have withdrawn dissolved carbon dioxide from the shallow water, but decaying plant remains almost certainly evolved carbon dioxide and thus led to the dissolution of any carbonates present. At the same time it was noted by Strahan (1901), that apparently a large part of the plant remains had escaped decay, and subsequently had been changed into coal. Both coal formation and the deposition of dolomite would have taken place under water.

As has been pointed out by Mentzel (1904), the detailed knowledge of many plants from the German coal layers is the result only of the excellent conservation of plant remains within coal balls. Only through "petrification" by calcium carbonate or by dolomite the plant remains were saved from conversion into coal. The dolomite nodules are generally lens-shaped, but spherical forms or even egg-like shapes have been found as well. Sizes vary from that of a pea to as much as 35 cm in diameter. Not much could be said concerning the mode of formation of the dolomite in the nodules, but Mentzel (1904) was convinced, that the dolomite must have precipitated from an aqueous solution at a moment preceding burial.[9] In the German coal layers of Westphalia as well as in the British coals from Yorkshire the coals containing dolomite nodules are directly overlain by marine sediments. The very good conservation of plant remains inside the coal balls of dolomite was therefore attributed by Mentzel (1904) to the action of sea salts, which would have prevented decay of the organic material. But the formation of dolomite would have taken place at a later stage, and would possibly be related to the formation of pyrite. The conservation of plant fragments in the dolomite concretions within the coal layers of Westphalia featured prominently in a paper by Kukuk (1909). Plants such as *Sigillaria*, *Lepidodendra*, *Calamites*, and *Stigmaria* could be recognized. The thin sectioned dolomite coal balls were seen to consist of haphazard aggregates of plant remains intergrown by various small roots. In many of the coal balls fruits such as the *Stigmaria* appendices (looking much like the modern pine apples) were found. Pieces of wood for example that from *Lyginopteris oldhamia* could be recognized in microscopic examination. The stratigraphic distribution of the dolomitic coal balls within the coal seams of Westphalia did not suggest, that their occurrence was restricted to one particular horizon (as for example Renier, 1909 had suggested). In this respect the dolomite concretions behaved distinctly different from the concretions of iron carbonate, which were restricted to the top of certain coal layers, overlain by marine sediments.

Stopes & Watson (1909), after analyzing a number of samples from "coal balls", found some of these to consist entirely of dolomite (mixed with some siderite in most instances). In the view of Stopes & Watson (1909) the formation of this dolomite had to be related to the influence of sea water during the deposition of the plants, that later changed into coal. Experiments by Murray & Irvine (1889, 1890) and Stocks (1902) were mentioned, in which the importance of bacterial sulfate reduction for the precipitation of calcium carbonate from sea water under the influence of organic matter, was demonstrated. Stopes & Watson (1909) suggested, that the same process of bacterial sulfate reduction would lead to the formation of dolomite and magnesite.

Like Stopes & Watson (1909), who had found many indications for an autochtonous origin of the dolomitic coal balls, Kukuk (1909) made several observations, all supporting this particular view and all of these contradicting the allochtonous origin suggested by Potonié (1899) and Stocks (1902). For example the gradual change of a bed of dolomitic coal balls into a thin, but continuous, layer of the same material was considered by Kukuk (1909) to be as good evidence as the finding of two dolomite coal balls connected by a plant's stem by Stopes & Watson (1909). Furthermore the dolomite coal balls were mostly found in arrangements parallel to the general bedding plane; which was another observation contradicting any rolling action in transport typical of an autochtonous origin. But the most convincing argument for an *in situ* origin was according to Kukuk (1909) the random orientation of the *Stigmaria* appendices within the coal balls. Only when the coal balls are *in situ* petrified pieces of root zone from a marsh, this particular structure could have resulted. Although Kukuk (1909) was not quite certain how the mineral dolomite had been formed in the coal balls, he had made various observations in support of Mentzel's (1904) theory. The fossils found in the sediments above coal layers containing dolomite coal balls, were invariably of marine origin. In this respect there was a clear parallel with the siderite concretions found in the roof of coal layers overlain by marine sediments. There where limnic sediments followed upon the coal layers, no dolomitic coal balls were found. Teichmüller (1955) found the same relation with overlying marine sediments, and cited in support the observations made by Mamay & Yochelson (1953) on the occurrence of marine invertebrates such as forminifera, pelecypoda, gastropoda, brachiopoda and ostracoda in coal balls from southern Illinois and southeastern Kansas (USA). Additional evidence has been given by Werner (1954): samples of a marine peat were measured to adsorb especially magnesium and calcium cations.

In the dolomite coal balls from the Ruhr area (Germany) the degree of conservation the Carboniferous plant remains is in general poor, except for those parts of the plants, that grew in the earth itself (Teichmüller, 1955). In these coal balls the remains of roots are predominant. From this observation, in combination with an abundance of pyrite, Teichmüller (1955) concluded, that the absence of oxygen must play a role in the formation of dolomite.[10] After analyzing dolomite samples from the Carboniferous coals of the Ruhr area, Eckhardt & Von

Gaertner (1955) concluded, that a transition from acidic pH values (typical of modern peat water) to definitely alkaline pH values had led to the precipitation of dolomite.

Gothan & Benade (1932) reported finding small, spherulitic concretions of dolomite in the Carboniferous coals of the Ruhr district. Linck & Köhler (1933) described coal balls of dolomite varying in size from about 1 cm diameter to one measuring several decimeters (Gothan & Oberste-Brink, 1931 had described dolomitic concretions in coal measuring up to 2 m in length and 30 to 50 cm thick; and Kukuk & Hartung, 1941 described finding a tree trunk 2.80 m long consisting entirely of dolomite in the coal deposits of the Ruhr area. The coal balls are often coated with a gleaming layer of coal; sometimes this outer coating consists of clay minerals. Nests of several coal balls separated by only a thin layer of coal have become known. The interior of coal balls consists of well preserved plant remains (stalks, leaves, roots, rhizomes), with little or no admixed coal. The plant remains are in general not at all coalified. The rest of such coal balls consists of Ca-Mg-Fe carbonate. Linck & Köhler (1933) had used chemical analyses as well as Debye-Scherrer diffractograms to investigate the mineralogy of the carbonates, and had found stoichiometric dolomite (*Normaldolomit*) to be predominant.

Gothan (1934) studied the replacement of various plant remains (including conifer wood, tree roots, and fungal spores) by dolomite from a brown coal mine at Malliß (Mecklenburg, Germany). From the same locality Schwab (1959) obtained a number of samples of dolomitized wood. The Miocene brown coal at Malliß contains especially pieces of conifers (*Cupressinoxylon* sp.). Shrinkage and deformation of the cell structure on a microscopic scale indicated decomposition of the wood under wet conditions. The loss of cellulose must have caused the shrinkage of the individual cells. Replacement by dolomite led to the fixation of this situation. Dolomite filled the pores of the wood structure, but did not affect the cell walls. Those parts of the wood that had not been replaced by dolomite were later compressed during burial and changed into (fusinite) coal. The dolomite crystallites are generally oriented perpendicular to the cell walls, and occur in concentric layers, giving the impression of a *periodic precipitate*. Not all of the wood had been filled with dolomite in a regular way: the dolomite is concentrated in small nodules (some 1.5 to 3 mm in diameter) arranged parallel to the tree rings, much like the siderite nodules in the fossil wood described by Stach (1927).

The occurrence of dolomite in coal is not restricted to the coal fields of England or Germany: in many other parts of the world dolomite has been found in coal. Boldireva & Slivko (1959) found dolomite in coals of the Ukraine; Asano et al.(1964), Murayama & Kobayashi (1965), Hosokawa (1966) and Matsumoto (1978) in Japanese coal; Taylor (1968) in Australian coal; Chandy (1970) in coal from India; and Rao & Gluskoter (1973) found dolomite in coal from the United States. After having studied carbonate concretions from various Japanese coal fields, Matsumoto & Iijima (1981) concluded, that the dolomite (and magnesite) must have formed in brackish water or sea water, and not in freshwater. Earlier Hoehne (1949) had drawn the conclusion, that some of the dolomite found in the German coal might well have formed under limnic conditions. Similarly Teichmüller et al. (1954) pointed out, that not in all cases a marine influence could be detected in the Carboniferous coals of Westphalia, and had consequently suggested, that some of the dolomite coal balls might have been formed under limnic conditions. A comparable conclusion was drawn by Gehl (1962) for the large bodies of dolomite in the brown coal deposits at Malliß. No definite geographical orientation could be detected in the distribution of the mega concretions of dolomite. In one respect at least the latter concretions are different from the dolomitic coal balls of the Carboniferous coals of the Ruhr area: Schwab (1959) observed, how the plant remains within the brown coals of Malliß were not very different from the surrounding brown coal with respect to their stage of coalification.

Hoehne (1949, 1954) concluded, thereby following the example of Mentzel (1904), Stopes & Watson (1909) and Kukuk (1909), that the dolomite found by him in different German coals, had to be an authigenous mineral (much like siderite, pyrite, quartz, kaolinite, and phosphorite found in this coal). A comparable paragenesis of kaolin, α-quartz, pyrite, iron sulfate, gypsum, calcite, dolomite, and anatase was described by Mukherjee & Lahiri (1953) from Indian coals. Chandy (1970) found dolomite together with kaolinite, apatite, quartz, anatase, siderite and gypsum in coals from the Laikdih Seam, Raniganj coalfield, India. But not all authors have shared the view of Mentzel (1904): for example Werner (1955) considered dolomite in coal to be a replacement product, requiring an external supply of magnesium cations, low concentrations of oxygen, the presence of organic compounds and a slightly elevated partial pressure of carbon dioxide.

