CHAPTER SEVEN

DOLOMITE SYNTHESES

INTRODUCTION

The dolomite problem is in more than one respect a unique problem. For more than 200 years it has puzzled generations of scientists. Very few problems of the natural sciences have ever reached such status. Meanwhile a tremendous amount of literature on the subject has been published. As has been explained before, not all of that published material can possibly be reviewed (or even mentioned) on these pages. The present chapter will have to be limited to a selection from known accounts on the synthesis of dolomite. Only those syntheses that were carried out at room temperature will be considered, because the scope of this publication has been restricted to the formation of dolomite (and magnesite) under conditions of room temperature & atmospheric pressure.

Linck (1912) classified the laboratory experiments conducted up to that time into 4 classes: 1) those experiments that had been conducted at room temperature & atmospheric pressure conditions (Scheerer, 1866; Pfaff, 1894); 2) experiments performed at room temperature, but at high pressure (Pfaff, 1907); 3) experiments conducted at low pressure, but at elevated temperatures (Forchhammer, 1849; De Sainte-Claire Deville, 1858; Bourgeois & Traube, 1892; Klement, 1894, 1895); and 4) experiments employing both high pressures and high temperatures (Von Morlot, 1847 A; Favre, 1849 A,B; Durocher, 1851; Hunt, 1859, 1866; Hoppe-Seyler, 1875). In the account given here only Linck's Class 1 experiments will be discussed: laboratory tests conducted under conditions similar to those of the sedimentary environment.

There have been authors, who claimed too much. Their claims on the successful low-temperature synthesis of dolomite invariably proved to have been without foundation, when those experiments were duplicated (if that was possible at all). Crucial point appears to be the *reproducibility* of the experiment; any claim will have to be checked by way of duplication.[1] In spite of many serious efforts the dolomite problem has remained for many years singularly unassailable.

There have been other authors, who were frank enough to recount their efforts leading to anything but dolomite; but they form rare exceptions. One example of this kind is Forchhammer (1849). In his first experiment calcium bicarbonate solution was mixed with seawater and the mixed solution was frozen. A precipitate formed, containing 7.55 wt.% $MgCO_3$ and 92.45 wt.% $CaCO_3$. Forchhammer's second experiment was also carried out with a calcium bicarbonate solution mixed with sea water, but this time it was left standing for 8 days at a temperature between 288 and 293 K. The precipitate contained 2.19 wt.% $MgCO_3$ and 97.81 wt.% $CaCO_3$. A second series of tests by Forchhammer (1849) consisted of mixing sea water with a calcium bicarbonate solution, to which sodium carbonate had been added. At a temperature of 323 K a precipitate formed, containing 13.10 wt.% $MgCO_3$. From his laboratory experiments Forchhammer (1849) drew the conclusion, that an increase in temperature led to higher percentage of incorporated magnesium carbonate. Another example of such a frank account is that of Hunt (1859). For example his experiment No.1 involved the addition of a solution of sodium hydrogen carbonate to a solution, containing equimolal amounts of calcium- and magnesium chloride. The gelatinous precipitate that formed initially, soon changed into a crystalline substance. Chemical analysis showed it to consist of calcium carbonate with only very small amounts of $MgCO_3$. In experiment No.3 a dilute solution of sodium hydrogen carbonate was added to a solution containing sodium chloride, calcium chloride, magnesium chloride, and sodium sulfate. After mixing the two different solutions, and stirring, a crystalline precipitate slowly formed, consisting of calcium carbonate with 3.3 wt. % $MgCO_3$. After describing various experiments, in which the effects of the presence of sodium sulfate or magnesium sulfate on the solubility of calcium bicarbonate had been investigated, Hunt(1859) turned his attention to high-temperature tests, which were notably more successful.

A third example is that of Hoppe-Seyler (1875), who started out his tests with attempts to duplicate the experiments of Von Gorup-Besanez (1851) with mixed magnesium/calcium bicarbonate solutions. The results were negative. Similarly negative were all efforts to react seawater with calcium carbonate or adding a calcium bicarbonate solution to seawater and subsequently pumping air through it. Even tests involving the freezing of a solution of magnesium sulfate or seawater saturated with calcium bicarbonate were carried out. At this point of his investigation Hoppe-Seyler concluded, that aqueous solutions such as those found in nature (seawater, river water, spring water, or ground water) would not, upon mere escape of dissolved carbon dioxide, lead to dolomite formation.[2]

The fourth example of an honest account describing negative results after trying to synthesize dolomite at room temperature has been provided by Pfaff (1894). That author described how he had tried: 1) To react magnesium- and calcium chloride solutions saturated with respect to sodium chloride with sodium carbonate. 2) Reacting a solution of magnesium sulfate, calcium sulfate and sodium chloride with sodium carbonate. 3) Desiccation of artificial seawater at elevated temperatures (below 373 K) while ammonium carbonate was being added from time to time. 4) Continuously bubbling carbon dioxide through a saturated sodium chloride solution, to which calcium carbonate and magnesium chloride had been added. 5) Continuously bubbling carbon dioxide through a saturated sodium chloride solution, to which calcium carbonate and magnesium sulfate had been added. 6) Adding magnesium chloride or magnesium sulfate to a calcium bicarbonate solution saturated with sodium chloride and, after adding ammonium carbonate, forcing its desiccation at elevated temperatures. 7) Dissolving magnesium oxide and calcium oxide in CO_2-rich NaCl-saturated water, and bubbling CO_2 through it during slow evaporation open to the air. 8) Dissolving magnesium oxide and calcium oxide in carbonated water saturated with sodium chloride, adding ammonium carbonate, and forcing its desiccation. 9) Desiccating concentrated solutions of calcium- and magnesium bicarbonate (prepared by dissolving $CaCO_3$ and magnesium hydroxide carbonate in water with excess CO_2) while leading carbon dioxide through the solution. 10) Desiccating the same concentrated, mixed Mg/Ca bicarbonate solution after ammonium carbonate had been added. In all of these experiments, as Pfaff (1894) noted with some regret, no carbonate formed capable of withstanding treatment with dilute acid.

Another example of unsuccessful attempts to synthesize dolomite at room temperature can be found in the account of Leitmeier (1915). There was for example the experiment, which consisted of adding a magnesium bicarbonate solution to powdered calcium carbonate. There was a series of tests, involving slow CO_2 escape from a number of mixed Mg/Ca bicarbonate solutions kept at various temperatures. The same series was also conducted with the same mixed bicarbonate solutions at the same temperatures, only this time sodium chloride had been added. Because no positive results were obtained in all these cases, magnesium chloride and/or magnesium sulfate were added to the mixed bicarbonate solutions. Still no dolomite would form, and therefore a slight carbon dioxide overpressure was applied. The duration of the experiments was increased from a few hours to periods as long as months or even one whole year. No dolomite formed. All these attempts were in vain, as it turned out. In the end Leitmeier (1915) concluded, that dolomite would not form by way of direct precipitation from a solution.

experiment number	amount of $CaCl_2$ solution	amount of $MgCl_2$ solution	amount of Na_2CO_3 solution	Mg/Ca ratio	precipitate
1	50 cm^3	0 cm^3	50 cm^3	0	C
2	40	10	50	0.25	C + N
3	30	20	50	0.67	C + N
4	20	25	50	1	C + N
5	20	30	50	1.5	C + N
6	10	40	50	4	C + N
7	0	50	50	∞	N

Table VII - Experiments (conducted at 298 K) with dropwise additions of a 0.5 mol/dm^3 sodium carbonate solution to mixtures of a 0.5 mol/dm^3 calcium chloride solution and amounts of a 0.5 mol/dm^3 magnesium chloride solution and the resulting precipitates (modified from Baron, 1960) (C = calcite; N = nesquehonite).

Unsuccessful attempts to synthesize dolomite at ambient temperature have been described by Mitchell (1923 B) as well. The first attempt by Mitchell (1923 B) consisted of adding a 1/25 N magnesium chloride solution and a saturated calcium bicarbonate solution (prepared by saturating a calcium hydroxide solution with carbon dioxide) to 500 cm^3 of artificial sea water. The artificial seawater was being stirred slowly, while the magnesium chloride solution and the calcium bicarbonate solution were being added drop by drop from two burettes placed opposite of each other above the beaker. But no precipitate formed in this manner. Six hours after adding 10 cm^3 of a 1/20 N sodium carbonate solution, a precipitate first formed. "The grains were of extremely irregular character and were so small as to prevent accurate determination of their optical properties, except that it was possible to see that the refractive index was slightly greater than 1.69, and the birefringence was very strong. The substance was neither hydrated nor basic in character (Found: CaO = 26.50 , 26.45 ; MgO = 25.10 , 25.10 ; CO_2 = 48.61 , 48.58 per cent)": Mitchell (1923 B, pp.1892-1893). But Mitchell (1923 B) refrained from claiming to have synthesized dolomite at room temperature, even though the precipitate formed in his opinion had a refractive index ".. very similar to that of dolomite" (Mitchell, 1923 B, p.1893). In a second series of experiments Mitchell (1923 B) added equal volumes of a mixed calcium- magnesium chloride solution (1/10 N) and a 1/10 N sodium carbonate solution, drop by drop, to 1 dm^3 of water. After 14 days some 300 cm^3 of the solution had evaporated, and a fine-grained precipitate had been formed. No crystalllites could be seen under the microscope, but the precipitate was definitely anisotropic. From the chemical analyses (H_2O = 14.81 , 14.62 , 14.75 ; CaO = 23.51 , 23.59 , 23.82 ; MgO = 16.20 , 16.14 , 16.23 ; CO_2 = 46.00 , 46.03 , 45.97 per cent) Mitchell (1923 B) concluded, that this precipitate consisted of "hydrodolomite", $CaCO_3.MgCO_3.H_2O$, similar to that described in Doelter's *Handbuch* (1912).

Halla (1937) tried to synthesize dolomite at room temperature through the addition of 1 part of a 0.059 mol $Ca(CN)_2$ solution to 2 parts of a 0.3 mol $Mg(HCO_3)_2$ solution. After a few days a white precipitate had been formed, which was found to consist of a mixture of $MgCO_3.3\ H_2O$ and $CaCO_3.6\ H_2O$. A second experiment, consisting of drop-wise additions of a 0.0177 mol $CaCl_2$ solution into 212 cm^3 of a 0.01385 mol solution of $K_2Mg(CO_3)_2.4\ H_2O$ dissolved in 20 % KCl in water, did not lead to dolomite formation either. A precipitate formed after the addition of 50.8 cm^3 of the calcium chloride solution, but in X-ray diffraction no dolomite was detected. Additional experiments by Halla (1937), involving the use of a calcium chloride solution of different molarity, changes in the procedure of drop-wise additions, the use of alcohol-water mixtures, or the use of $Na_2CO_3.MgCO_3$ instead of the potassium magnesium double carbonate, did not lead to successful results either.

Meanwhile papers describing unsuccessful attempts to synthesize dolomite at room temperature have become rare; one of the few to be found, is that by Baron (1960). Amounts of a sodium carbonate solution in water (0.5 mol/dm^3) were added drop by drop to a mixed solution of calcium chloride and magnesium chloride (each with 0.5 mol/dm^3). The tests were conducted at a temperature of 298 K. Nitrogen was being bubbled through the reaction vessel in order to ".. avoid contact with the air". In almost all instances calcite would precipitate, followed later by $MgCO_3.3\ H_2O$. Only in those instances where pure calcium chloride solution reacted with the sodium carbonate solution, calcite precipitated, and when using magnesium chloride with sodium carbonate in solution, nesquehonite precipitated (see Table VII). From these negative results Baron (1960) drew the conclusion, that the ions Cl^- , CO_3^{2-} , Ca^{2+} , Mg^{2+} and Na^+ were possibly involved in the formation of dolomite, but that these ions as such were insufficient to create the mineral at a temperature of 298 K and under atmospheric pressure. Castanier et al. (1990) performed experiments on the possible low-temperature formation of dolomite with the help of various microorganisms: peptone plus magnesium and calcium acetate were added to a small freshwater pond. Despite enhanced microbial activity (notably by sulfate reducing bacteria and denitrifying bacteria) during the 8 days of the outdoor experiment, the precipitates formed (at temperatures varying from 283 to 301 K), whether in dialysis tubes or on glass slides, did not resemble dolomite at all. Instead "… amorphous, maybe hydrous, magnesium and calcium carbonates which may be possible dolomite precursors" (Castanier et al., 1990, p.126) were found. No X-ray diagrams were presented in order to substantiate the claim.