Dolomite replacing wood has been described from petrified wood in the Mio-/Pliocene deposits of Kern County, California (USA) by Adams (1920). All of the samples studied, showed a characteristic partition: the outer layer of the stem, which must have belonged to the sapwood, contained almost pure dolomite. The inner layers of the petrified wood, more dark colored and with tree rings, consisted entirely of silica. The structure of the petrified wood made it possible, to determine the specimen as having once been part of a coniferous tree. The usual aspect seen in thin-section analysis is, that some of the dolomite rhombs had a core of silica. At the same time it could be seen, how dolomite rhombs (of about 1 mm) had squeezed the surrounding cells of the wood. Adams (1920) did not hesitate to describe dolomite formation in wood as a process, that had taken place simultaneous with actual plant growth: "Judging from the secondary enlargement of dolomite with a cell as center, the initial crystallization occurred within the cell, in some cases at least" (Adams, 1920, p.362). Because a living tree will effectively prevent any penetration by crystals of dolomite or by silica, Adams (1920) suggested, that crystallization could have taken place only after the bark of a tree had been injured and part of the wood would have started to rot. This conclusion seems to be substantiated by the observation of Kukuk & Hartung (1941), that tree trunks in coal are not of an *in situ* origin. Such large pieces must have accumulated as driftwood; to be changed into dolomite only after their incorporation into the sediment. Dolomite has been reported by Ismailov et al. (1964) from petrified trees of the *Taxodioxylon albertense* sp. from the Taskhent area (Russia). The dolomite found by Alonso-Zarza et al. (1998) near root cells in Miocene paleosols of the Madrid Basin (Spain), contributes additional evidence concerning the relation between plant growth and the low-temperature formation of dolomite.

DOLOMITE IN DOGS

Undoubtedly one of the most curious occurrences of dolomite has been described by Mansfield (1979, 1980). Dolomite, distinctly of Recent age (most probably not older than 8 months), was found in the form of uroliths in the bladder of a Dalmatian dog. Not only did this dolomite not contain any admixture, it even showed in X-ray diffraction the superstructure lines typical of dolomite *sensu stricto*. Uroliths consisting of dolomite had never before been described, but Von Gorup von Besanez (1871)[11] as well as Sutor & Wooley (1970) reported uroliths consisting of magnesium calcite.

On two different occasions a 4-year old, male Dalmatian dog (*Canis familiaris*) had developed numerous small urinary stones. In September 1975 the first symptom, the dog's inability to urinate, had been relieved by catheterization. At the same time the dog's urine and blood had been sampled and analyzed. Blood was found in the urine, along with proteins, epithelial cells, small amounts of mucus and a few bacteria. Blood urea nitrogen was not higher than the normal average value (250 mg/dm^3 was measured, whereas 100 to 300 mg/dm^3 is the normal range: Mansfield, 1980). The white blood cell count was markedly higher than the usual average values. A bacterial test (standard aerobic thioglycolate culture) did not reveal any bacterial infection. The day after catheterization the uroliths were removed by way of cystotomy (= abdominal surgery reaching into the bladder). The uroliths recovered were not analyzed. Eight months after this operation the dog again showed symptoms of urolith trouble. In May 1976 cystotomy was again carried out, and this time the uroliths found in the dog's bladder were analyzed with X-ray diffraction. No blood or urine analyses were performed on this occasion. The numerous rounded, nodular uroliths (one reached a diameter of 8 mm) consisted of pure dolomite: superstructure reflections at 25.4 and 20.7 nm were present in the X-ray diffractogram (see Fig.2, p.833 in Mansfield, 1980).

Concerning a plausible cause for this particular occurrence of dolomite, Mansfield (1980) mentioned three possibilities: 1) renal alkalosis, 2) infection by urease-producing bacteria, and 3) infection by uric acid fermenting bacteria. There can be no doubt that a bacterial infection of the urinary tract would have caused "... an intense alkalinization of the urine, with the precipitation of calcium, magnesium, ammonium, and phosphate salts and subsequent formation of ... renal stones" (Harrison et al., 1978, p.465). But in this particular instance there were no indications of any bacterial infection. In Mansfield's (1980) paper mention is made of two different standard bacterial cultures with a negative outcome. The possibility of renal, respiratory or metabolic alkalosis was rejected by Mansfield (1980), because the Dalmatian's diet was such, that the dog should have a hyper-acidic urine. And moreover "Renal, respiratory and other systematic alkaloses are terminal if not treated quickly; thus, the Dalmatian's continued good health without such treatment precludes their likelihood": Mansfield (1980, p.834). Mansfield's own conclusion was, that urease-producing bacteria must have been responsible for the low-temperature formation of dolomite.[12] Although Dalmatian dogs are notorious producers of high levels of ureum in their urine, and consequently often suffer from ureate uroliths[13], the ureum combines in most cases with ammonia to form ammonium ureate as the precipitate. What a suggested bacterial infection cannot explain, is the fact that the uroliths found, consisted of dolomite instead of more usual compounds such as ammonium ureate, Ca-Mg-NH_4-phosphate, calcium oxalate or cystine. Mineral concretions found in the kidneys or in the bladder of dogs consist in most cases of calcium-, ammonium- or magnesium phosphate. According to Osborne et al. (1972) phosphate makes up some 60 to 90 % of all canine uroliths. To a much lesser extent ureate uroliths occur (in only 10 % of the cases), calcium oxalate uroliths (in approximately 10 % of the cases), or cystine (an amino acid) uroliths (the latter in only 5 % of the cases) (Osborne et al., 1972). Mansfield's suggestion of an infection by urease-producing bacteria is undermined by the laboratory analyses described ("... urease-producing bacteria ... were not detected in a standard (aerobic, thioglycolate) culture": Mansfield, 1980, p.834). In low-temperature laboratory experiments by Hedelin et al. (1985) urease-induced uroliths were found to consist of magnesium ammonium phosphate hydrate (struvite) and/or crystalline calcium phosphate(s).

DOLOMITE IN PEARLS

Dolomite of obvious Holocene age has been found by Tanaka et al. (1960) in cultured pearls (3 years old) and in pearl oysters (2 years old) from the cultures of the Nippon Pearl Company in Matoya Bay, near Kashikojima, Japan. For more than 90 % these pearl oysters (*Pinctada martensii* Dünker) consist of calcium carbonate, and a few percent of a protein (conchiolin) are invariably present as well. Chemical analyses and X-ray diffraction showed that the mineral dolomite was present in the pearl nacre, in the nacreous layer of the oyster, and especially in the prismatic layer of the oyster's shell. The presence of dolomite in the nacre of cultured pearls and in the pearl oyster is the more surprising, since the nacre layer consists entirely of aragonite. In contrast finding dolomite in the prismatic layer seems more probable, since that layer consists of calcite. The prismatic layer shows evidence of deposition in a distinctly rhythmic manner. At the same time this rhythmic character is also a characteristic property of the nacre layer. It is this rhythmic character, caused by periodic changes in size and orientation of the micro-crystallites forming the nacre, that makes possible the distinction between cultured pearls and natural ones in X-ray photographs (see for example: Webster, 1983, p.507). The pronounced concentric structure of natural pearls finds its origin in fluctuations caused by seasonal growth. The few nacre layers that surround the (artificial) core of *cultivé* pearls exhibit the same concentric, rhythmic character. It was in these outer nacre layers of cultured pearls, that Tanaka et al. (1960) found traces of dolomite.

DOLOMITE AND ALGAE

As early as 1852 the possible relation between dolomite formation and the activity of algae has been suggested by Ludwig & Theobald.[14] The water of the warm springs of Bad Nauheim (Germany) investigated by Ludwig & Theobald (1852), contained calcium in the form of its bicarbonate, but magnesium in the form of chloride. The withdrawal of dissolved carbon dioxide from the water by the numerous algae would cause the precipitation of calcium carbonate. The calcareous sinters thus formed, contained up to 11.69 wt.% magnesium carbonate. The change of magnesium chloride in solution into magnesium carbonate would have been brought about by the living cells of the algae as well: Ludwig & Theobald (1852) observed, that clearly the algae were not capable of precipitating any chlorides. Högbom (1894) had suggested, that leaching of for example the calcareous alga *Lithothamnium* (which may contain up to 13 mol % $MgCO_3$) would lead to dolomite. Much the same mechanism was proposed by Skeats (1905), who suggested that especially calcareous algae consisting initially of aragonite would be prone to "dolomitization".

Rivière (1939 B) supposed, that the removal of CO_2 from sea water by living algae would increase its pH to values of 9 or more. A different role for the algae was suggested by Kirchof (1966): the chlorophyll of green plants such as algae contains magnesium, and it would be this magnesium, that gives rise to dolomite. [It is perhaps of some interest to note, that Willstätter (1906) has suggested active participation of the magnesium ion of the chlorophyll molecules in the process of photosynthesis. In his view the assimilation of carbonic acid would be catalyzed by a reaction between the basic metal magnesium and carbon dioxide in aqueous solution. A reaction that is comparable to the Grignard synthesis, in which magnesium metal reacts with alklyl halogenides to form alkyl magnesium halogenides. The latter organo-magnesium compounds form useful intermediates in numerous syntheses of organics such as alcohols, ketones, aldehydes, and silicones.]

Withdrawing carbon dioxide from sea water and thus causing the precipitation of a carbonate such as dolomite, is not the only role played by algae in the sedimentary environment. Black (1933) pointed out, how he had observed filamentous algae (such as *Schizotrix, Symploca,* and *Phormidium*) permeate and bind a newly deposited layer of several millimeter thickness in modern carbonate sediments of the Bahamas. Other algae notably *Scytonema* would be growing only on the exposed top of such a layer, forming there a dark colored, mucilaginous layer protecting the sediment underneath from subsequent erosion. The distinctly rhythmic aspect of these "algal mats" was, in the explanation of Black (1933), not only the result of annual changes in sedimentation rate (in which autumn storms of the Bahamas play a considerable role), but also in part the result of tidal sedimentation effects. Only in the tidal zone laminae composed of relatively coarse carbonate grains passing upwards each time into a fine mud, were being found.