The present discussion will be restricted to those experiments, which are by standard of Playfair's *Principle of Actualism*, compatible with the conditions prevailing in the sedimentary environment. This quest for an actualistic approach excludes at once a relatively large number of laboratory tests. Experiments in which temperatures exceeding 333 K were used, need not be considered here. The well-known tests described by Medlin (1959; where temperatures of 473 K and higher were used), by Siegel (1961; carried out at 351 K, and duplicated by Fritz & Smith, 1970), and Gaines (1974; conducted at 373 K) will not be discussed.

Mitchell (1923 B) had, according to *Chemical Abstracts* Vol.18 (1924), precipitated dolomite crystals from artificial sea water at room temperature. The dolomite contained some 55 % $CaCO_3$ and up to 44 % $MgCO_3$. Dolomite also formed in water in contact with calcite and nesquehonite. But Mitchell had used in all instances carbon dioxide pressures of 20 bar. Similarly Baron (1958, 1960) produced dolomite from a solution containing 0.5 mol $CaCl_2$, 0.5 mol $MgCl_2$ and 1.0 mol Na_2CO_3 , at a temperature of 423 K, but under carbon dioxide pressure of 3.2 bar. High carbon dioxide pressures were also used by Yanateva et al. (1973), who claimed to have synthesized dolomite (and magnesite) from a mixed Mg/Ca bicarbonate solution, to which had been added calcium- as well as magnesium sulfate and kept under carbon dioxide pressure of 4 bar. It will be clear, that the details of the tests by Mitchell, Baron, and Yanateva and co-workers can be left out of consideration. The same reasoning must be applied to experiments intended to change the dielectric constant of the seawater used in laboratory syntheses. Amounts of dioxane[3] have been used by Oomori & Kitano (1987) to mix into sea water, to which sodium carbonate had been added (at 313 K). The addition of 5 vol. % dioxane led, according to Oomori & Kitano (1987), to "well-crystallized protodolomite". "Decrease in dielectric constant, change in mineral solubility, modification of hydrogen bonding structure and change in hydration state of ions through addition of dioxane seem to be effective for protodolomite formation. The role of dioxane in the protodolomite formation, however, remains unsolved": Oomori & Kitano (1987, p.61).

Very low temperatures will also be disregarded. Therefore the claim of Müller & Fischbeck (1973), that freeze-drying of bicarbonate solutions during glaciations might well account for at least a number of occurrences of modern dolomite, will be left out of consideration. Freeze-drying was only a part of a more complex procedure used by Müller & Fischbeck. After dissolving pure dolomite in CO_2-saturated water and freeze-drying the bicarbonate solution, water was added and the mixture heated to 328 K. Strictly speaking therefore the experiments of Müller & Fischbeck (1973) cannot be considered to be truly *low* temperature syntheses.

Other experiments that will not be discussed are those experiments, which have nothing to do at all with dolomite formation as such. One such experiment has been described by Hsü & Siegenthaler (1969, 1971). Filling an aquarium partly with quartz sand, adding a 3 % NaCl solution and coloring the solution with $KMnO_4$, may be of some significance in hydrological studies, it has no consequence whatever for the low-temperature synthesis of the mineral dolomite. Nor has the outcome of a tank experiment on migrating dyed water, supposed to illustrate the reflux of concentrated sea water (Simms, 1984).

IRREPRODUCIBLE RESULTS

A number of claims has to be left out of consideration, because these were either published in a virtually inaccessible form, or simply because essential information required in any attempt at duplicating these tests, is lacking in the descriptions. The paper by Cornu (1907) was not only published in a rather inaccessible form (the *Oesterreichische Zeitschrift für Berg- und Hüttenwesen* cannot be found in every library), but it also lacks any details on the experiment itself. Cornu (1907) claimed to have observed dolomite in the precipitate, which formed from a calcium bicarbonate solution, to which an amount of magnesium sulfate had been added.[4] Identification had taken place only by way of the colouring method of Lemberg (1888). The amount of magnesium sulfate in the solution was not specified. And, apart from mentioning that the solution had been left standing in a conical flask for three months (at room temperature), no details were given.

An example of the second type is to be found in the paper by Kohlschütter & Egg (1925). The publication as such appeared in a well-known journal (*Helvetica Chimica Acta*), but essential details on the experiment itself are absent. In their paper, dealing mainly with the morphology of $CaCO_3$ crystals as influenced by certain ions in solution, Kohlschütter & Egg (1925) casually remarked, that in one of their tests "... perhaps dolomite had been formed". Perhaps indeed because this impression was based solely on the observation, that the product formed would not be easily dissolved in dilute hydrochloric acid. That was the only criterion used for identification: no X-ray evidence at all was presented. The precipitate as such had been formed in a calcium bicarbonate solution mixed with relatively large amounts of magnesium and subjected to slow CO_2-escape at room temperature. The carbonate was found to be adhering strongly to the glass. No specification whatever of the concentrations of calcium bicarbonate or magnesium chloride was given (except for the indication that "high concentrations" had been used[5]); this in clear contrast to other parts of the same paper, where all experimental procedures were explicitly described. Although it might have been possible to devise a series of experiments with a certain resemblance to the experiment described by Kohlschütter & Egg (1925), no such attempt was made. This decision was at least in part prompted by the conviction, that comparable tests described by Pfaff (1894) and Leitmeier (1915) had been unsuccessful.

Dolomite crystals as large as 1 mm have been found by Neher & Rohrer (1958) in core samples from a drilling at Laufen, near Koblenz (Aargau, Switzerland). The dolomite together with some calcite formed small "nests" in the top of a biotite gneiss underlying (Triassic) Buntsandstein strata. The idiomorphic habitus of these crystals demonstrated, that the dolomite was most probably of authigenic origin. In every instance the dolomite crystals were surrounded by a dark rim containing not only organic compounds, but also *live* bacteria.[6] After isolating these bacteria (which were not identified) from core samples, Neher & Rohrer (1958) were able to cultivate these bacteria in an inorganic medium and obtained dolomite crystals. No dolomite formed in sterile controls.[7] Although Neher & Rohrer (1958) stated, that in a subsequent paper in the same journal all the details would be revealed, their 1959 paper did not much to clarify the conditions used. Anaerobic cultures on the basis of dissolved gneiss samples kept at temperatures from 328 to 331 K after 6 weeks apparently led to the formation of dolomite. Such cultures gave rise to dolomite crystals of more than 1 mm in diameter.[8] The difficulty encountered here, when trying to duplicate the experiments of Neher & Rohrer (1958, 1959), lies of course in obtaining samples of the bacteria from the original drilling.

Comparable difficulties will be encountered, when trying to duplicate the experiment of Vasconcelos et al. (1995). For "the active microbial community" found in the black mud of Lagao Vermelha, Brazil was not analyzed by way of the pure culture technique. No attempt was made to identify the micro-organisms involved (in later papers this omission has been made good, if only by the introduction of a new *genus* of sulfate reducing bacteria: Warthmann et al., 2000). But a much more serious objection against this particular claim on the low-temperature formation of dolomite, is the fact, that the carbonate precipitated is not dolomite but ankerite. In the paper by Vasconcelos et al. (1995) the X-ray diffractogram of what has been claimed to be "a fully ordered dolomite", features only one of the three superstructure reflections. One of the missing other two superstructure reflections should have virtually the same relative intensity as the one featured. Why is it absent? After enlarging Fig.3 from the paper by Vasconcelos et al. (1995) to a somewhat more practical size, measurement of all of the diffraction peaks present becomes possible. The peaks identified in the diffractogram as belonging to "a fully ordered dolomite" were measured by me to be located at 23.8° , 30.8° , 34.78° , 37.15° , 41.0° , 44.7° . But other peaks can be recognized, located at 24.85° , 27.3° , 27.5° , 38.5° , 41.8° and 50.7° . Especially the latter peak at 50.7° is quite clear and cannot be overlooked. But it is not part of the dolomite diffraction pattern; it is in fact the second strongest line of the mineral *ankerite* $Ca(Fe,Mg)(CO_3)_2$. When consulting JCPDS-ICDD card No. 41-586 the conclusion seems inevitable, that the other peaks assigned by Vasconcelos et al. (1995) to "a fully ordered dolomite" should in fact be attributed to ankerite. (Apart from peaks belonging to α-quartz, peaks at 24.85° , 27.3° , 27.5° , 38.5° , 41.8° and 49.0° remain, but these belong probably to vaterite.) This re-interpretation is in fact supported by the EDAX analyses given by Vasconcelos et al. (1995), in which Mg, Ca and Fe were found. In another paper on the same subject Warthmann et al. (2000) claimed to have synthesized dolomite in anaerobic cultures of sulfate-reducing bacteria. However identification took place only by way of EDAX analysis, and not in X-ray diffraction. (Identification of minerals by way of EDAX is virtually impossible; to my regret I speak from experience!) Nonetheless Warthmann et al. (2000) claimed to have identified the mineral formed as “nonstoichiometric dolomite.”

The low-temperature experiment described by Kocurko (1986), in which ordered dolomite had been formed, will be difficult to duplicate because of two different reasons. In the first place a sample of the original algal community would have to be used. The second argument against any attempt at duplication is more serious: as Kocurko (1986) described it, the experiment took approximately five years.

In a relatively large number of publications claiming the low-temperature formation of dolomite, not even the barest fundamentals concerning the procedures used, can be found. But perhaps the language barrier and incomplete, or even erroneous, translations of these publications are to be blamed. Chilingar & Bissell (1963) took the trouble to translate the findings of Valyaskho (1962) (published in a nonaccessible[9] book described as "Geochemical regularities in the formation of potassium salt deposits: Izd.Mosk.Univ., A.P.Vinogradov, editor, 397 p., illus."). In the view of Valyaskho the speed of the reaction between calcium bicarbonate and magnesium sulfate would be crucial with regard to the dolomite problem. In most cases this reaction would proceed fast and lead to calcium sulfate and magnesium hydroxide carbonate as the end products. However if very small amounts of magnesium would be present, no such reaction would take place. Instead calcium carbonate would form. At low concentrations the following reaction would take place:

$$2\ Ca(HCO_3)_2 + MgSO_4 = CaMg(CO_3)_2 + CaSO_4 + 2\ H_2O + 2\ CO_2\ . \qquad \text{(eq. 30)}$$

"*Valyaskho (1962, p.55) and his associates obtained individual, isolated rhombohedrons of dolomite in some of their experiments. The dolomite was identified by V.B. Tatarsky and V.N. Dubinina, utilizing crystallo-optical analytical methods. Obviously, it would have been better if this dolomite had been identified by X-ray analysis. All experiments were conducted in equilibrium with atmosphere (low* CO_2 *pressure)*": Chilingar & Bissell (1963, p.801). Even though Chilingar & Bissell (1963, p.801) intended to "... check the validity of this reaction", the obvious lack of experimental details (obvious even in this apparently first-hand translation) must have prohibited such attempts.

Other experiments that will be left out of consideration are those, in which dolomite was not only found in the end products, but had been present in the starting material. It is most astonishing, to put it mildly, to note how scientists can seriously claim to have synthesized dolomite under conditions of low temperature, when it had been there from the very start. One such extraordinary claim has been put forward by Chazen & Ehrlich (1973). In their test pure dolomite and artificial sea water, made up from distilled water and quantities of reagent grade chemicals (NaCl, $MgCl_2$. 6 H_2O, $MgSO_4$.7 H_2O, $CaCl_2$.2 H_2O, KCl, and KBr), were used. The dolomite was ground to a very fine powder and dissolved in the artificial brine. After several days reaction time the newly formed phase appeared to be aragonite. According to the original text of the paper by Chazen & Ehrlich, dolomite could be prepared in the following manner: "*Aragonite-bearing samples were produced by reaction of powdered dolomite with solutions of 2.5 times normal salinity. After 8 days some of the samples were filtered, dried, and analyzed by X-ray diffraction and the microprobe, and the presence of aragonite was confirmed. The remaining beakers were uncovered and allowed to equilibrate at room conditions for approximately 7 wk. This primarily involved evaporation, but rehydration due to the salts removing water vapor from the air occurred occasionally. At the end of this time the solids were filtered, dried, and analyzed. Comparison of diffraction peak areas indicated that the amount of dolomite increased greatly with respect to aragonite*" (Chazen & Ehrlich, 1973, p.3632).

Assessment of the claim on successful low-temperature synthesis of dolomite put forward by Davies et al. (1975) will also encounter the problem of identification, but it is not entirely comparable. The dolomite would have been formed in a mixture of calcite and nesquehonite interbedded with decaying algal mats in a sea water-filled aquarium. The claim of Davies, Ferguson & Bubela (1975) was illustrated in their paper with a X-ray diffractogram. However the small part of a diffractogram reproduced there, shows apart from calcite and fluorite peaks the pattern of magnesium hydroxide carbonate. The rather complex diffractogram of magnesium hydroxide carbonate effectively obscures the possible presence of small amounts of dolomite. In this case the main peak of dolomite at 28.86 nm (JCPDS file card 11-78) has to be distinguished from three closely spaced peaks of magnesium hydroxide carbonate at 29.19 , 28.99 and 28.40 nm (JCPDS file card 25-513). No mention was made of the second (in decreasing order of intensity) diffraction peak of dolomite at 21.91 nm, nor of any other peaks of the dolomite signal. Although the same three authors, in 1977, even enlarged their claim on successful low-temperature synthesis of dolomite, their factual evidence became even more dubious, because in their tank experiments large amounts of powdered dolomite had been used as a starting material.

A different sort of difficulty will be encountered in attempts to duplicate the experiments described by Usdowski (1989, 1991, 1994). In 1964 Usdowski had reported the synthesis of dolomite in hydrothermal experiments carried out at 453 K and 12 bar pressure. In his book Usdowski (1967) had described syntheses of dolomite and magnesite carried out in sealed glass tubes at a temperature of at least 393 K. But in 1989 Usdowski claimed to have found dolomite and magnesite, formed as the result of the reaction between magnesium chloride (plus calcium chloride) solution and aragonite powder in sealed glass tubes after keeping the glass tubes at 333 K during 7 years.[11] Perhaps future investigators will take the trouble to duplicate tests involving 7 years reaction time; I was in no position to perform that kind of experiment.

SCHEERER'S EXPERIMENT

Scheerer (1866) dissolved limestone fragments and (separately) dolomite powder in water by bubbling carbon dioxide through it. After complete dissolution the separate solutions were mixed in varying proportions. The mixed Mg/Ca bicarbonate solutions were subsequently subjected to slow desiccation at room temperature.[12,13] Under identical conditions a pure calcium bicarbonate solution and a pure magnesium bicarbonate solution were desiccated. The calcium bicarbonate solution developed clear rhombs of calcite; the magnesium bicarbonate solution gave rise to needle aggregates of what Scheerer described as "hydrated magnesium carbonate". The mixed bicarbonate solutions yielded "crystals of calcium-magnesium carbonate", as subsequent chemical analyses revealed. These crystals consisted of rhombs with numerous faces, while other crystals were more rounded, of a more polyedric form, and were grouped together like a string of pearls.

Numerous authors have since repeated Scheerer's experiment, and in all those tests no dolomite at all formed. It is however important to note, that Scheerer did not claim the formation of any dolomite in his experiments (Scheerer, 1866, p.12 spoke of "*Krystalle von Kalk-Magnesia Carbonat*"). On the other hand Scheerer did not hesitate to interpret the results of his experiments in terms of dolomite formation. The tests with mixed magnesium-calcium bicarbonate solutions were duplicated for example by Von Gorup-Besanez (1872) and Hoppe-Seyler (1875). In none of their experiments dolomite was formed: mixtures of $CaCO_3$ and $MgCO_3.3\ H_2O$ or $MgCO_3.5\ H_2O$ were invariably the result.

Von Gorup-Besanez (1872) not only analyzed a number of mineral waters from dolomite regions, but also dissolved samples of dolomite into CO_2-rich water and desiccated the thus obtained mixed Mg/Ca bicarbonate solution at room temperature (or at slightly elevated temperature: Von Gorup-Besanez was not particularly clear concerning the temperature used). Such solutions behaved as "mixtures of both bicarbonates"; under no condition whatever dolomite precipitated from the mixed solutions.[14] What Von Gorup-Besanez did find upon slow desiccation of such solutions was, that at first a multitude of needle-shaped crystallites of calcium carbonate formed (floating on the solution in the form of a membrane), and only much later, when a large part of the solution had evaporated, a light, flaky precipitate was formed, consisting of a form of magnesium carbonate (magnesium hydroxide carbonate to judge from the description).

As mentioned before, Hoppe-Seyler (1875) also duplicated the tests of Scheerer (1866) and obtained much the same negative results, that had been reported by Von Gorup-Besanez (1872). Whether magnesium bicarbonate solution was mixed with an equimolal amount of a calcium bicarbonate solution and slowly desiccated at room temperature, or mixed in any other ratio with a calcium bicarbonate solution, no dolomite whatever could be obtained in this manner even after months of slow desiccation at room temperature.[15] The same conclusion was reached by Leitmeier (1915), who dissolved dolomite in CO_2-rich water and subjected the thus formed solution to gradual escape of CO_2 at various temperatures. In this case too no dolomite formed: mixtures of calcite and hydrated forms of magnesium carbonate had been formed instead.

Kazakov et al. (1957) have tried to precipitate dolomite at 293 K from a mixed Mg/Ca bicarbonate solution, to which NaCl had been added. No dolomite (or magnesite) precipitated: the solids formed were calcite and nesquehonite. Comparable observations have been made by Baron & Favre (1958). Their mixed solutions had been prepared by separately dissolving calcium carbonate and magnesium carbonate in water under carbon dioxide

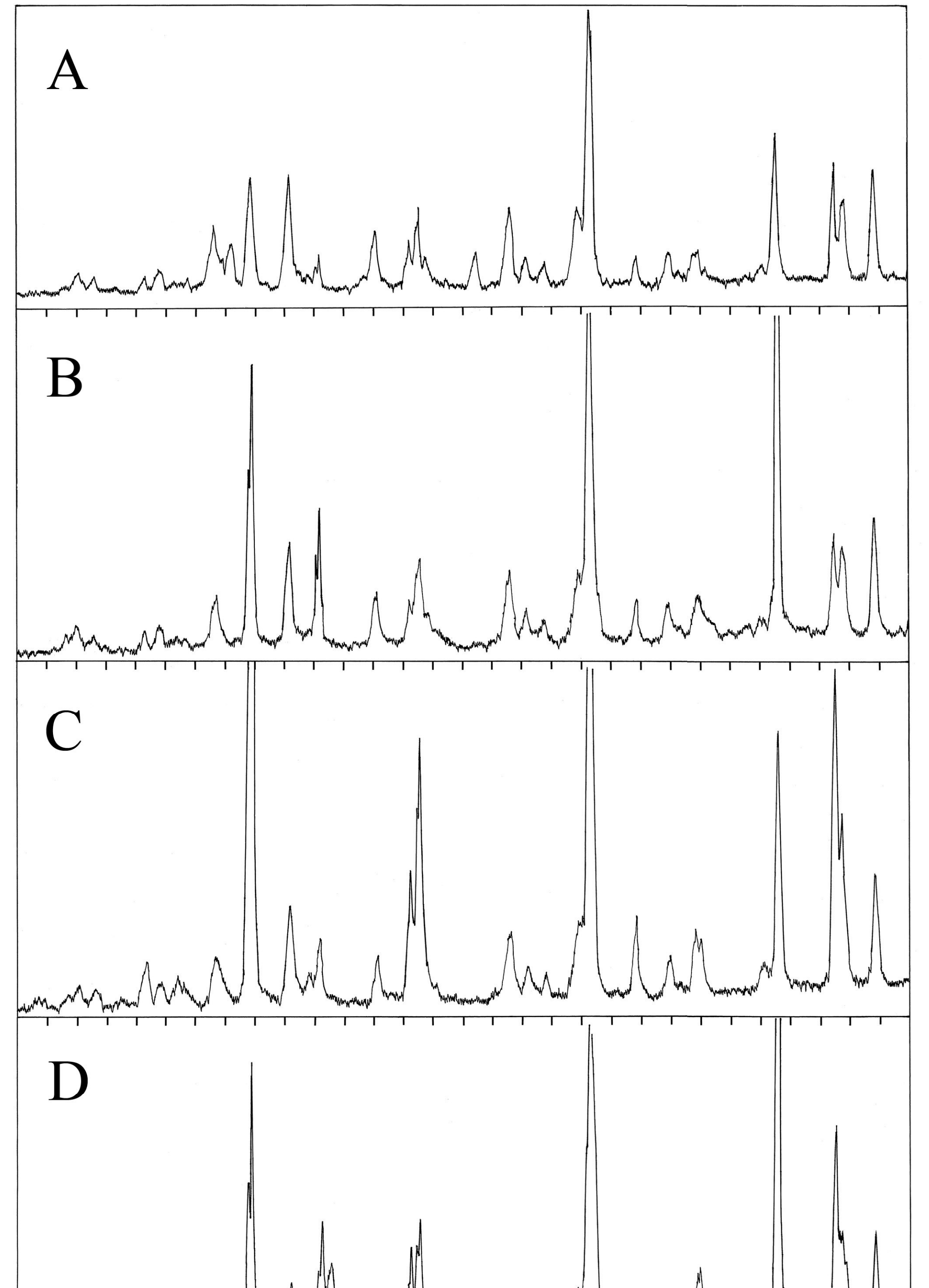

Fig.30 – Precipitates formed upon static desiccation of mixed Mg/Ca bicarbonate solutions at 303 K; A – Mg/Ca = 1; B – Mg/Ca = 2; C – Mg/Ca = 3; D – Mg/Ca = 4.

pressure of 1.9 bar. Ten different mixtures were made up, ranging from a pure calcium bicarbonate solution, via 0.1 magnesium bicarbonate + 0.9 calcium bicarbonate, in steps to bicarbonate + 0.1 calcium bicarbonate, and ultimately a pure magnesium bicarbonate solution. After desiccating the solutions at a temperature of 298 K, the minerals calcite, aragonite, vaterite, monohydrocalcite and nesquehonite were found.

Not directly discouraged by the conclusions reached by others, but with the hope, that perhaps a trace of dolomite might develop, I have tried to duplicate Scheerer's experiment. A series of 8 different mixed Mg/Ca bicarbonate solutions, each with a specific Mg/Ca ratio, was prepared by weighing an amount of $CaCO_3$ powder (calcite)[16], and adding an amount of magnesium hydroxide carbonate.[17] In every instance the ingredients were added to 1 dm^3 of demineralized water, and were dissolved by bubbling carbon dioxide through the water. Bubbling continued until all carbonate had been dissolved; in most cases 24 hours proved sufficient. As soon as a clear solution had been formed, the glass beaker containing it, was placed in a thermoconstant box: desiccation took place at a constant temperature of 303 K. After desiccation the dry precipitate was scraped off the glass, powdered, and could be used directly in X-ray diffraction. In the first test Mg/Ca = 1 was attained by dissolving 0.40 g $CaCO_3$ and 0.46 magnesium hydroxide carbonate. The minerals formed after desiccating the bicarbonate solution at a constant temperature of 303 K were calcite, aragonite and nesquehonite (Fig.30 A). When using a Mg/Ca ratio of 2, by way of dissolving 0.24 g $CaCO_3$ with 0.56 g magnesium hydroxide carbonate, aragonite and nesquehonite formed (Fig.30 B). In the case of a Mg/Ca of 3, created by dissolving 0.18 g $CaCO_3$ together with 0.62 g magnesium hydroxide carbonate, aragonite and nesquehonite were formed (Fig.30 C). The same two minerals precipitated from a mixed bicarbonate solution with Mg/Ca = 4 , prepared with 0.14 g $CaCO_3$ and 0.66 g magnesium hydroxide carbonate (Fig.30 D). Aragonite and nesquehonite were also found in the precipitate, that formed after the desiccation of a mixed bicarbonate solution with Mg/Ca = 5 (with 0.12 g $CaCO_3$ and 0.68 g magnesium hydroxide carbonate) along with a small amount of magnesium hydroxide carbonate (Fig.31 A). The same three minerals formed, when desiccating a solution with Mg/Ca = 7 at a constant temperature of 303 K (the latter bicarbonate solution had been prepared by dissolving 0.08 g $CaCO_3$ and 0.72 g magnesium hydroxide carbonate in 1 dm^3 carbonated water) (Fig.31 B).