Algal mats are not really restricted to the tidal zone; algal mats can be found in the lower supra-tidal environment too. There highly saline conditions prevail and even precipitation of salts may take place. Such high salt concentrations do not inhibit microbial activity in all instances. There are halophilic microbes, that will thrive when the level of dissolved salts exceed that of normal sea water. Examples are to be found among the bacteria (*Halobacterium*, *Halococcus*, and *Ectothiorhodospira*), the cyanobacteria (Synechococcus = *Coccochloris*, *Synechocystis* and *Dactylo-coccopsis*), and eukaryotic photosynthetic flagellates of the genus *Dunaliella* and related genera such as *Chlamydomonas* and *Asteromonas* (see also Reed, 1986). What really controls the possible occurrence of algal mats is the absence of grazing metazoans such as Pelecypoda. Another factor controlling algal growth is light, because it enables photosynthesis. In algal mats only the very top layer of algae receives sufficient light; underlying algae are inevitably doomed. The organic compounds of the algae will be decomposed by bacteria, for example by sulfate reducing bacteria. Precipitation of carbonates takes place in a rhythmic manner, not only caused by the day/night alternation between photosynthesis and respiration, but also by the tidal rhythm of the sea. Because of their position mainly in the intratidal environment algal mats periodically receive a new supply of calcium cations and carbonate anions.

Phleger (1969), in his description of the Laguna Ojo de Liebre (Mexico), where Kinsman (1969) and Pierre et al. (1984) had found modern dolomite, was surprised by the wealth of organisms living on the algal mats on top of the evaporite deposits. The brine there contains dense populations of chlorophytes, giving it a reddish color. Even in the halite deposits high concentrations of algae occur. This high organic productivity would be caused by the excessive supply of nutrients in the form of concentrated seawater, replenished every time by the incoming tide and wind-driven flooding (Phleger, 1969).

A close relation between dolomite and algae has also been invoked by Gebelein & Hoffman (1971, 1973), to explain alternations between dolomite and limestone on a millimeter scale. Mudcracks, truncated ripple marks and stromatolites all pointed to an environment, consisting of very shallow water or even to intratidal conditions. Authors such as Sander (1936), Fischer (1964) and Laporte (1967) had previously described the same association, but Gebelein & Hoffman (1971, 1973) were the first to add experimental observations to support their claim, that these interbedded dolomite-calcite laminae would have been formed by algae. Observations on Recent algal mats formed the main part of their paper. The layers of stromatolites consisting mainly of algal filaments, had been formed as surficial mats during periods of non-deposition. Such algal layers originated in ponds of seawater, occurring in most instances in the intratidal zone. Salinity of the seawater in these ponds changes with the season. The underside of the algal mats contains bacteria in extremely high concentrations. As a result the rate of decomposition of algal mucilage is quite high underneath the algal mat. This layer of partially decomposed algal material is the site of carbonate precipitation. Large amounts of minute carbonate crystals (measuring about 1 to 4 micrometer) were found in the layer. The carbonate consists of magnesium calcite with 14 to 19 mol % $MgCO_3$. "All crystals grow attached to the surface of mucilaginous sheaths of the blue-green algae; thus, a clear-cut genetic relationship between algal mucilage, bacterial decomposition and Mg carbonate nucleation and crystal growth can be demonstrated in these mats": Gebelein & Hoffman (1973, p.607). In their laboratory experiments with blue-green algae (*Schizotrix calcicola*) Gebelein & Hoffman (1973) noted, that the living algae are capable of concentrating magnesium to values 3 to 4 times higher than the concentration of the surrounding solution. For example if normal sea water with Mg/Ca = 4.5 was used for culturing the algae, the algal cells would be measured to possess Mg/Ca = 15 . When using a culture medium with Mg/Ca = 8 , the algal sheaths were found to have attained Mg/Ca = 25 to 30 . Despite the more than 200 different experiments conducted by Gebelein &

Hoffman (1973), no dolomite precipitated in their algal cultures. The laboratory tests carried out with these cultures, consisted essentially of adding small amounts of filtered algal sheath material to quantities of natural or artificial sea water with different salinities and Mg/Ca ratio's. In all of the experiments small amounts of ammonium carbonate (0.004 to 0.006 mol/dm^3) were added. All solutions had been sterilized before adding the algal material, "... to minimize any possible effects of particulate organic matter and bacteria" (Gebelein & Hoffman, 1973, p.610). The only precipitate formed were very small crystallites of Mg calcite with 17 to 20 mol % $MgCO_3$. No dolomite at all was found, and therefore Gebelein & Hoffman (1973) reached the conclusion, that the dolomite found associated with algal mats and stromatolites must have a secondary origin.

The relation between algal activity and dolomite formation has been documented on many occasions. To give only a few examples (see also Chapter 4): Davies (1970) reported on algal mats associated with modern dolomite in the South Gladstone tidal flats (Shark Bay area), Australia. Davies et al. (1975) had found algal mats in a small semi-permanent pool on One Tree Reef (southern Great Barrier Reef), Australia, where modern dolomite occurs. Cook (1973) reported on algal mats and dolomite in the siliciclastic tidal flats of Broad Sounds (Queensland), Australia. Stromatolites and Recent dolomite have been described by Shinn et al. (1965) from the supra-tidal flats of western Andros Island, Bahamas. The same association was found by Bourrouilh-Le Jan (1973 A) in small lakes near Fresh Creek, Bahamas. Algal mats cover most of the sediments in the Lagoa Vermelha, Brazil, where Höhn et al. (1986) and Moreira et al. (1987) had found modern dolomite. Algal activity occurs in the pools on the island of San Andres, Colombia, where Kocurko (1979) found modern dolomite. Wolff & Füchtbauer (1976) reported the presence of bioherms of blue-green algae in the dolomite-bearing sediments, that fill two meteoric impact craters in southern Germany. Durgaprasada Rao et al. (1978) found dolomite crystals in carbonate nodules, that had been precipitated by algae. Aharon et al. (1977) as well as Krumbein & Cohen (1977) described algal mats on the sediments of Solar Lake, Isreal, where they had found modern dolomite. Algal mats cover the sediments of a brine pan near Ras Muhammed, from which modern dolomite had been reported by Gavish (1980), Gavish et al. (1985), Friedman (1980) and Friedman et al. (1985). Baltzer et al. (1982) found modern dolomite in the sediments underlying algal mats in the delta of the Mehran River, Iran. Modern dolomite associated with algal mats on Sugar Loaf Key, Florida (USA) has been described in detail by Shinn (1968 B). Algal mats on the tidal flats of Laguna Madre, Texas (USA) together with modern dolomite have been described by Miller (1975).

DOLOMITE AND BACTERIA

Bacteria precipitating calcium carbonate

Murray & Irvine (1889, 1890) described how they had mixed sea water with urine and kept it at temperatures ranging from 289 to 300 K. "After a time the whole of the lime present in sea-water was thrown down as carbonate and phosphate": Murray & Irvine (1890, p.164). In analyses of the "liquor" of living oysters and fresh mussels high concentrations of ammonia salts were found, exceeding by far the concentrations found in normal seawater. Because urea can react with two molecules of water to give one molecule of ammonium carbonate, Murray & Irvine (1889, 1890) became convinced of the importance of ammonia compounds toward the precipitation of calcium carbonate from sea water. Temperature of the water would be of considerable importance: in cold water the decomposition of nitrogen-containing organic compounds would be very slow or even absent, whereas in tropical seas this form of decomposition would be proceeding at considerable speed. The amount of animal life (the producers of the nitrogen-containing organics) would be another determining factor in the possible precipitation of calcium carbonate.[15]

After analyzing numerous samples of "mud-waters" and comparing these with analyses of the overlying sea water, Murray & Irvine (1895, p.485) found "The alkalinity of the mud-waters (evidently due to the presence of carbonates) was increased in a most striking manner when compared with the water immediately overlying the mud, and depended directly upon the chemical changes that had taken place in the sea-water salts in the water associated with the Blue Mud." Originally Murray & Irvine (1889, 1890) had explained the formation of ammonium carbonate as being caused by the activity of multi-cellular organisms, but Murray & Irvine (1895) were inclined to conclude, that "... the principal increase of alkalinity is due to the de-oxidation of sulfates by the organic matters in the mud" (Murray & Irvine, 1895, p.485). Later Murray (1900) made the suggestion, that perhaps bacteria could have played a role in the deposition of the calcareous sediments of the Black Sea.[16] The same reaction responsible for the precipitation of calcium carbonate by bacteria had been invoked earlier by Steinmann (1889).

In experiments Baur (1902) has shown, how precipitation of calcium carbonate by denitrifying bacteria takes place, when calcium in the form of its humate, oxalate, formiate or citrate was used in the culture media. Similarly Söhngen (1906) observed in his experiments the precipitation of calcium carbonate, when using calcium butyrate or calcium formiate in his media. Boquet et al. (1973) noted in their laboratory experiments, that a multitude of soil bacteria is capable of precipiating calcite ("From this we infer that crystal formation is a common phenomenon and that its occurrence is simply a function of the composition of the medium used": Boquet et la., 1973, p.528). Drew (1911, 1913) attributed the precipitation of calcium carbonate in his experiments as well as in the sea near the Bahamas and the Florida Keys, to denitrifying bacteria. In samples taken *in situ* Drew (1913) found "enormous numbers" of the bacterium, that he thought to be responsible for the deposition of $CaCO_3$. Samples from the sediments from the Great Salt Lake and from various marine sediments near Florida and the Bahamas were used by Kellerman (1915) to inoculate "mixed cultures" of bacteria. If initially soluble salts of calcium were present in the culture medium, calcium carbonate precipitated. "The most important natural precipitation is probably the transformation of calcium carbonate by the combined action of ammonia, produced by bacteria either by the denitrification of nitrates or by the fermentation of protein, together with carbon dioxide, produced either by the respiration of large organisms or the fermentation of carbohydrates by bacteria" (Kellerman, 1915, p.58).