EXPERIMENTS BY PFAFF

Pfaff (1894) claimed successful low-temperature synthesis of a mixed carbonate, that resembled dolomite in its behavior toward dilute acid and in optical properties. The procedure used, involved the dissolution of calcium carbonate and magnesium hydroxide carbonate ("magnesia alba") in a solution of hydrogen sulfide plus ammonium sulfide in water (*Schwefelammon*), and desiccating the solution at elevated temperature on a water bath.[18,19] After complete desiccation several additions of ammonium carbonate were made, followed by forced desiccation until the precipitate would be quite dry. The mixture formed was washed with 1 % hydrochloric acid. Only when heating the precipitate in concentrated hydrochloric acid, it would start to dissolve. Chemical analysis revealed, that the precipitate contained "... a high amount of magnesia as well as some lime".[20] Repeating the experiment led to identical results. Because Pfaff had found only small amounts of calcium carbonate in the analysis of the final precipitate, he tried to dissolve pure $CaCO_3$ into a H_2S solution. Considerable amounts of calcium carbonate were found to dissolve in that manner. In additional tests Pfaff established,

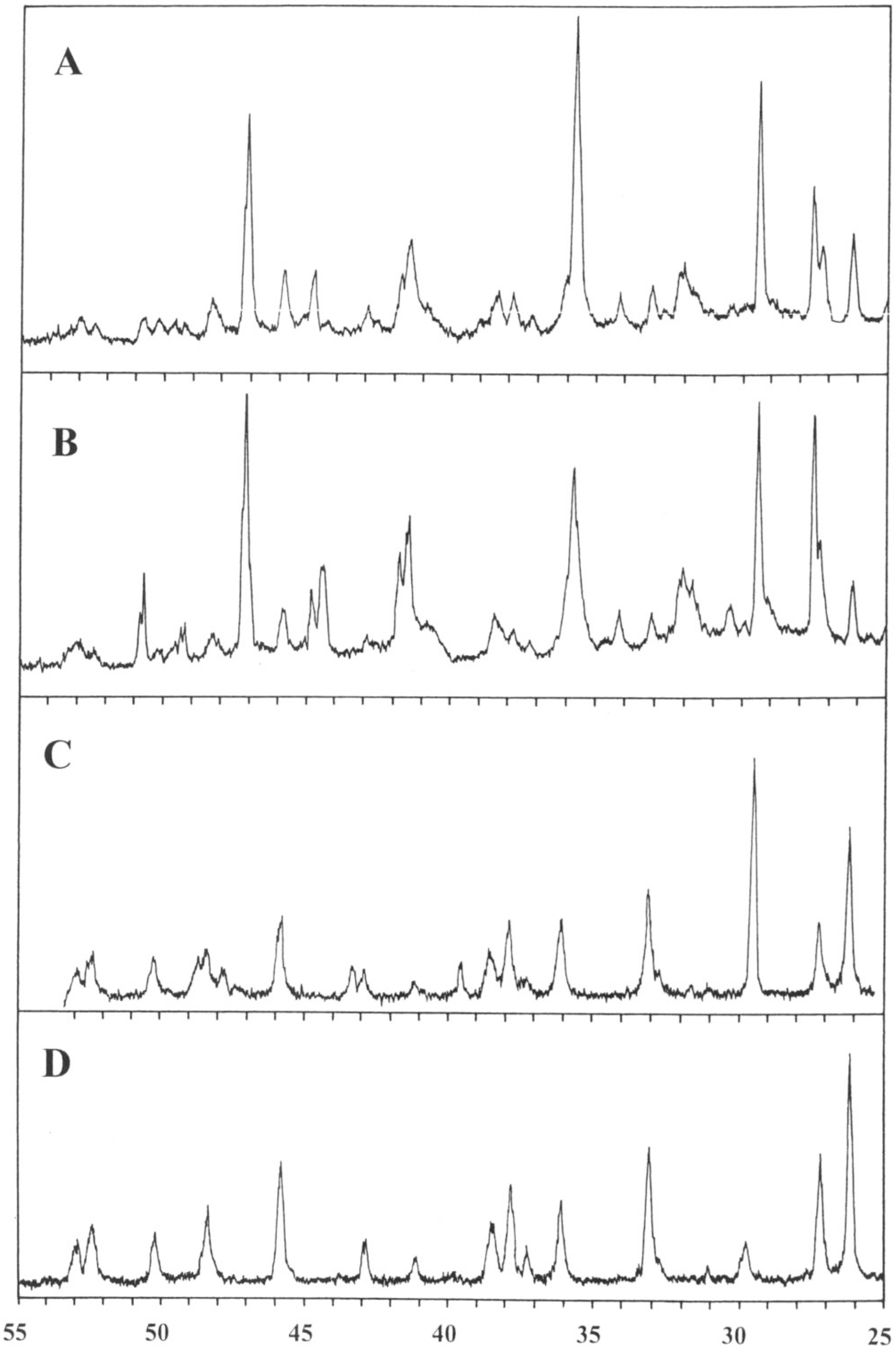

Fig.31 – A & B: Precipitates formed upon static desiccation of mixed Mg/Ca bicarbonate solutions at 303 K (A – Mg/Ca = 5; B – Mg/Ca = 7). C & D: Precipitates formed upon duplication of the experiments by Pfaff (1894).

that magnesite would not be easily dissolved in a H_2S solution, but that magnesium hydroxide carbonate would dissolve quite well. After describing several tests, in which a crystalline form of magnesium carbonate capable of withstanding treatment with dilute acid had been formed, Pfaff proceeded to recount his success in synthesizing dolomite. Calcium carbonate had been dissolved in a solution of hydrogen sulfide in water, and magnesium hydroxide carbonate had been dissolved in a solution of hydrogen sulfide plus ammonia in water. The cation concentration of each of these two solutions was determined, after which the solutions were mixed in such a way, that the mixture contained twice as much calcium as magnesium. Reagent grade sodium chloride was added (as Pfaff had used in all of his experiments). Carbon dioxide was then bubbled slowly through the solution, while it gradually desiccated at room temperature. The experiment took about two months; after that period, a dry precipitate was obtained. After washing it several times with water, as well as with dilute acid, followed by desiccation at 393 K, wet chemical analysis was performed. The remainder of the precipitate contained 43.7 wt.% $MgCO_3$, 52.0 % $CaCO_3$, and 3.8 % of an insoluble residue. Under the microscope the substance showed rather strong double refraction. It was insoluble in dilute hydrochloric acid. After initially giving off some CO_2, it would not dissolve further in even a rather concentrated solution of hydrochloric acid. Pfaff (1894) observed, that this behavior was comparable to that of a finely powdered natural dolomite.

Because in all his experiments Pfaff (1894) had used aqueous solutions saturated with sodium chloride, the actual role of NaCl was studied by way of repeating several tests without any NaCl. All of those tests proved to be negative: in all tests carried out without NaCl precipitates formed, which would readily dissolve in dilute HCl. It is therefore only logical, that Pfaff concluded, that sodium chloride must be actively involved in the low-temperature formation of magnesite and dolomite.[21] The same role could be played by large amounts of ammonium salts.

Although initially Pfaff hesitated to describe the mixed Mg/Ca carbonate obtained as dolomite, and described it as a "... dolomite-like substance" instead, later on in his paper no such hesitation remained. The conditions required for the low-temperature synthesis of dolomite were summarized by Pfaff (1894) as follows: 1) sodium chloride or ammonium salts should be present in high concentrations; 2) after dissolving calcium and magnesium in aqueous solutions of hydrogen sulfide (or ammonium sulfide), conversion into carbonates required the addition of carbon dioxide; and 3) the magnesium solution should be prepared only by way of bubbling hydrogen sulfide through an aqueous suspension of magnesium hydroxide carbonate.

In a second publication on the same subject Pfaff (1903) stated frankly, that he no longer considered the low-temperature formation of dolomite by way of the reaction between CO_2 and dissolved calcium and magnesium sulfides as very likely to take place in nature. Now Pfaff had become convinced, that because of the well-known association between dolomite and gypsum, the latter compound would be involved in the process of dolomite formation. In laboratory tests Pfaff had been able to procure evidence in support of this view. The experiment that created a mixed Mg/Ca carbonate, resembling dolomite (because it did not dissolve in dilute hydrochloric acid), was not exactly described in great detail.[22] In my interpretation of the rather cryptic German text, Pfaff (1903) had heated amounts of $MgSO_4.7\ H_2O$, $MgCl_2.6\ H_2O$, $CaCl_2.2\ H_2O$ and NaCl in water, resulting in the precipitation of gypsum from the solution. After cooling down, CO_2-rich water would be added, and the solution would slowly desiccate at a temperature of 293 to 298 K. After "numerous repetitions" of desiccation and re-wetting with CO_2-rich water, the dolomite-like substance would have been formed. The claim that a dolomite-like substance would have formed, was certainly undermined by two chemical analyses of the precipitate. In the first analysis Pfaff (1903) found 62.7 % $MgCO_3$ and 38.1 % $CaCO_3$.[23] In a second analysis these percentages were 12.3 and 88.0 respectively. Because even the most essential information is lacking in Pfaff's (1903) paper (for example concerning the amounts of chemicals used), no possibility exists to duplicate this particular experiment.

At least one attempt to duplicate the tests of Pfaff (1894) has become known. Balló & Jugovics (1915) reported, that the addition of hydrogen sulfide gas to solutions containing calcium chloride, magnesium chloride, sodium chloride and sodium carbonate in water (at 291 to 293 K) did not lead to the precipitation of dolomite. Similarly bubbling ammonia through such a solution did not lead to the low-temperature formation of dolomite. Apart from the futile attempts by Balló & Jugovics (not all of the details are clear, because the original publication was not accessible to me), no serious efforts to duplicate the tests of Pfaff seem to have been made. Perhaps the reason is to be found in the prejudice expressed by Leitmeier (1915), that Pfaff's experiments were "... somewhat unrealistic".[24]

Because no need exists to duplicate tests in which temperatures exceeding 333 K were used, a relatively large number of experiments described by Pfaff (1894) can be left out of consideration. Nevertheless several attempts to duplicate certain experiments of Pfaff (1894) have been made by me.

In a first attempt 1.0 g $CaCO_3$ plus 1.18 g magnesium hydroxide carbonate (approximately equivalent molal amounts) were dissolved in 1 dm^3 distilled water with the aid of compressed H_2S gas bubbled through. Dissolution was quite rapid: after only 48 hours both carbonates had disappeared from the bottom of a large conical flask and a clear, if somewhat greenish, solution had been obtained. After pouring the solution into a large, shallow glass bowl, 400 g NaCl were added. The amount of sodium chloride appeared to be enough to give a supersaturated solution: not all of the sodium chloride would dissolve. Above the bowl an infrared lamp was placed, and its voltage regulated in such a way, that the temperature near the surface of the solution was a constant 303 K. While the solution was desiccating, carbon dioxide gas (industrial grade) was slowly bubbling through it. From time to time the salt crust that had formed, was broken up into pieces to facilitate further desiccation. After only a few days the solution had disappeared altogether, and a dry salt crust remained. Added were 2 dm^3 of distilled water, dissolving again almost all of the sodium chloride. A slightly greenish precipitate was obtained upon filtering through a paper filter, and it was washed with another 2 dm^3 of distilled water. After drying the filter paper (at room temperature), the 0.4 g of precipitate were X-rayed. It turned out, that magnesium calcite (with a quite narrow main peak at 30.2 nm) together with aragonite had been formed (Fig.31 C).

A negative result was obtained also in a second experiment, designed to verify Pfaff's (1894) claim on the formation of dolomite. In this second experiment 0.5 g $CaCO_3$ (calcite powder) and 1.68 g magnesium hydroxide carbonate were dissolved in 1 dm^3 distilled water with the aid of H_2S gas bubbled through it during 10 days. After pouring the clear solution into a large glass bowl and adding 400 g NaCl, carbon dioxide was slowly bubbled through. At the same time a heat lamp secured desiccation at a temperature of 303 K. After only 5 days the water had vanished, and a thick salt crust remained. Addition of 2 dm^3 distilled water dissolved the salt crust again, and the solution obtained was left to settle in two high glass cylinders for at least 24 hours. Then most of the clear solution was siphoned off, and distilled water added again. This decanting was repeated 5 times, after which the fine suspension obtained was desiccated in a large Petri dish at 303 K. X-Ray diffraction showed the precipitate to consist mainly of aragonite together with minor amounts of a magnesium calcite with its main peak at 30.0 nm (Fig.31 D).