Sulfate-reducing bacteria

Not only urea-decomposing bacteria or denitrifying bacteria are capable of precipitating carbonates. Beijerinck (1895) described how bacterial sulfate reduction was often seen to lead to precipitates of calcium carbonate and iron (II) carbonate. The production of hydrogen sulfide, followed by its oxidation to sulfur, and the downward infiltration of CO_2-containing water, were the results. The process of sulfate reduction was found to be caused by a bacterium isolated from the black mud at the bottom of a ditch or from soil solution. The new group of bacteria[17] was found to be strictly anaerobe. Special glass retorts were used by Beijerinck (1895) to isolate the new anaerobes from the large amounts of aerobe and facultative anaerobe bacteria. Pure cultures of *Desulfovibrio* can best be obtained, according to Van Delden (1904), when following the method of Trenkmann (1898): a small amount of hydrogen sulfide gas dissolved in the culturing medium will prevent the development of almost any other bacterium.

By way of culturing *Microspira desulfuricans* bacteria (identical with those described originally by Beijerinck, 1895) from the mud of a lake near Odessa in media with different salinities, Rubentschick (1928) was not able to distinguish it from the *Microspira aestuarii* of Van Delden (1904). Only a difference in salt tolerance was found to exist between the two species. Both supposedly different species were found to be capable of considerable adaptation with regard to salinity. Baars (1930) showed the "marine" *Vibrio aestuarii* (isolated originally by Van Delden, 1904 from the black mud of a Dutch tidal flat) as well as the *Vibrio thermodesulfuricans* of Elion (1924) to be identical with Beijerinck's *Spirillum desulfuricans*. In this way Baars (1930) not only established the capacity of this sulfate reducing bacterium to thrive under marine conditions (3 % salinity) and somewhat elevated temperature (according to Elion, 1924 it would still be active at 328 K), but also found a wide variety of organic compounds suited as hydrogen-donor (ranging from alcohol such as ethyl alcohol via sugars such as glucose and mannose to the nitrogen compounds α-alanine or asparagine). The high amounts of hydrogen sulfide found in the deeper water (> 180 m) of the Black Sea have been attributed by Issatchenko (1924) to the activities of the *Microspira aestuarii* described originally by Van Delden (1904).

The microbial benthic community present in Solar Lake, Israel (where Aharon et al., 1977 and Lyons et al., 1984 have found modern dolomite) has been studied by Jørgensen & Cohen (1977). The Solar Lake sediments consist of a cyanobacterial mat (stromatolite) up to 1 m thick. The microbial community is made up of organisms such as the unicellular *Aphanocapsa littoralis* and *Aphanothece halophytica*, and the filamentous cyanobacteria *Microcoleus* sp. and *Oscillatoria* spp. together with diatoms (*Amphora coffeaeformis* and *Nitzschia* sp.), photosynthetic and colorless sulfur bacteria and various heterotrophic bacteria. "Seasonal changes in their growth and relative abundance cause a lamination of the mat, with an annual layer thickness of about 1.2 mm" (Jørgensen & Cohen, 1977, p.657). Measurements included bacterial counts and the rates of sulfate reduction and of oxygen exchange. Active bacterial sulfate reduction in Solar Lake takes place only in the upper 20 cm of the sediment. Bacterial counts showed the sulfate reducing bacteria (*Desulfovibrio* sp.) to be concentrated in the topmost millimeters of the sediment. Centimeters lower these counts were a factor 100 less, and at depths of more than 20 cm very few *Desulfovibrio* colonies were encountered. The rate of sulfate reduction depended entirely on the primary production of organic compounds by the benthic cyanobacterial community. Concentration of H_2S is the highest in the same upper 20 cm of the sediment; deeper in the sediment hydrogen sulfide concentrations gradually decrease. From calculations it was concluded, that calcium carbonate precipitation must take place at depths of 50 to 80 cm (at 80 cm depth a layer of "almost pure carbonate silt" was found).

Brooks et al. (1968) measured the almost complete disappearance of calcium in solution from sediments exhibiting reducing conditions. Numerous analyses made on two cores from marine sediments off the coast of Southern California by Presley & Kaplan (1968) showed dissolution of calcium carbonate taking place in the interstitial water near the sedimentary interface of reducing sediments, and supersaturation with calcium carbonate at greater depths. On the basis of isotope measurements Presley & Kaplan (1968) concluded, that in reducing sediments an increase in dissolved carbonate with depth must be due to metabolic activity. The presence and the activity of sulfate reducing bacteria in environments where modern dolomite was found, has been documented in a relatively large number of instances. To mention only a few examples: Höhn et al. (1986) found bacterial sulfate reduction taking place in the Lagao Vermelha (Brazil), where they had found modern dolomite. Aharon et al. (1977) had noted the same association between active bacterial sulfate reduction and Recent dolomite in the Solar Lake, Israel; Perthuisot (1971, 1974) found it in sabkha El Melah, Tunesia; Friedman (1966) noted the same relation in the Salt Flat Graben, Texas and Hein et al. (1979) noted the association between dolomite and bacterial sulfate reduction in the cores of Quaternary sediments from the Bering Sea. Carballo et al. (1987) described, how large areas of dolomitic crusts had formed in a pond at Sugarloaf Key (Florida, USA), where the sediment itself was dark colored, anoxic, and smelling of hydrogen sulfide. Laboratory analyses of the water from this pond revealed active bacterial sulfate reduction. Gregg et al. (1992) noted the presence of H_2S in a core sample with Holocene dolomite from Tomas Savannah, Belize.

Bacterial sulfate reduction requires relatively high concentrations of organic materials to be available for the decomposition process. But as Lalou (1957) noted, the nature of such organics is not particularly critical. In his tests Lalou (1957) had used glucose; but it turned out, that additions of all sorts of organic matter containing carbon could be used, even pure cellulose worked well. However when using pure peptone or urea, no carbonates would form. The end products formed in bacterial sulfate reduction are gases such as hydrogen sulfide and methane and liquids, which can be described as kerogen precursors. Koppenol et al. (1977) reported the occurrence of gas bubbles of methane, emerging from the organic-rich carbonate, in which they had found modern dolomite.

In addition to the ubiquitous *Desulfovibrio desulfuricans* and the genus *Desulfotomaculum*, several new genera of bacteria capable of sulfate reduction have been described such as *Desulfobacter, Desulfonema*, *Desulfobulbus* (see for example Postgate, 1984).

Bacterial sulfate reduction is often characterized by a black color of the sediment: the black colour is due to finely disseminated iron sulfide (Beijerinck, 1895; Van Delden, 1904). According to Rubentschick (1928) not FeS, but rather the (colloidal) hydrate $FeS.H_2O$ would be the colouring agent. The source of the iron ion can be found in the iron content of clay minerals: Drever (1971) has shown iron to be extracted from clay minerals under anaerobic conditions, followed by the incorporation of magnesium from the sea water into the clay minerals (thereby changing the notronite component of montmorillonite into a saponite component).

Methane-producing bacteria

The anaerobic decomposition of cellulose gives rise to large amounts of methane and carbon dioxide gas as Hoppe-Seyler (1886) has shown. In 1887 Hoppe-Seyler described, how a small amount of calcium acetate dissolved in river water and infected with a trace of river mud, would lead to the microbial production of calcium carbonate, carbon dioxide and methane according to:

$$Ca(C_2H_3O_2)_2 + H_2O \rightarrow CaCO_3 + CO_2 + 2\ CH_4\ . \qquad \text{(eq. 5)}$$

Omelianski (1903) found, that similarly the bacterial decomposition of calcium butyrate under anaerobic conditions gives rise to calcium carbonate, carbon dioxide plus methane:

$$Ca(C_4H_7O_2)_2 + 3\ H_2O \rightarrow CaCO_3 + 2\ CO_2 + 5\ CH_4\ . \qquad \text{(eq. 6)}$$

When using calcium formiate in the same experiment, Omelianski (1903) observed the formation of hydrogen (along with calcium carbonate and carbon dioxide) and described the micro-organism responsible as *Bacillus formicicus*.

Isolation of two different bacteria capable of methane-production was first achieved by Söhngen (1906, 1910). One of these was described as an immotile, Gram-negative rod-shaped bacterium, and named originally *Bacillus methanicus* (later known as *Methanobacterium*). The other was much larger and immotile, and occurred invariably in the form of a distinct aggregate of eight spherical cells arranged in neat packets; it is now known as belonging to the genus

Methanosarcina. Because Söhngen (1906) succeeded in obtaining monocultures of the methane-producing bacteria, conclusions regarding the exact mechanism of methane production became possible. Laboratory experiments established how methane together with carbon dioxide, is produced, whether acetate, acetone, butyrate, ethanol or propionate are used as the substrate. The formation of CO_2 in organic decomposition reactions is not at all surprising, but the concurrent formation of methane is (Barker, 1956). The explanation was found by Van Niel (1931): the "carbon dioxide reduction model" involves the complete oxidation of organic substrates to carbon dioxide, followed by a (possibly partial) reduction of CO_2 to CH_4 . For example in the case of acetate being the substratum used:

$$CH_3COOH + 2\,H_2O \rightarrow 2\,CO_2 + 8\,H \text{ (oxidation)} \qquad \text{(eq. 7)}$$

$$8\,H + CO_2 \rightarrow CH_4 + 2\,H_2O \text{ (reduction)} \qquad \text{(eq. 8)}$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \; . \qquad \text{(eq. 9)}$$

The fermentation of most organic compounds by methane-producing bacteria leads in most cases to the simultaneous formation of methane and carbon dioxide, but not in all. As for example Barker (1956) stressed, in some of these bacteria the oxidation step is coupled with the available amount of CO_2 , and in the presence of only a limited amount of CO_2 no methane will be formed. Laboratory experiments involving radioactive tracers have shown methane to originate from the methyl group of acetate (Buswell & Sollo, 1948; Stadtman & Barker, 1949).

In their laboratory experiments Stephenson & Stickland (1933) found, that organic 1-carbon compounds are anaerobically reduced to both methane and carbon dioxide. For example when using formic acid (0.5 %) in the monoculture, the reaction would take place according to:

$$4\,H.COOH \rightarrow CH_4 + 3\,CO_2 + 2\,H_2O \; . \qquad \text{(eq. 10)}$$

When placing the same monoculture in an hydrogen atmosphere, bacterial reduction of the formic acid (present in the medium as the sole carbon source) to methane without the formation of any carbon dioxide was seen to take place:

$$4\,H.COOH + 3\,H_2 \rightarrow CH_4 + 2\,H_2O \; . \qquad \text{(eq. 11)}$$

Therefore Stephenson & Stickland (1933) concluded that the bacterial reduction of formic acid takes places in two different steps (each catalyzed by a specific enzyme):

first $$H.COOH \rightarrow H_2 + CO_2 \; , \qquad \text{(eq. 12)}$$

and then $$4\,H_2 + CO_2 \rightarrow CH_4 + 2\,H_2O \; . \qquad \text{(eq. 13)}$$

The same monoculture of methane-producing anaerobic bacteria of Stephenson & Stickland (1933) demonstrated the capacity to reduce sulfate into sulfide in the presence of hydrogen, according to:

$$H_2SO_4 + 4\,H_2 \rightarrow H_2S + 4\,H_2O \; . \qquad \text{(eq. 14)}$$

The formation of methane in laboratory cultures of sulfate-reducing bacteria has been confirmed by Sisler & ZoBell (1951) and Postgate (1969). But according to Martens & Berner(1974) and

Postgate (1984) the formation of methane and the activities of the sulfate-reducing bacteria are incompatible. A different type of anaerobe bacterium (*Methanococcus* sp.) would be responsible for the production of methane according to Abram & Nedwell (1978 A). Field observations in combination with laboratory experiments by Cappenberg (1974 A,B) have shown the distribution pattern: the methane-producing bacteria are invariably active in the layer beneath that, where sulfate reduction takes place (thereby confirming the observations made by Liebmann, 1950). Martens & Berner (1974) and Bernard (1979) noted the same spatial distribution between an upper zone of sulfate reduction and an underlying anoxic environment with methane production in cored marine sediments: "... significant production of methane does not begin until dissolved sulphate concentrations approach zero" (Martens & Berner, 1974, p.1167). In laboratory experiments Cappenberg (1974 B) showed the toxic effect of H_2S on the methane-producing bacteria. According to Hines & Buck (1982) the distribution of methane-producers and sulfate-reducers in near-shore marine sediments would be somewhat more complex. In a number of cores from marine sediments the zone of bacterial sulfate reduction overlies the zone of the methane-producing bacteria. But in other instances the two will be concomitant: the sulfate-reducing bacteria are accompanied by methane-producers such as *Methanobacterium*, *Methanococcus* and *Methanospirillum* sp. in the upper 10 to 20 cm of the sediment. In the marine sediments from the Blake Outer Ridge, Atlantic Ocean (DSDP Site 533) the upper 15 m comprises the zone of sulfate reduction and from 15 to 100 m core depth methane formation predominates (Claypool & Threlkeld, 1983). Biogenic methane formation concomitant with bacterial sulfate reduction taking place in salt marsh sediments in the San Francisco Bay near Palo Alto, California has been described by Oremland et al. (1982). According to Zeikus & Winfrey (1976) the production of methane in the sediments of Lake Mendota (Wisconsin, USA) depends on the temperature of the sediment. A marked seasonal change takes place every year in the number of methane-producing bacteria and in the amount of methane released.

The reduction of carbon dioxide by hydrogen in solution leading to the production of methane has been claimed by among others Koyama (1964), Nissenbaum et al. (1972), Whelan (1974), Claypool & Kaplan (1974), and Deuser et al. (1973). Under anaerobic conditions organic compounds such as carbohydrates, proteins and lipids will all be transformed into CO_2 plus CH_4 (Mah et al., 1977). From the breakdown of amino acids and long-chain lower fatty acids, alcohol and CO_2 plus H_2 result. Sulfur-containing amino acids such as methionine must be responsible not only for hydrogen sulfide, but also for part of the methane formed in anaerobic lacustrine sediments (Zinder & Brock, 1978). Hydrogen is seldom detected, because it can be used by all of the known methane-producing bacteria for the reduction of CO_2 to CH_4 (Wolfe, 1971). *In situ* observations in salt marsh sediments by Abram & Nedwell (1978 A) showed the necessity of both H_2 and CO_2 for methanogenesis. The availability of hydrogen may well be the limiting factor. Experiments by Abram & Nedwell (1978 B) demonstrated how the presence of hydrogen stimulated sulfate reduction by *Desulfovibrio* spp. The competition between *Desulfovibrio* and other anaerobes such as the methane-producing bacteria would be won in most instances by *Desulfovibrio*, because of its greater ability to utilize hydrogen. Competition for hydrogen between *Desulfovibrio* and methane-producing bacteria is capable of explaining the distribution pattern of methane in anaerobic sediments (Abram & Nedwell, 1978 B). Near the surface the sediment contains usually little or no methane; but this methane-depleted surface layer is found only in marine sediments (Reeburgh & Heggie, 1977). In lacustrine sediments the concentration of methane increases immediately with depth. Although a number of the methane-producing bacteria are facultative anaerobe, actual production of methane requires strict anaerobic conditions (Zeikus, 1977). At the same time many species are known to be autotrophic: for their growth and proliferation CO_2 can be used as the sole source of carbon. Methane-producing bacteria have been detected in the rumen and the gastro-intestinal tract of animals, in marine and lacustrine muds and sediments, in flooded soils and in sewage-sludge digesters (Zeikus, 1977). According to Mah et al. (1977) and Zeikus (1977) the reduction of CO_2 into CH_4 coupled with the oxidation of hydrogen is characteristic of the methane-producing bacteria. Not only *Methanobacterium* would be capable of this reaction, but also various species of the genus *Clostridium*. The end product of this bacterial reduction process is acetic acid, which does not accumulate either, because in black muds, marshes and swamps it will be converted directly or indirectly into CH_4 and CO_2 (Mah et al., 1977). Calculations by Jeris & McCarty (1965) showed some 67 % of the initial organic carbon of the substratum to be converted into acetate first (later to be changed into methane), and only 33 % of the methane produced to be the result of the reduction of CO_2 by hydrogen. According to Bryant et al. (1977) the sulfate reducing *Desulfovibrio vulgaris* and the methane-producing *Methanobacterium formicicum* may well occur in association, but only as long as sulfate ions are present in a high concentration. As soon as sulfate ions have disappeared, the methane-producing bacteria become more effective in the transfer of hydrogen. When using anaerobic cultures under nitrogen, methane-production and sulfate reduction take place simultaneously: the two processes are apparently not mutually exclusive (Oremland & Taylor, 1978). *In situ* measurements in lake sediments by Lovley et al. (1982) showed methane-production to be the dominant process during such a co-existence. Addition of sulfate ions was seen to decrease the microbial production of methane. At the usual concentrations of sulfate in freshwater lakes the sulfate reducing bacteria seem to "out-compete" the methane-producing bacteria (as Lovley & Klug, 1983 put it).

Isotope-labeled bicarbonate and acetate were used by Crill & Martens (1986) *in situ* in anoxic marine sediment to measure the relative contributions of CO_2 reduction and acetate fermentation to the process of methane production. Sulfate reduction constitutes the predominant anaerobic process in the upper 10 to 35 cm of the sediment at this location (Cape Lookout Bight, North Carolina USA), and the mineralization of organic carbon in the deeper sediments accounts for methane production. In the view of Crill & Martens (1986) the two processes would involve two different types of bacteria: the sulfate reducers and the methane-producers. Field evidence ("... the highest rates of methane production were found beneath this zone of high sulfate concentrations": Crill & Martens, 1986, p.2095) as well as evidence from *in situ* experiments (consisting of the addition of hydrogen or acetate to lake sediments, in which both sulfate reduction and methane production had been found: Winfrey & Zeikus, 1977) support the conclusion of two different microbial populations being responsible for the two different processes. "The distribution of methanogenic bacteria and their activity are restricted to anoxic environments where associated bacteria maintain a low E_h and produce methanogenic substrates as well as other nutrient factors": Mah et al. (1977, p.325). As long as sulfate is present, sulfate-reducing bacteria will predominate over the methane-producing bacteria. The presence of sulfide in marine sediments caused by sulfate reducers, will largely inhibit the activities of methane-producing bacteria (Cappenberg, 1974 B). Laboratory experiments by Martens & Berner (1974) confirmed this principle. In other words: separate depth zones exist in lacustrine as well as marine sediments for sulfate reducing bacteria and for the methane-producing bacteria. In some instances the rate of methane production in the zone beneath that of the sulfate-reducers is so high, that gas bubbles of pure methane will escape from shallow sediments (Martens, 1976).

The vertical distribution of methane and methane-producing bacteria in lake sediments in general shows an increase with depth up to a certain maximum, followed by a gradual decrease (Cappenberg, 1974 A; Reeburgh & Heggie, 1974; Winfrey & Zeikus, 1977). At the same time seasonal variations in the distribution profile of methane and of Eh were measured (Cappenberg, 1974 A). Periodic alternations between oxygen-rich and anoxic conditions in shallow sediments have been measured by Martens (1976).

Philp & Calvin (1975) described, how a kerogen-like material is being formed in algal mats on carbonate sediments of the Laguna Madre, Baja California (USA). Kelts & McKenzie(1982) related, how the drilling of Hole 479, Leg 64 (Gulf of California) of the Deep Sea Drilling Project into dolomite-rich diatomaceous muds had to be stopped prematurely, because of a dangerously high content in kerogen ("The hole was actually terminated because of an omnious increase in thermocatagenic hydrocarbons C_1 - C_8": Kelts & McKenzie, 1982, p.555).