EXPERIMENTS BY LINCK

In his first communication concerning laboratory synthesis of dolomite, Linck (1909 A) refrained from describing the exact conditions of his experiments. Not only were the conditions not explained, the exact nature of the compound synthesized was not fully revealed either. Linck claimed it to be an anhydrous mixed crystal of both magnesium and calcium carbonate. Under certain conditions this double salt would change into a compound quite similar to dolomite. This calcium-magnesium carbonate would form upon adding ammonium carbonate to solutions of both calcium and magnesium salts. The amount of incorporated magnesium carbonate would depend on the concentration of the magnesium salt in solution, because always a large part of the water-soluble magnesium salt would remain in solution. The use of equimolal amounts of calcium and magnesium salts would initiate the formation of a compound very similar to dolomite. Linck stressed the possibility, that this dolomite-like mixed crystal could be precipitated directly from solution only if certain conditions such as low carbon dioxide pressure, presence of hydrogen sulfide, et cetera were met. Ultimately Linck (1909 A) did not doubt the fact, that he had been able to synthesize dolomite at low temperature, since the second half of his paper was devoted to a historical review of many of the preceding attempts by others to explain the low-temperature formation of dolomite.

In a second paper published in 1909 Linck gave more details. But even so it still is impossible to establish unambiguously the experimental conditions of his tests. The difficulty lies in the exact amount of chemicals used by Linck (1909 B). In the original text reference is made to "... 1 mol (2.4 g) $MgCl_2$ and 1 mol $MgSO_4$" dissolved in 50 cm^3 water, mixed with 1.5 mol ammonium sesquicarbonate in 150 cm^3 . In turn this mixture had to be added to 100 cm^3 H_2O containing 1 mol $CaCl_2$.[25] Linck's student Diesel (1911) finally revealed, that Linck had actually used 5.08 g $MgCl_2.6\ H_2O$, 3.66 g $MgSO_4.7\ H_2O$, 10.20 g $(NH_4)H_2(CO_3)_3.H_2O$, and 2.77 g $CaCl_2$ in his experiment. After dissolving the magnesium chloride and the magnesium sulfate in 50 cm^3 water and mixing it with 150 cm^3 water containing the ammonium sesquicarbonate, Linck had added 100 cm^3 water with the calcium chloride dissolved in it. Carbon dioxide would be emitted, and a thick, gel-like paste formed. Heating the paste to 303 K would start the crystallization process, and upon heating it to temperatures between 323 and 333 K, crystallization would be quite rapid. After filtering off the precipitate, microscopic analysis showed Linck, that a mass of needle aggregates resembling spherolites had been formed. Chemical analyses showed the precipitate to possess "nearly precisely" the composition of dolomite.

It is important to note, that Linck (1909 B) frankly admitted, that not dolomite as such, but an anhydrous mixed crystal of calcium and magnesium carbonate had been formed.[26] In a subsequent experiment true dolomite was made, but there Linck applied high temperatures as well as elevated pressure. The precipitate had been made from calcium chloride, magnesium chloride, magnesium sulfate and ammonium carbonate, heated in closed glass tubes during several hours to temperatures between 313 and 323 K. Chemical analyses, optical properties and specific weight all showed, that the precipitate formed was true dolomite. From this Linck concluded, that the anhydrous Mg/Ca carbonate formed under conditions of low temperature was a necessary intermediate in the formation of dolomite (the parallel with a precursor phase that has been known as "protodolomite", is obvious!).

In his 1937 paper on the same subject Linck stated to have found support for his ideas on the existence of a mixed Mg/Ca "gel" in the views expressed by Mayer (1932). The latter author had suggested, that the precipitation of calcium carbonate inside organisms would invariably take place in the form of an amorphous gel. Linck (1937) explained, that after "mutual absorption" of the $CaCO_3$-gel and a $MgCO_3$-gel, there were two different possibilities:

either the magnesium would disappear, and thus would not be available for the incorporation into $CaCO_3$, or it would be incorporated into the calcite lattice. Even so Linck (1937) thought, that large amounts of dolomite would not be created in this manner, because the problem would be to find the required amounts of magnesium bicarbonate. A second possibility seemed more likely: dolomite would receive its magnesium from the dissolved magnesium sulfate and magnesium chloride present in normal seawater. But the problem remained, how dolomite would really form. New inspiration seemed to come from the observations by Linck & Köhler (1933) on the processes taking place in tidal (salt) marshes.[27] There dolomite was being formed as the result of the reactions of calcium carbonate with a solution of magnesium sulfate and magnesium chloride, with carbon dioxide as well as ammonia dissolved in it.

Prior to the year 1913 Linck had been convinced, that he had really found the solution to the dolomite problem[28], but after that time Linck appears to have taken a more modest standpoint. Most likely the reason for that change was the outcome of laboratory research by Linck's own students Schmidt and Spangenberg. After duplicating the tests described by Linck, Schmidt (1913) had not found any dolomite at all. Schmidt (1913) showed, that the "*Linck'sche Mischsalz*" was at best a mixed crystal of $CaCO_3$ with relatively large amounts of magnesium carbonate incorporated in it. Similarly Spangenberg (1913) had demonstrated in experiments, that a mixed anhydrous Mg/Ca carbonate would form, but not dolomite, after adding a solution of ammonium carbonate to one of magnesium chloride and calcium chloride at room temperature. True dolomite would be formed only when these ingredients would react under considerable pressure in closed glass tubes subjected to temperatures of at least 323 K. Three years earlier both Fischer (1910) and Meigen (1910) had drawn the conclusion, that the experiments described by Linck (1909 A, B), when conducted at ambient temperature and under atmospheric pressure, did not lead to dolomite formation. Fischer's (1910) first experiment consisted of adding an ammonium carbonate solution (of 1.75 g/dm^3) to natural seawater at room temperature. The precipitate was filtered off after four weeks reaction time, and subjected to wet chemical analysis. The precipitate consisted of 98.4 % $CaCO_3$ and 1.6 % $MgCO_3$. In Fischer's second experiment the ammonium carbonate solution was added to concentrated seawater (concentrated from 500 cm^3 to 200 cm^3 by heating). The chemical analysis of the precipitate formed after 14 days gave 97.6 % $CaCO_3$ and 2.4 % $MgCO_3$. In a third experiment even more concentrated sea water was used (concentrated by heating until the precipitation of gypsum started); added to it were 100 cm^3 of the ammonium carbonate solution, while keeping the temperature at 303 K. The precipitate contained only 3.2 % $MgCO_3$ and 96.8 % $CaCO_3$. Markedly more $MgCO_3$ was found in the precipitate, that formed in Fischer's fourth experiment, but there a temperature of 373 K had been used. Meigen (1910) stated, that all his attempts to duplicate Linck's experiments had been without success. The precipitates obtained would dissolve quickly in cold, dilute acetic acid.

The claims of Linck have also been criticized by Leitmeier (1915), who stressed especially the lack of adequate identification. Much like Meigen (1910) Leitmeier arrived at the conclusion, that no true dolomite had been formed. Leitmeier was especially critical of the use of an unspecified "dilute acid" to distinguish dolomite from mixed Mg/Ca carbonates. Leitmeier (1915) argued that even pure dolomite, when finely powdered, will dissolve quickly in dilute hydrochloric acid (even showing effervescence). Leitmeier (1915) suggested, that optical measurements such as that of the refractive index, would offer instead a more reliable means of distinction between dolomite and the "*Linck'sche Mischsalz*".

Köhler (1931) checked the claims of Linck and had to conclude, that unless high pressure and/or high temperatures were used (333 K at least), no dolomite formed. At the same time Köhler confirmed the essential role played by the ammonia radical. The role of ammonia had

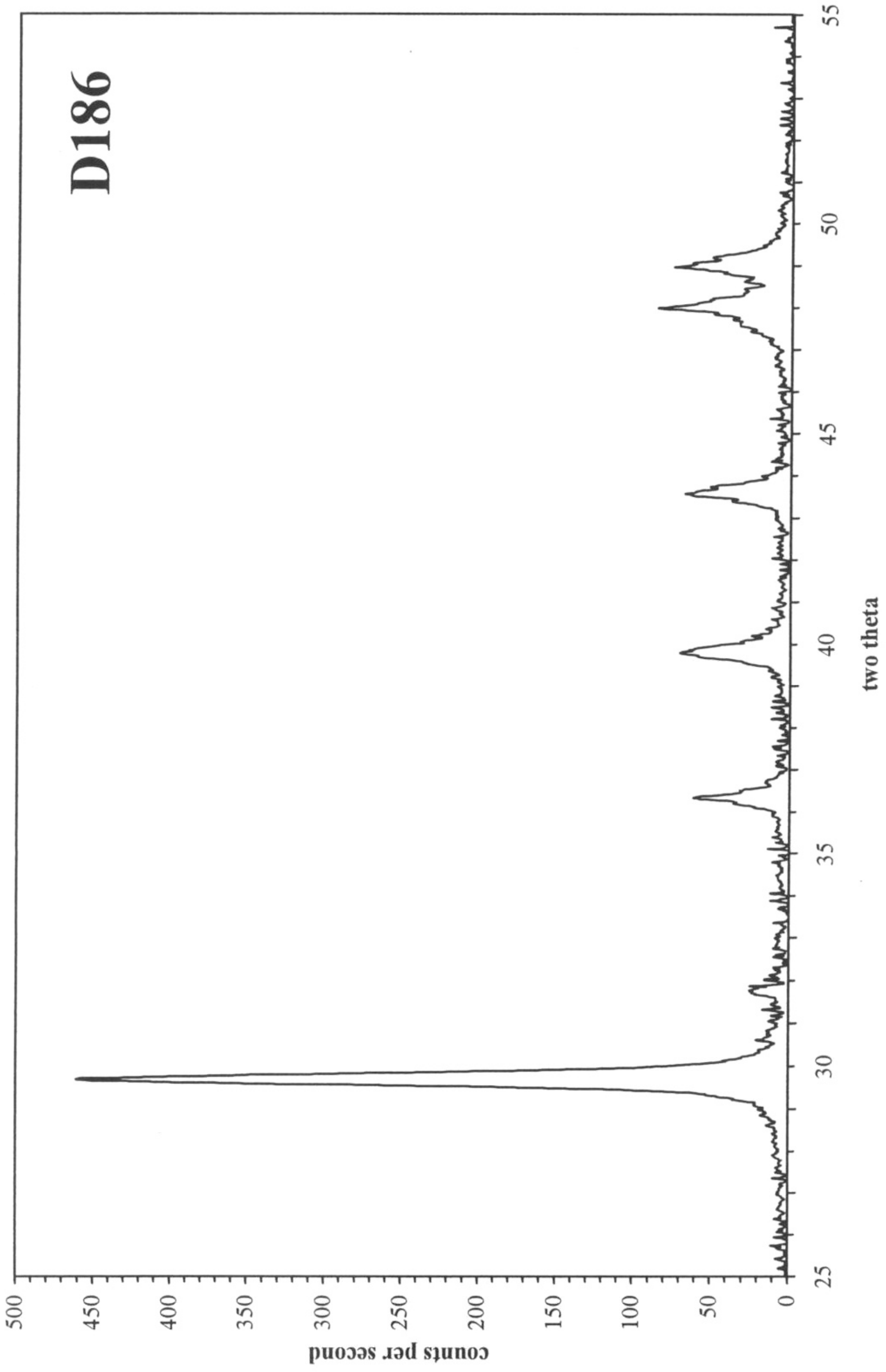

Fig.32 A – Precipitate formed upon duplication of the experiment of Linck (1909).