Other bacteria

The postulation of a new species of "calcareous bacterium" (*Bacterium calcis*) by Drew (1913) lacked a foundation in adequate physiological observations, as for example Lipman (1924) has pointed out. In addition Lipman (1924) was surprised to note, how no attempt at all had been made by Drew (1913) to let his bacteria precipitate $CaCO_3$ from pure sea water. Kellerman & Smith (1914) were convinced that the "*Bacterium calcis*" of Drew (1913) instead had to belong to the *Pseudomonas* genus. Bavendamm (1932) noted, that Drew's description of *Bacterium calcis* would equally apply to for example *Bacterium Brandti*, *Bacterium Bauri*, *Bacterium Grani*, and *Bacterium Feiteli*. Lipman (1924) doubted, whether Drew's *Bacterium calcis*, the *Pseudomonas calcis* introduced by Kellerman & Smith (1914), the *Pseudomonas calciphila* or any other denitrifying bacteria, would be capable of precipitating $CaCO_3$ from normal sea water, not enriched in calcium compounds, in organic material, or in nitrate. Because the culture media contained relatively large amounts of calcium as organic salts, the breakdown of these salts by any bacterium would lead to the precipitation of $CaCO_3$ ("... I can reproduce the results obtained by Drew on the precipitation of calcium carbonate in sea-water if the proper medium is used, namely, if to the sea-water there is added a salt of calcium with some organic acid": Lipman, 1924, p.187). Another argument used by Lipman (1924) was, that bacteria could not be found in high concentrations in sea water. The latter argument is only partly true, because extremely high amounts of bacteria occur in the topmost centimeters of most marine sediments (Russell, 1892[18] ; Smith, 1926; Bavendamm, 1931, 1932; ZoBell, 1946).

Marine sediments may contain in places high concentrations of bacteria (especially of the genera *Pseudomonas*, *Vibrio*, *Spirillum*, *Achromobacter*, and *Flavobacterium*) in the upper few cm's of cores taken. Biochemical degradation of source organic compounds in such sediments takes place at measurable rates, but the complete removal of oxygen, nitrogen and sulfur atoms does not usually take place (Stone & ZoBell, 1952). In general compounds such as carbon dioxide, hydrogen sulfide, hydrogen, ammonia and low-molecular fatty acids, alcohol and amines result upon decomposition of organic compounds by marine bacteria (ZoBell, 1946).

Mechanism of $CaCO_3$ precipitation

In the view of Van Delden (1903) bacterial sulfate reduction would not only affect any dissolved calcium sulfate, but it would convert magnesium sulfate as well. When using sodium lactate as the main nutrient of the medium, the following reaction would take place:

$$2\ C_3H_5O_3Na + 3\ CaSO_4 \rightarrow 3\ CaCO_3 + Na_2CO_3 + 2\ CO_2 + 3\ H_2S + 2\ H_2O. \qquad \text{(eq. 15)}$$

Elion (1924) gave the more general reaction equation as:

$$2\ C + MeSO_4 + H_2O \rightarrow MeCO_3 + CO_2 + H_2S \qquad \text{(eq. 16)}$$

(in which Me can be Ca or Mg).

Mixed cultures of bacteria were made responsible for the precipitation of calcium carbonate in the experiments by Kellerman & Smith (1914). The mechanism for the precipitation of calcium carbonate would consist of bacterial formation of large amounts of ammonia, which would react with calcium bicarbonate in solution:

$$Ca(HCO_3)_2 + 2\,NH_4OH \rightarrow CaCO_3 + (NH_4)_2CO_3 + 2\,H_2O\,. \qquad \text{(eq. 17)}$$

A second mechanism was found in the production of "traces of carbon dioxide" (but CO_2 might as well come from plants or higher animals) by one kind of bacteria, whereas another kind would be producing ammonia, either from the decomposition of proteins or by the reduction of nitrate to nitrite. The resulting ammonium carbonate would subsequently react with dissolved calcium sulfate, and so lead to the formation of $CaCO_3$:

$$CaSO_4 + (NH_4)_2CO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4\,. \qquad \text{(eq. 18)}$$

A third mechanism was found by Kellerman & Smith (1914) in the decomposition by bacteria of organic calcium compounds used in the culture media such as calcium succinate, calcium acetate or calcium malate.

Berner et al. (1970) described four different mechanisms contributing to an increase in carbonate alkalinity (defined as the total concentration of all dissolved bicarbonate species plus twice the total concentration of all dissolved carbonate species). The first would be the dissolution or the precipitation of calcium carbonate under the influence of carbon dioxide present in water. The second would be bacterial reduction of sulfate leading to H_2S and HCO_3^- in solution. The third mechanism contributing to an increase in carbonate alkalinity would be bacterial production of ammonia. The fourth mechanism would involve the formation of authigenic silicates:

$$3\,Al_2Si_2O_5(OH)_4 + 2\,K^+ + 2\,HCO_3^- \rightarrow 2\,KAl_3Si_3O_{10}(OH)_2 + 2\,CO_2 + 5\,H_2O \qquad \text{(eq. 19)}$$

(and comparable reactions involving Na^+ or Mg^{2+}). In chemical analyses of pore water squeezed from anaerobic, sulfide-rich sediments Berner et al. (1970) measured alkalinities up to 30 times as high as that of the overlying sea water. But even so no marked degree of calcium carbonate precipitation could be noted; it was suggested, that possibly dissolved organic matter would inhibit the precipitation of $CaCO_3$.

After carrying out a multitude of laboratory experiments Novitsky (1981) reached a fundamental conclusion regarding the actual role of marine bacteria in the precipitation of calcium carbonate: solely the pH of the solution controls the precipitation of $CaCO_3$. Marine bacteria would be able to influence the pH in different ways, but an active biochemical participation of bacteria in $CaCO_3$ precipitation as suggested by for example Morita (1980) could not be detected.

Formation of dolomite

From his laboratory experiments Pfaff Jr. (1907) concluded, that bacteria would have to be involved in the precipitation of dolomite even in the non-marine environment. The suggestion has been made by Drew (1913), that notably the ammonia producers such as the denitrifying bacteria would be instrumental in the precipitation of calcium carbonate from sea water. Jourdy (1914) suggested that denitrifying bacteria would be involved in the decomposition of calcareous algae, and so be instrumental in the formation of dolomite.

The importance of ammonium carbonate, a compound formed in high concentrations during the bacterial decomposition of vegetable or animal tissues, in the low-temperature formation of dolomite has been stressed by Linck (1909 B). In Linck's view especially those limestones that had accumulated high concentrations of organic matter, would be prone to dolomite formation. Several authors have suggested, that hydrogen sulfide would play an active role. Both Nenadkevich (1917) and Vernadskii (1917) described, how they had found measurable amounts (up to 0.01 wt.%) of H_2S in dolomites. Vernadskii added that perhaps the hydrogen sulfide would have originated from the reduction of sulfate. This possible role of H_2S seems to be contradicted by the laboratory experiments of Balló (1913), who noted that hydrogen sulfide gas, when bubbled through a solution containing $CaCl_2$, $MgCl_2$, Na_2CO_3 and NaCl kept at room temperature, leads to the formation of $MgCO_3.3\ H_2O$, but NH_3 gas bubbled through it favors the formation of an anhydrous mixed Mg/Ca carbonate. More evidence on the significance of ammonia came from Russell (1934), but his evidence was circumstantial: when heating dolomite fragments in a glass tube, an oil-like substance formed and ammonia would evolve. Paul & Meischner (1991), after studying in detail the Pleistocene deposits of a former lake in Germany, came to the conclusion, that the dolomite there had been formed in still water permanently void of oxygen and rich in H_2S .

From black mud collected in the Weissowo salt lakes (Charkov region, southern Russia), Nadson (1928) was able to isolate a number of $CaCO_3$-precipitating bacteria. The fact that microbes were responsible for processes involving the migration of not only calcium in the $CaSO_4$-rich sediment, but also migration of silicon and iron, was checked by Nadson with the aid of sterile blanks. A cultivation medium of 2 ‰ peptone inoculated with this black mud, led to the deposition of $CaCO_3$ (as a film floating the medium) together with abundant *Proteus vulgaris* bacteria that had caused the phenomenon. These bacteria would induce carbonate precipitation through the conversion of the proteins into NH_3 and H_2S . From other tests Nadson concluded, that bacteria such as *Bacterium albo-luteum* and *Bacillus mycoides* also precipitated calcium carbonate, but to a much lesser degree. Especially when *Bacillus mycoides* would be cultivated on broth, on agar-agar or gelatine medium, or better still on an alkaline meat-peptone broth, carbonate would form as the result of the decomposition of protein into NH_3 . But not only bacteria were found to cause the precipitation of $CaCO_3$: Nadson (1928) observed how three different species of *Actinomycetes* would do much the same. Especially older cultures of *Actinomyces albus*, *Actinomyces verrucosus* and *Actinomyces roseolus* showed, when cultured on peptone/agar or peptone/gelatine media, the precipitation of notable amounts of calcium carbonate.[19] A comparable observation had earlier been made by Molisch (1925), who added, that not only *Actinomycetes* species were capable of precipitating calcium carbonate, but that even two different yeasts (*Saccharomyces olexudans* and an undetermined pink yeast) would possess the same faculty. Bersa (1920, 1926) found calcium carbonate in the vacuoles of three different species of sulfur bacteria.

Nadson (1928) left little or no doubt concerning the cause of carbonate formation: in all cases production of ammonia took place upon the microbial decomposition of proteins of the medium. The presence of calcium sulfate in the sea water media was a strict prerequisite, as Murray & Irvine (1890) had noted earlier. In most cases Nadson (1928) found, that virtually magnesium-free calcium carbonate had been formed in his experiments. Only in two instances a magnesium calcite had been formed. Nevertheless Nadson tried to bring his experiments into relation with the low-temperature formation of dolomite, at least in theory.[20] Various authors have taken up the suggestion. For example Müllers (1930) invoked the bacterial production of ammonia and carbon dioxide to explain the Devonian dolomites near Gerolstein (Eifel Mountains, Germany). Reuling (1934) suggested the same origin for the dolomite in the lower part of the Funafuti core. Brise (1928) described the correlation between the dolomite content of Palaeozoic limestones in Manitoba (Canada) and the former existence of reducing conditions. In the dark colored horizons, which must have formed under reducing conditions, the percentages of incorporated $MgCO_3$ were markedly higher than that of the lighter parts of the same limestone formed under oxidizing conditions. Similarly Steidtmann (1917) interpreted the omnipresence of FeO in dolomites and dolomite-containing limestones as proof of the fact that the dolomite must have formed under reducing conditions. Udluft (1929), while studying German Zechstein dolomites, found a relation between dolomite and the occurrence of Fe^{2+}, as well as a relation between dolomite and "a certain amount of bitumen". From these two different observations Udluft (1929) drew the conclusion, that iron had not been part of the original sediment, but that it had been introduced after sedimentation, and that reducing conditions must have prevailed during the formation of the dolomite. Sander (1936) gave a detailed account on the association between dolomitic limestones and bitumen. Somewhat indirect evidence was cited by Charles (1948): in the petroleum-producing strata of the Pyrenean Mountains (France) there is a correlation in dolomites and a black color of the rock, a distinct smell of H_2S and the presence of oil. In Recent deposits of dolomite too, such as in the Kara-Bogaz-Gol (Russia), a correlation between dolomite and sulfate reduction brought about by bacteria has been noted (Nuryagdyev & Sedelnikov, 1966). Even from the descriptions of the cores from the Deep Sea Drilling Project this relation becomes clear. For example Lancelot & Ewing (1972) attributed the large amounts of natural gases (mainly CH_4, but also CO_2 and H_2S along with traces of C_2H_6) found at DSDP sites 102, 103, 104 and 106, to bacterial sulfate reduction. In these predominantly siliclastic grey muds local concentrations of calcite, dolomite and siderite occur in the form of lenses, nodules or layers. Davies & Supko (1973) explained, that "... fluctuating geochemical conditions" were involved in the low-temperature formation of authigenic dolomite, and that those fluctuations would have been caused by the *cyclical reducing nature* of certain deep-sea environments.

Gieskes (1973) noted in a study of interstitial water from samples of the Deep Sea Drilling Project the following changes caused by bacterial sulfate reduction: depletion of calcium as well as magnesium, increase in alkalinity, increase in ammonia, and an increase in phosphate. Brown & Farrow (1978) pointed out, that sulfate reducing bacteria were active in the conversion of calcium carbonate in the burrows of crustacea into dolomite, taking place at the bottom of Loch Sunart, Scotland. Bacterial sulfate reduction would influence the mineralogy of Mg/Ca carbonates in the view of Sayles et al. (1973) especially by the simultaneous production of HCO_3^- and H_2S . According to Baker & Kastner (1981) bacterial sulfate reduction would aid in the low-temperature formation of dolomite in several ways: 1) by the removal of sulfate anions, 2) by increasing the alkalinity, and 3) by the production of NH_4^+ ions, that would "... aid in the release of adsorbed Mg^{2+} cations" (Baker & Kastner, 1981, p.215). Kelts & McKenzie (1982) were convinced that dolomite formation requires low sulfate concentration, high alkalinity, and high ammonia content. The process would not be taking place in the zone of active bacterial sulfate reduction itself, but a few meters below it in the zone of methane-production. In the view of Slaughter & Hill (1991) bacterial sulfate would aid in dolomite formation especially through the decomposition of proteins and other nitrogen-containing compounds, during which ammonia would be formed. The liberation of this strong base increases the alkalinity of the solution, thereby leading to a predominance of carbonate anion groups over bicarbonate anions. As the four factors promoting dolomite formation Slaughter & Hill (1991) mentioned: 1) high concentrations of protein-rich organic matter; 2) alkaline conditions; 3) high ionic strength; and 4) absence (or removal) of sulfate and phosphate anions. In the view of Andrews (1991) high alkalinity in combination with the removal of all organic matter as caused by active bacterial sulfate reduction, would be responsible for dolomite formation. In active algal mats (of Florida Bay) no dolomite was found; there only magnesium calcite (with up to 23 mol % $MgCO_3$) were found.

In recent years a number of authors have reported on the formation of dolomite in experiments with bacterial cultures. For example Rivadeneyra et al. (1993) noted the precipitation of small amounts of dolomite in cultures of *Bacillus* sp. isolated from saline soils, Rivadeneyra et al. (2000) in cultures of halophilic bacteria (*Nesterenkonia halobia*), and Rivadeneyra et al. (2006) noted the presence of dolomite in cultures of *Chromohalobacter marismortui.* Concerning the mechanism involved Rivadeneyra et al. (1996, 1998) stressed the role of the production of carbon dioxide and ammonia during the bacterial decomposition of nitrogen-containing ingredients of the medium used. The claim of Wright & Wacey (2005) that bacterial sulfate reduction would lead to the low-temperature formation of dolomite through the release of magnesium and calcium from neutral ion pairs and generating elevated carbonate concentrations, is difficult to evaluate since their identification of the “dolomite-like phase” appears to be wanting.[21]

Roberts et al. (2004) have described the formation of dolomite in a laboratory experiment involving sulfate-reducing bacteria and methane-producing bacteria. The laboratory experiments involved petroleum-contaminated groundwater from Bemidji (Minnesota, USA). To water samples taken under anaerobic conditions, fragments (0.5 – 5 mm) of local basalt substratum were added. Five gram of sterilized rock fragments were put in 40 ml of groundwater, and a small amount of petroleum as a carbon source. Fragments of dolomite (!) and calcite were allowed to contact the solution, but remained separated by way of dialysis tubing. A concentrated bacterial population (described as iron-reducing and methane-producing bacteria) from the same groundwater was used to inoculate the sterilized mixture. After 8 months of storage under anaerobic conditions at 298 K newly formed phases were separated and X-rayed. Calcite plus dolomite were found (amongst others[22]); “Dolomite ordering is indicated by the presence of superstructure reflections …. No evidence of other secondary carbonate minerals (e.g., siderite) was found by using XRD and SEM. In sterile controls only calcite precipitated …”: Roberts et al. (2004, p.279).

The relation between dolomite and the occurrence of bitumen and oil is well known. Papers for example by Daly (1907), Fulda (1931), Stuart (1932), Stockfish & Fulda (1933), Linck (1937), Dmitrieva (1951), Heady (1952), Hunt (1953), Hartwig (1955), Yagishita (1955), Fujiwara (1956), Kimpe (1956), Marr (1957), Kornfeld (1959), Bausch & Wiontzek (1961), Chepikov et al. (1964), Spiro & Danyushevskaya (1964), Mattavelli et al. (1969), Bokov & Veneva (1971), Mogharabi (1971), Ali-Zade et al. (1972), Meyer & Yen (1974), Kovacheva et al. (1977), Abou-Khadrah & Khaled (1978), and Friedman (1980), all described this relation. Daly (1907) attributed the formation of dolomite and magnesite, as well as the formation of oil and natural gas, to the bacterial decomposition of organic compounds, much like Jourdy (1914). The latter author recalled the observations made by Renault (1900) on the occurrence of micro-organisms in oil. Bastin et al. (1926) observed how many of the waters found in oil wells were very low in dissolved sulfate. This chemical indication of the activities of bacteria has been substantiated in cultures made by Bastin et al. (1926) from samples of connate water: even from Silurian and Ordovician strata sulfate-reducing bacteria could be cultured. The presence of sulfate-reducing bacteria in brines associated with oil wells has been reported by Gahl & Anderson (1928), Bastin & Greer (1930) and Ginter (1930). Part of the Zechstein dolomite deposits of Thuringia (Germany) not only contains oil, but abundant fossil plants and animals as well (Linck, 1937). The formation of hydrocarbons in cultures of sulfate-reducing bacteria has been described by Jankowski & ZoBell (1944) and Oppenheimer (1965). Methane-producing bacteria are of special interest towards the formation of oil, because these bacteria "... represent a previously unrecognized source of multi-branched hydrocarbons found in sediments and petroleum" (as Wolfe, 1979, p.362 noted).

DISCUSSION

Déodat de Dolomieu (1791) in his description of the new mineral, that would later become known as dolomite, noted the smell coming from the fractured rock. De Dolomieu therefore suggested to include the new rock in the category of the evil smelling rocks (such as bituminous limestones).[23] Freshly collected samples of dolomite-containing nodules from the Atlantic Ocean smelled, according to Philippi (1907), of tri-methyl amine and ammonia. Therefore Phillipi stressed the role of organic compounds in the formation of dolomite.[24] Similarly Linck (1909 B) noted the relation between recent dolomites and organic activity.[25] Klähn (1924) performed extensive experiments in an attempt to unravel the relations between carbonate precipitation and organic activity. Klähn's conclusion was, that in nature the possible escape of carbon dioxide in an inorganic manner would always be surpassed by far by the production of carbon dioxide by organisms living in that environment. Skinner (1963) concluded, because of dolomite occurrences in the lakes of Southeastern Australia, that a direct relation exists between dolomite and plant growth.[26] In other words: purely inorganic precipitation of carbonates would be a rare exception under natural conditions. But the precipitation of carbonate by organisms does not always lead to the formation of dolomite. For example Wetzel (1926) analyzed the carbonate crust formed by *Oscillaria* and *Nostoc* algae together with *Crenothrix*-like bacteria on boulders in a river in northern Chile, measured 37.8 (wt.) % $CaCO_3$ and only 4.2 (wt.) % $MgCO_3$, and found no dolomite. But other scientists were quite convinced of the role played by for example algae in the low-temperature formation of dolomite. Schlanger (1957) observed in samples from the drilling on Eniwetok Atoll, that notably coralline algae had been changed into dolomite, more so than corals or foraminifera. A close relation between plant growth, in particular of *Ruppia maritima* Linn., and the occurrence of dolomite of Recent age in an intermittent lake in south-east Australia has been postulated by Alderman & Skinner (1957). During the dry summer months Kingston Lake would desiccate completely, but after the first rains of winter, water accumulates to a depth of 30 to 60 cm, and plant (and animal) life begins to reappear. During November and December the weather becomes warmer and plants proliferate. Fine white sediment consisting of calcite and dolomite, forms during these months of the year. The precipitation of these carbonates would, in the interpretation of Alderman & Skinner (1957), be the result of a rise in pH. The presence of abundant plant growth in the shallow water of Kingston Lake would exert a considerable influence on the pH of the solution. In this regard Alderman & Skinner (1957) mentioned the observations of Baas-Becking (1934), that the photosynthesis of plants, through its effects on the partial pressure of CO_2 in solution, could change a nighttime pH of below 8 to a value of 9.3 during the day. Because *Ruppia maritima* was the most abundant water plant present in Kingston Lake (although sedges and algae were found as well), its effects on the changes in pH would be predominant. Dolomite precipitation took place, when plant growth was most plentiful. "That there is a close relation between plant growth, rise in pH, and precipitation of dolomite in Kingston Lake seems certain ... More or less continuous records of pH changes and correlation with precipitation and such factors as sunlight, temperature and salinity appear to be necessary": Alderman & Skinner (1957, p.566).