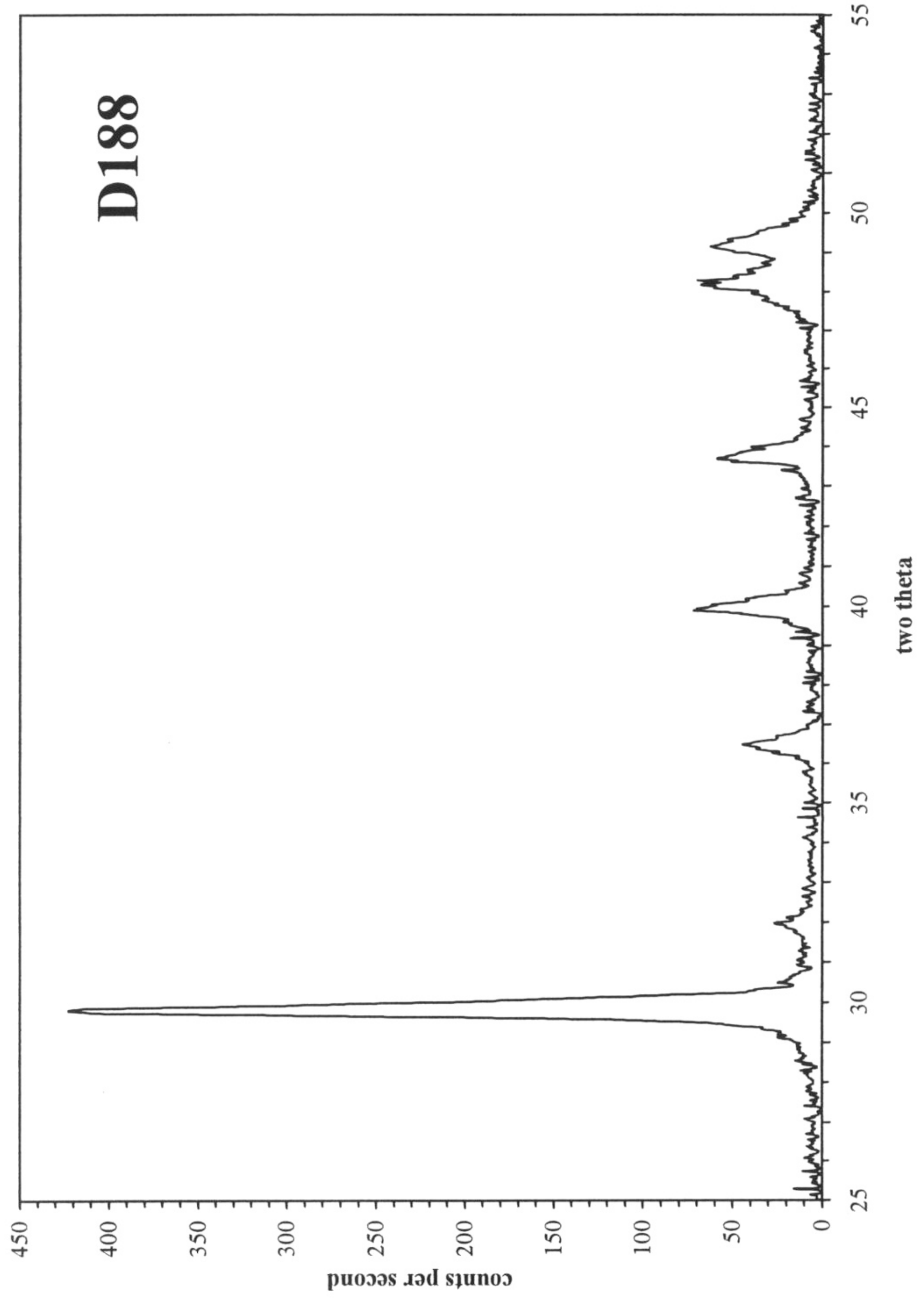

Fig.32 B – Precipitate formed upon duplication of the experiment of Linck (1909).

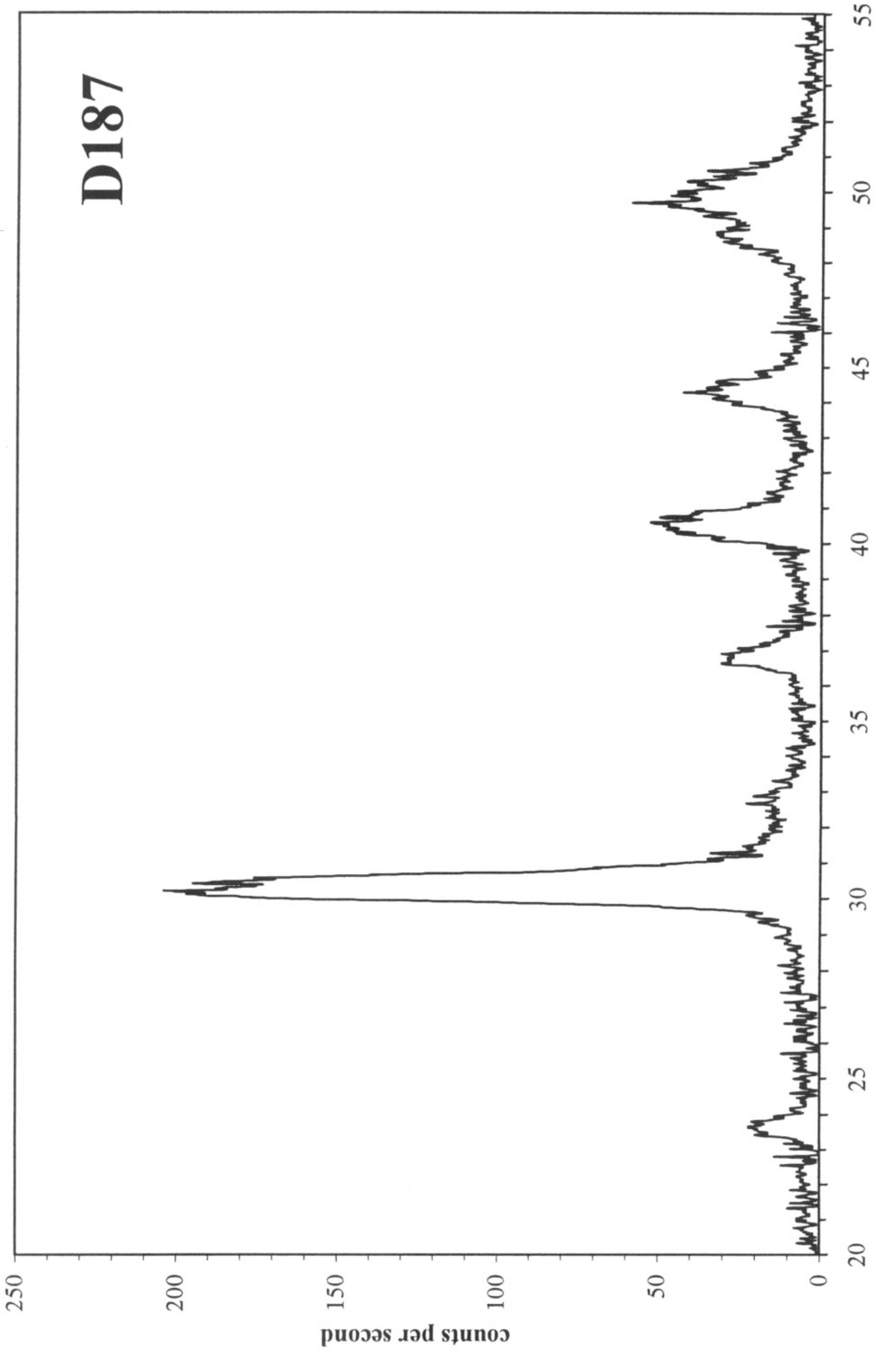

Fig.32 C – Precipitate formed upon duplication of the experiment of Linck (1909).

been hinted by Linck in 1903 and discussed in some detail by Adolf, Pulfrich & Linck in 1921. Linck's experiments furthermore have been duplicated by Berg & Borisova (1959). Those two authors showed with the aid of X-ray diffraction, that the substance synthesised by Linck (1909 B) was most probably magnesium calcite ("a solid solution of calcite in dolomite" as Berg & Borisova, 1959 described it).despite the observations previously made by several authors, I have tried to duplicate Linck's experiments. The attempt was hampered to some degree by the relative difficulty in obtaining one of the necessary chemicals. Ammonium sesquicarbonate, $(NH_4)_2CO_3.2\ NH_4HCO_3.H_2O$, is not a compound, that can be obtained easily. But at closer look it is not really necessary to use this very compound. For upon dissolution in water NH_4^+ , CO_3^{2-} and HCO_3^- will be formed. Therefore it must be possible to use an addition of equivalent amounts of ammonium carbonate and ammonium hydrogen carbonate instead. Duplication of Linck's experiment (following the description of Diesel, 1911) involved 5.08 g $MgCl_2.6\ H_2O$ and 3.66 g $MgSO_4.7\ H_2O$ in 50 cm^3 distilled water; a second glass beaker containing 6.02 g $(NH_4)_2CO_3.H_2O$ (DAB, FLUKA art. 09698) and 4.17 g NH_4HCO_3 (purum p.a., FLUKA art. 09832) dissolved in 150 cm^3 water; and a third with 2.77 g $CaCl_2.2\ H_2O$ in 100 cm^3 H_2O . The three beakers were put in a thermoconstant box to reach a temperature of 303 K. After half an hour of equilibration, the magnesium chloride/magnesium sulfate solution was poured into the ammonium bicarbonate/ammonium carbonate solution and immediately after that the calcium chloride solution was added. The result was an instantaneously turbid solution; precipitation started at once. After some 2 hours the precipitate had settled: the remainder of the solution had become clear. The precipitate was filtered off, and washed with 1 dm^3 of distilled water. After drying the sample at room temperature, X-ray diffraction was performed: the precipitate consisted of a magnesium calcite with its main diffraction peak located at 29.69 nm (Fig.32 A).

Because Linck and his students had stressed the importance of an elevated temperature, the experiment has been repeated at a temperature of 333 K. What resulted was a magnesium calcite with a relatively well-defined maximum intensity at 29.9 nm (Fig.32 B). Not even after performing the same experiment at 373 K dolomite appeared; instead a magnesium calcite with the main diffraction peak at 29.6 nm was found (Fig.32 C).

LEITMEIER'S EXPERIMENTS

Leitmeier (1910 A) claimed to have found dolomite in tests consisting of the gradual escape of carbon dioxide from a calcium bicarbonate solution, to which magnesium chloride or magnesium sulfate had been added. Initially the experiments had been intended to study the conditions under which the polymorphs of calcium carbonate will be deposited. In this sense Leitmeier carried further the experiments described by Cornu (1907), who had set out to study the same problem and who had claimed low-temperature formation of dolomite in his experiments.

Eight different tests with a calcium bicarbonate solution containing small amounts of magnesium chloride or magnesium sulfate were carried out during three months at a temperature of 275 K (in which only calcite formed). But Leitmeier (1910 A) discovered dolomite crystals in the precipitate from the solutions kept at a temperature of 283 or 293 K. In all experiments 0.1 g $CaCO_3$ was dissolved in 100 cm^3 water with the aid of carbon dioxide bubbled through. Amounts of $MgCl_2.6\ H_2O$ (0.005 , 0.01 , 0.05 , or 0.1 g) were added, or amounts of $MgSO_4.7\ H_2O$ (0.005 , 0.01 , 0.05 , or 0.1 g), and each solution was left standing in an open retort for 3 months at nearly constant temperature. The first time Leitmeier (1910 A) thought to have observed dolomite in these experiments (the carbonates would float on the

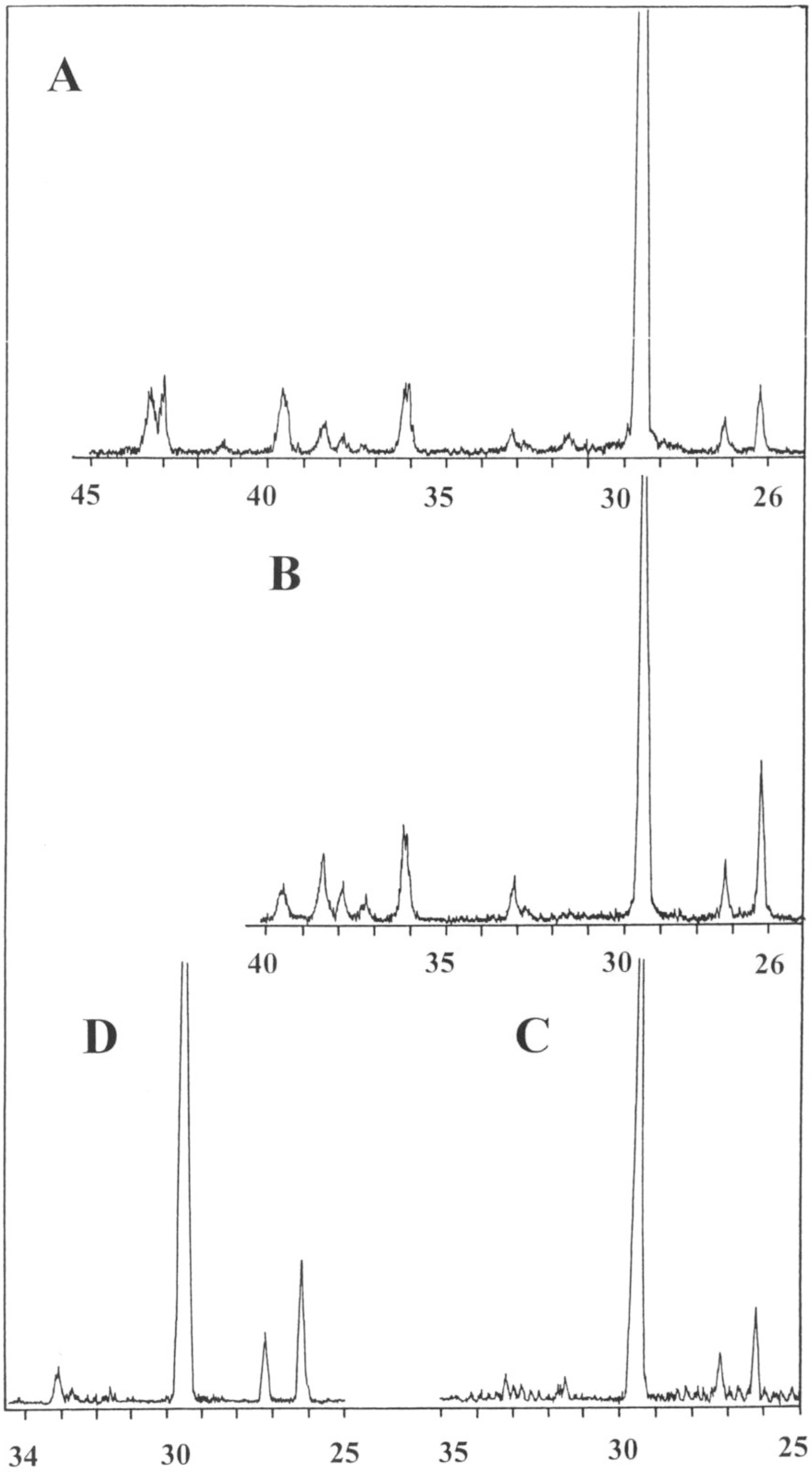

Fig.33 – Precipitates formed upon duplication of the experiments of Leitmeier (1910).

surface of the solution), was upon analysis of the precipitates from solutions with 0.01 g magnesium chloride or 0.01 g magnesium sulfate kept at a temperature of 283 K for 3 months. Identification of this dolomite took place with the microscope only, aided by the colouring method of Lemberg (1887,1888). In the precipitates from the bicarbonate solutions dolomite would have been formed. In this case Leitmeier (1910 A) even used dissolution into dilute hydrochloric acid to distinguish the dolomite rhombs from calcite and aragonite in the precipitate. But the dolomite rhombs were very small, and not even the use of oil immersion objectives on the microscope enabled unequivocal identification of its optical properties. Therefore Leitmeier (1910 A) expressed some doubts as to his claim on the formation of the mineral dolomite. The more so because Cornu (1907), who had conducted much the same experiments and who had claimed initially to have found dolomite, but later changed his mind and had stated, that aragonite had been formed (an opinion reached after Cornu had sent his samples to H. Vater, who had been able to observe only aragonite). At the same time Leitmeier (1910 A) was convinced, that the precipitates did not contain any magnesium carbonate trihydrate. In addition Leitmeier had observed tiny needles consisting of gypsum.[30] After analyzing the precipitates from the different retorts after a period of 3 months, Leitmeier (1910 A) left the solutions standing for another 3 months. Gradually the outdoor temperature rose (apparently Leitmeier had started his tests in the winter), and the solutions initially kept at 275 and 283 K reached higher temperatures. After 6 months titrations showed, that all of the dissolved calcium carbonate had disappeared from the solutions. In the series of retorts containing amounts of 0.05 respectively 0.1 g magnesium chloride or 0.05 respectively 0.1 g magnesium sulfate, dolomite formation had continued. More and more dolomite would form in these solutions as time went by.

From his laboratory experiments Leitmeier (1910 A) drew the conclusion, that dolomite would have been formed (much as in nature) by the reaction between pre-deposited calcium carbonate and magnesium salts in solution. This interaction would require considerable time at ambient temperature.[31] At the end of his 1910 paper Leitmeier announced "*Die Untersuchungen werden fortgesetzt*", and after 5 years of additional research Leitmeier published a second paper on the subject. But there Leitmeier (1916 A) expressed serious doubts, whether in his experiments of 1910 any dolomite had been formed at all. This doubt found its origin in two different observations: in the first place experiments by Mahler (1906) had shown, that the hot iron chloride solution of Lemberg's reagens not only attacks aragonite, but also calcite and dolomite. Consequently it could not be used as a reliable means to distinguish between calcium carbonate and dolomite. In the second place Leitmeier (1910 A) had not been able to measure the optical properties of his precipitates under the microscope. After duplicating his earlier tests Leitmeier (1916 A) was able to measure these optical properties, but he could not measure any properties typical of dolomite. In other words Leitmeier (1916 A) now doubted all of his earlier observations on dolomite formation at room temperature.

Despite the fact, that Leitmeier had renounced his own laboratory observations, I have tried to duplicate the experiments. To this end 10.0 g calcium carbonate[32] were dissolved in 10 dm^3 distilled water with the aid of excess carbon dioxide (industrial grade) bubbled through it. After completely dissolving the calcium carbonate, four different polyethylene bottles were each filled with 1 dm^3 of the calcium bicarbonate solution. To the first 0.5 g $MgCl_2.6\ H_2O$; to the second 1.0 g $MgCl_2.\ 6\ H_2O$; to the third 0.5 g $MgSO_4.7\ H_2O$; and to the fourth 1.0 g $MgSO_4.7\ H_2O$ were added. The four polyethylene bottles were not truly open; a plug of cotton wool kept dust (and insects) out. During three months the solutions were kept at room temperature, which varied slowly in day/night rhythm during the period from 291 to 296 K. After three months the solutions were filtered off, and the four different precipitates were dried

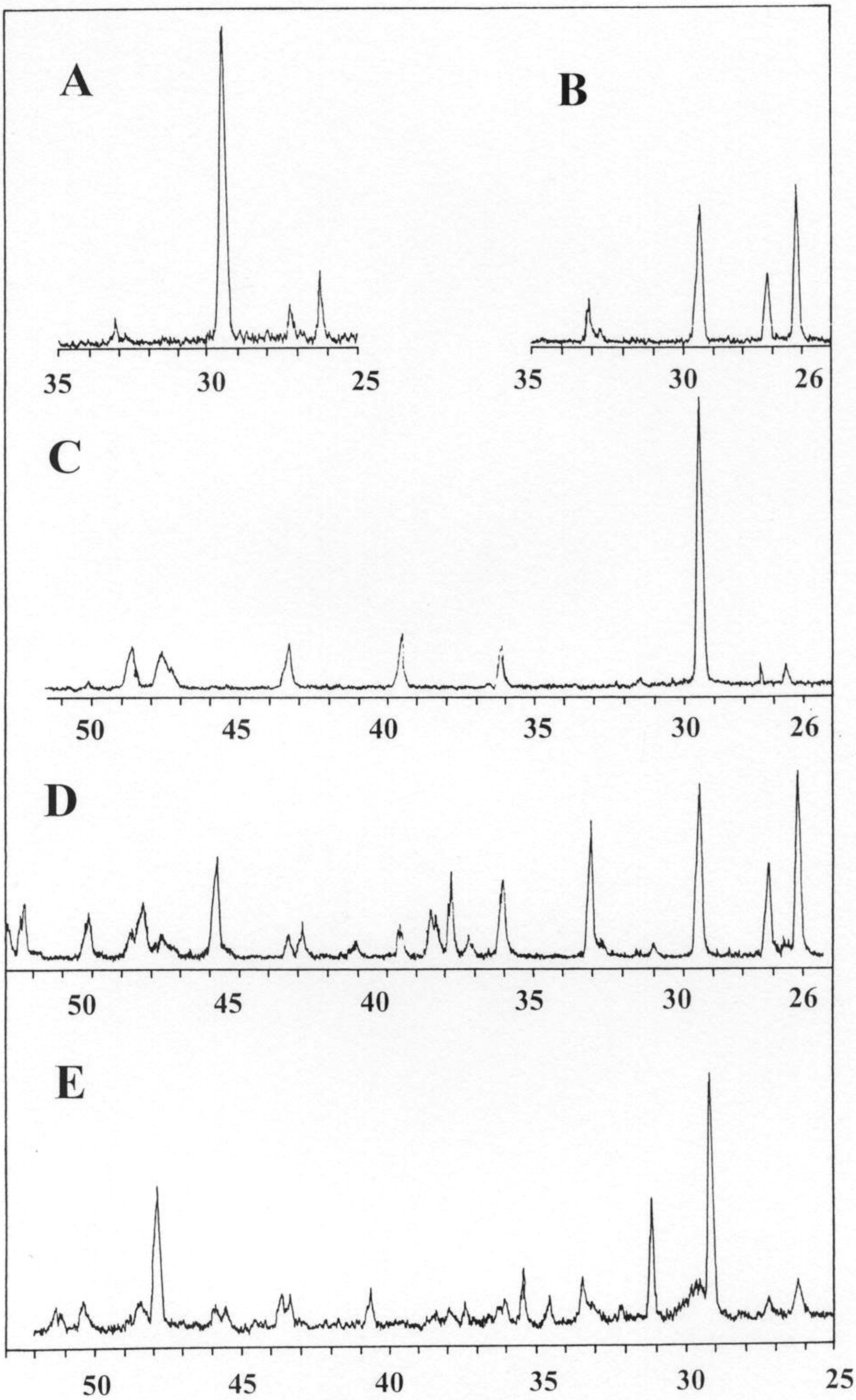

Fig.34 – Precipitates formed upon duplication of the experiments of Leitmeier (1910) (= A & B); of Lalou (1957) (= C & D); and Zeller et al. (1959) (= E).

at room temperature. X-Ray diffraction showed the formation of mainly a magnesium calcite with its main diffraction peak at 30.19 nm and a trace of aragonite in the first three solutions (Fig.33 A). Only in the calcium bicarbonate solution with 1.0 g magnesium sulfate a different assemblage had been formed: a magnesium calcite with its main diffraction peak at 30.27 nm along with a noticeable amount of aragonite (Fig.33 B).

After filtering off, the four different solutions were poured into the respective polyethylene bottles again (which had not been cleaned in between from adhering carbonates) and kept at room temperature for another period of three months. Room temperature during this time of the year fluctuated from 291 to 301 K. After filtering off and air drying the precipitates, the first solution was seen to have formed minor amounts of aragonite together with a magnesium calcite with its main diffraction peak at 30.28 nm (Fig.33 C). From the second solution a small amount of aragonite had precipitated along with magnesium calcite with a main diffraction peak at 30.29 nm (Fig.33 D). The third solution had given rise to somewhat less magnesium calcite (as compared to the first two samples), with a main peak at 30.34 nm, in combination with a comparably small amount of aragonite (Fig.34 A). The amount of the Mg-calcite formed from the fourth solution, seemed even less. It appeared almost equal to the amount of aragonite formed. The main diffraction peak of this last magnesium calcite was located at 30.29 nm (Fig.34 B).

EXPERIMENTS OF LALOU

Lalou (1957) described, how he had taken a sample of the euxinic muds from the bottom of the Mediterranean Sea in the Bay of Villefranche-sur-mer (Côte d'Azur), had added sea water and some glucose. After a few weeks a film floating the surface was noted, containing not only aragonite and calcite, but also some dolomite.[33] In more detail: Lalou had put about 1 kg of the black, H_2S-rich mud in an aquarium, added 3 to 4 dm^3 of normal sea water and 0.5 % glucose (15 to 20 g). After 3 days an iridescent film appeared on the liquid's surface. One day later the solution as a whole became turbid and emitted a "... strong smell of fermentation"; at about the same time, a vigorous production of gas bubbles took place. This production of gas ceased on approximately the eighth day of the experiment, and an ochre-colored film could be seen floating the surface. It was analyzed and found to consist of carbonate(s) and some iron. Subsequently the solution became dark-colored, virtually black. Numerous very small, black particles in suspension were seen to be responsible for that dark color. At the same time a strong smell of hydrogen sulfide emanated from the aquarium. At this stage a white, solid film of carbonates appeared on the solution's surface.