The occurrence of dolomite in coal might well be related to bacterial activity. For as Hoppe-Seyler (1886) has pointed out, the bacterial decomposition of cellulose leads to the formation of methane plus carbon dioxide. Lieske & Hoffmann (1929) and Lipman (1931) reported the presence of bacteria in coal samples. Van Iterson (1904) stressed the need to make a distinction between the aerobe and the anaerobe decomposition of cellulose. As soon as the latter prevails, the strictly anaerobe *Desulfovibrio's* will come into action. Under anaerobic conditions cellulose will be decomposed into methane plus carbon dioxide by the methane-producing bacteria such as *Methanococcus*, *Methanobacterium* and *Methanospirillum* sp. "Methane found in coal mines is believed to have been trapped there when the coal was formed, and the Carboniferous swamps must have been an ideal environment for methane bacteria": Wolfe (1971, p.108). An important observation in this regard has been made by Zeikus & Henning (1975), who found a facultative anaerobe methane bacterium (*Methanobacterium arbophilum*) in the heartwood of living trees (and in freshwater sediments and soils). Wood infested with these bacteria differs from normal wood in that it possesses an alkaline pH, no free oxygen and a high moisture content ("wet wood") (Zeikus, 1977). Synthetic lignin labeled with C^{14} isotopes was not decomposed, when immersed in anaerobic lake sediment (Hackett et al., 1977). Reducing conditions are responsible for the conservation of at least part of ancient biomass. Oxidation inevitably results in gases such as carbon dioxide, nitrogen oxides et cetera.

Most soils under water become anaerobic as the result of bacterial activity notably by the sulfate reducing bacteria. In such anaerobic soils methane-producing bacteria flourish, and methane together with carbon dioxide will be produced. Water plants using such underwater soils as a substratum, may contribute to dolomite formation because of the carbon dioxide cycling by plants. At the same time water plants such as *Potamogeton* and *Spirogyra* are known to absorb considerable amounts of methane, emanating from the anaerobic part of the underwater soil (as Söhngen, 1906 noted). The actual presence of bacteria in for example the dolomite concretions found in coal is not a point of discussion. For example Teichmüller (1955) cited an observation made originally by E. Daub in 1949, on the presence of a multitude of bacteria replaced by pyrite in the dolomite coal balls of a coal layer from the Carboniferous in the Ruhr area. In short there can be little doubt, that the presence of dolomite in ancient coal deposits as much as in modern deep-sea sediments must be related to the process of bacterial sulfate reduction. Lumsden (1985), who had been looking for large-scale variations in the distribution of dolomite in a multitude of core-samples, noted a relation with what was described as "anoxic events". But that was the only correlation to be found amongst the 844 different samples from the Deep Sea Drilling Project; no positive correlation between the presence of dolomite and for example an increase in age of the cored sediments or with depth in individual bore holes could be detected.

Perhaps the mechanism by which sulfate reducing bacteria are capable of forming dolomite consists merely of the increase in alkalinity or (as Compton, 1988 claimed), or an increase in alkalinity in combination with the removal of almost all sulfate anion groups. A direct relation between the degree of bacterial sulfate reduction and the titration alkalinity or between sulfate concentration and the amount of insoluble carbonate has been found by Abd-el-Malek & Rizk (1963 A,B). The decrease in the amounts of dissolved magnesium and calcium cations coincided in their laboratory experiments with a decrease of the bicarbonate ion at the expense of the carbonate group. "The characteristic features accompanying sulphate reduction in waterlogged soils are: a decrease in sulphate content; an increase in titratable alkalinity, and in the concentrations of carbonate and soluble sulphide; a decrease in the concentration of Ca^{2+} + Mg^{2+} , and significant increases in the counts of sulphate reducers": Abd-el-Malek & Rizk (1963 B, p.19). However Abd-el-Malek & Rizk (1963 B) could not observe the formation of any dolomite in their experiments. No undue emphasis is to be placed on the possible relation between sulfate reducing bacteria and dolomite formation.[27] For not only the experiments by Lalou (1957), but in particular those by Roman, Vasconcelos & McKenzie (2003) have shown low-temperature formation of "Ca-dolomite and high Mg-calcite" while using aerated bacterial cultures. However the fact remains, that up to now an adequate explanation for the mechanism of dolomite formation in bacterial cultures is wanting.

Detailed investigations into algal mat communities, including the inherent bacteria, led Dupraz et al. (2004) to describe four differently timed, chemical transformations given by the following equations:

1) $2\,HCO_3^- + Ca^{2+} \rightarrow [CH_2O] + CaCO_3 + O_2$ (= photosynthesis) (eq. 20)

2a) $[CH_2O] + CaCO_3 + O_2 \rightarrow 2\,HCO_3^- + Ca^{2+}$ (= aerobic respiration) (eq. 21)

2b) $3\,[CH_2O] + CaCO_3 + H_2O \rightarrow 2\,HCO_3^- + Ca^{2+} + C_2H_6O$ (= fermentation) (eq. 22)

3) $2\,[CH_2O] + SO_4^{2-} + Ca^{2+} \rightarrow CaCO_3 + CO_2 + H_2O + H_2S$ (eq.23)
(= sulfate reduction)

4) $H_2S + 2\,O_2 + CaCO_3 \rightarrow SO_4^{2-} + Ca^{2+} + H_2O + CO_2$ (eq. 24)
(= sulfide oxidation).

Two of these processes [i.e., photosynthesis (1) and bacterial sulfate reduction (3)] give rise to the precipitation of calcium carbonate, but the remaining processes [aerobic respiration (2a), fermentation (2b) and sulfide oxidation (4)] in effect cause the dissolution of calcium carbonate. During daylight hours photosynthesis predominates in the algal mat community, and reactions 1 and 3 predominate. However during the night microbial consumption of oxygen will take place, and reactions 2 a & b and 4 combine to dissolve, at least in part, calcium carbonate again. Dupraz et al. (2004) not only measured a marked difference in amounts of dissolved oxygen vs. depth between lithified (calcified) and non-lithified algal mats, but observed pronounced fluctuations with changes in light intensity. “During occasional cloud cover, the O_2 profile collapsed within seconds (especially in the lithifying mat), which indicates very high rates of O_2 consumption and that the surface of the mat encounters oxic-anoxic fluctuations throughout the day”: Dupraz et al. (2004, p.751). As a result of this dynamic phenomenon caused by changes in light intensity, especially of course by the day/night rhythm, optimum conditions for the low-temperature formation of dolomite are being created.

The relation between bacterial sulfate reduction and anaerobe (anoxic) conditions will have to be reconsidered, for Jørgensen & Cohen (1977), Skyring (1987), and Canfield & Des Marais (1991) have found how sulfate reduction may take place in the presence of dissolved oxygen. For example, in hypersaline bacterial mats from Baja California (Mexico) sulfate reduction was measured to be taking place in the well-oxygenated zone.[28] Diurnal cycles in the process of bacterial sulfate reduction have been measured by Fründ & Cohen (1992) to take place in a hypersaline pond. Day / night changes in light (at constant temperature in the tests) will control algal (cyanobacterial) growth and so influence the activities of the sulfate-reducing bacteria.

Even so questions remain, notably concerning the occurrences of modern dolomite in bladder stones in a Dalmatian dog, and dolomite in pearls. To which may be added the presence of dolomite in tapeworms, in freshwater snails and in human beings. For Scott et al. (1962) have described minute particles of dolomite in tape-worms of the species *Taenia taeniaeformis*. Later Von Brand & Weinbach (1975) published details on the occurrence of dolomite as cestode corpuscles in the tape-worms *Cysticercus bovis* and *Cysticercus tenuicollis* (the first worms live as parasites in calves, and the second species in pigs or sheep). Dolomite in freshwater snails of the *Belgrandiella fontinalis* and the *Belgrandiella kuesteri* species has been described by Medaković et al. (2003). The outer layer of the shells of both species invariably contained aragonite only, but the inner layer consisted mainly of calcite. In addition this inner layer was found to contain dolomite, in the two different species of freshwater snails from one locality only, however (the Vidmar Spring near Prodkraj and Hrastnik, northeastern Slovenia).

Truly fascinating is the discovery of dolomite in the form of tiny particles (of some 5 to 15 micrometer) in cervical nodes and in the gallbladder wall of two different human patients described by Reid & Anderson (1988). Although by far the majority of granulomas in patients suffering from sarcoidosis has been found to consist of calcium oxalate or phosphate, the endogenous origin of the two granulomas of modern dolomite in humans cannot be doubted according to Reid & Anderson (1988). The occurrence of dolomite in human tooth enamel has been hinted by Driessens & Verbeeck (1985). Gault et al. (1993) found dolomite in calculi from the urinary tract (kidney, bladder) from at least five different human patients. But Gault et al. (1993) warned that identification had taken place with infrared spectroscopy only, and that X-ray diffraction would be required to confirm these occurrences of modern dolomite.