In a second experiment Lalou used 3 dm^3 of seawater, added the euxinic mud, and kept all other conditions the same. This test was different, in that Lalou removed the carbonate film every time it formed. The experiment, and the harvesting of the carbonates, was continued for a period of one month. Lalou checked in a blind test, that the addition of glucose was responsible for the development of the carbonate film. In an aquarium containing a quantity of the euxinic mud plus seawater, but without any glucose, no film of carbonates would develop. After applying X-ray diffraction to the material of the crusts formed, Lalou stated, that aragonite, calcite, and dolomite were present.

Lalou made no attempt to explain the formation of this dolomite ("The conditions of formation of the dolomite have not yet been established": Lalou, 1957, p.193). However Lalou stated, that the abundant production of CO_2 by "various bacteria", followed by the production of relatively large amounts of H_2S, would be instrumental. "This escape of H_2S leads to an increase of the pH value; whence the magnesium and calcium ions, free in a medium saturated with CO_2, give a formation of bicarbonates, then, at the water/air interface, where the CO_2 tension decreases, a formation of crystalline carbonates": Lalou (1957, p.191). Because he had measured pH, sulfate anion concentration, dissolved H_2S and the amounts of carbonates formed every day during his experiments, Lalou was able to conclude, that the carbonate started to form, with a few days delay, upon the disappearance of the sulfate anions from the solution. As soon as all sulfate had been reduced to H_2S, the process of carbonate deposition halted abruptly. Lalou was able to explain the origin of these carbonates: in one of his experiments daily measurements of Ca^{2+} and Mg^{2+} were made. There it was found, that during the first few days after the start of the experiment (the time of abundant CO_2 production), the Ca^{2+} concentration increased sharply (from about 0.44 mg/dm^3 to 0.85 mg/dm^3). Such high concentrations of calcium indicated, that dissolution from the (carbonate-rich) mud must have taken place.

A fine grained carbonate sand from the Mediterranean Sea[34] was used by me in an attempt to duplicate the tests of Lalou (1957). To 1 dm^3 of artificial sea water (according to the recipe of Lyman & Fleming, 1940)[35] 50 g of this carbonate sand were added, after which 5 g glucose and a small quantity of "black mud" from a Dutch tidal flat were added. After some 4 months a white, friable film was seen floating on the seawater in its glass beaker. After removing the film, washing it several times with distilled water and drying it at room temperature, X-ray diffraction showed it to consist mainly of a magnesium calcite with its main diffraction peak at 30.2 nm (Fig.34 C). The beaker was left to itself for another 2 months at room temperature, when the second carbonate film was removed, washed and analyzed. This time not only aragonite and a magnesium calcite with its main peak at 29.9 nm, but also a carbonate mineral with its major diffraction peak at 28.8 nm had formed (Fig.34 D).

EXPERIMENTS OF ZELLER, SAUNDERS & SIEGEL

The paper by Zeller et al. (1959), claiming the low-temperature synthesis of a "dolomite-like carbonate", is so short, that it will be reprinted here in its entirety: "Carbonate materials yielding X-ray-diffraction patterns characteristic of the dolomite-type carbonates have been precipitated from solutions in the laboratory. This dolomite-type material has been produced at standard pressure and at temperatures and digestion periods that are much less than those previously reported in the literature. Starting materials included calcium nitrate, magnesium sulfate, and sodium carbonate. The maximum concentration of each was 1.5 M. X-Ray patterns made after substitution of other salts (for example, magnesium chloride for magnesium sulfate) showed no reflections from dolomite-type material. Results of experiments, including those in which the order of addition of reagents was changed, indicate that the presence of sulfates is essential. The rate of reaction that affects the formation of the dolomitic precipitate may be controlled by the insolubility of certain of the reactants. If the sulfates or the rate of reaction as controlled by the insolubility relations are important to the precipitation of "primary" dolomite, the genesis of dolomite, both in evaporitic and other environments, may be more clearly explained."

Although the paper by Zeller, Saunders & Siegel is not particularly rich in its experimental details, an attempt has been made to duplicate the test. In 100 cm^3 distilled water 35.4 g $Ca(NO_3)_2.4\ H_2O$ (= 1.5 mol/dm^3) were dissolved. To another 100 cm^3 of distilled water 36.9 g $MgSO_4.7\ H_2O$ (= 1.5 mol/dm^3) were added. In a third small glass beaker 100 cm^3 water were mixed with 15.9 g Na_2CO_3 anhydr. (= 1.5 mol/dm^3). After all three salts had dissolved

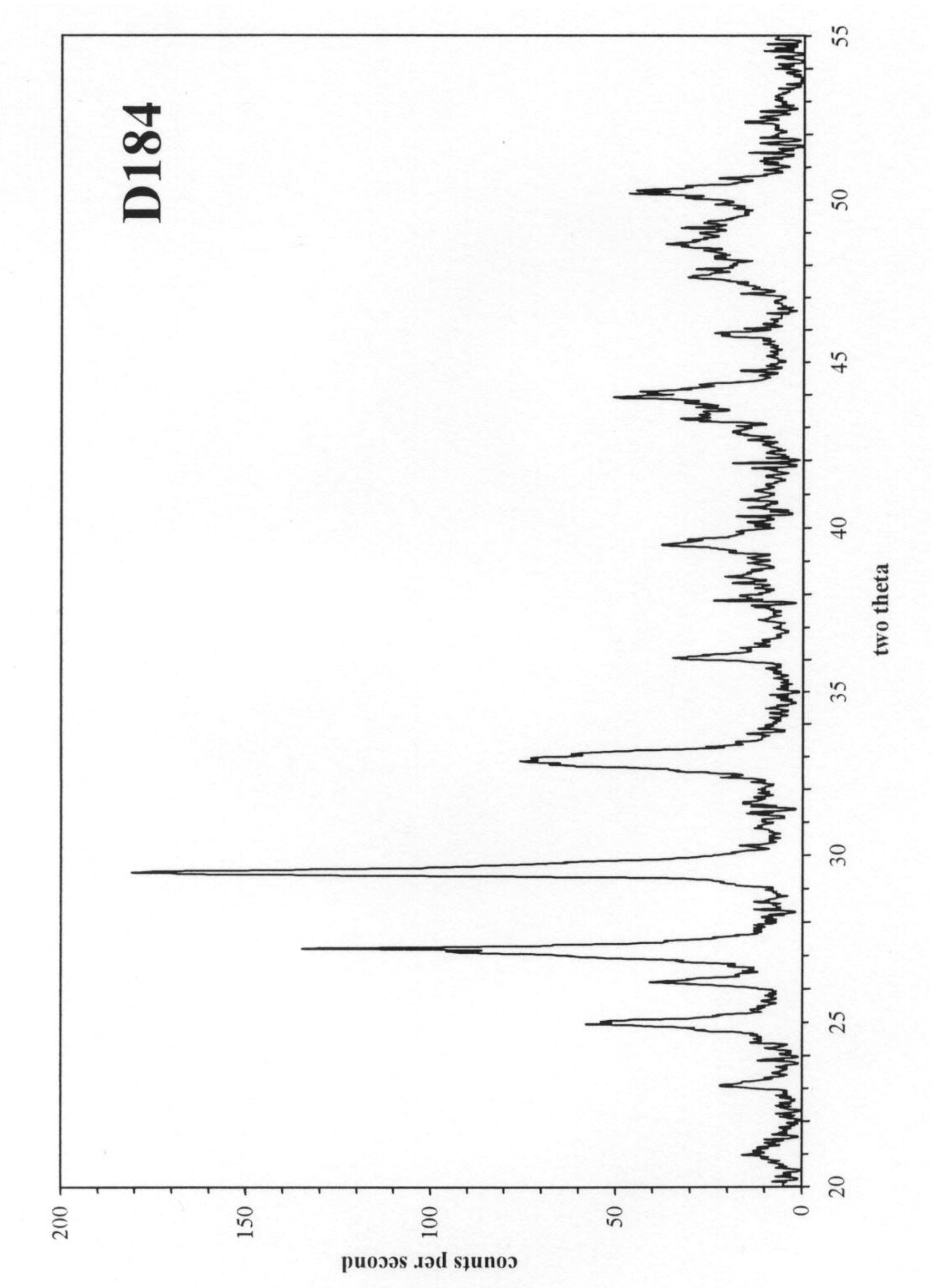

Fig.35 A – Precipitate formed upon duplication of the experiment of Zeller et al. (1959).

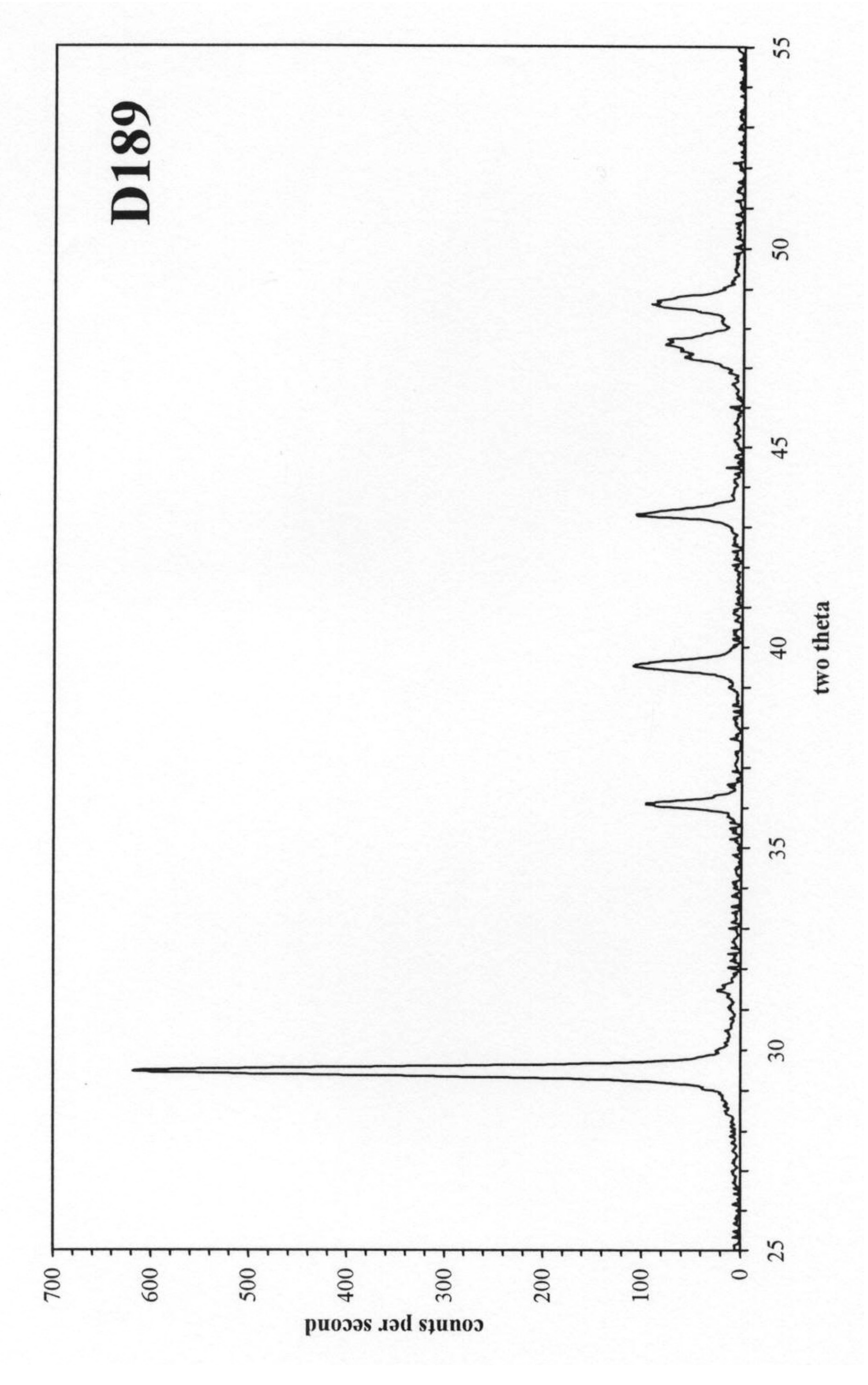

Fig.35 B – Precipitate obtained upon duplication of the experiment of Zeller et al. (1959).

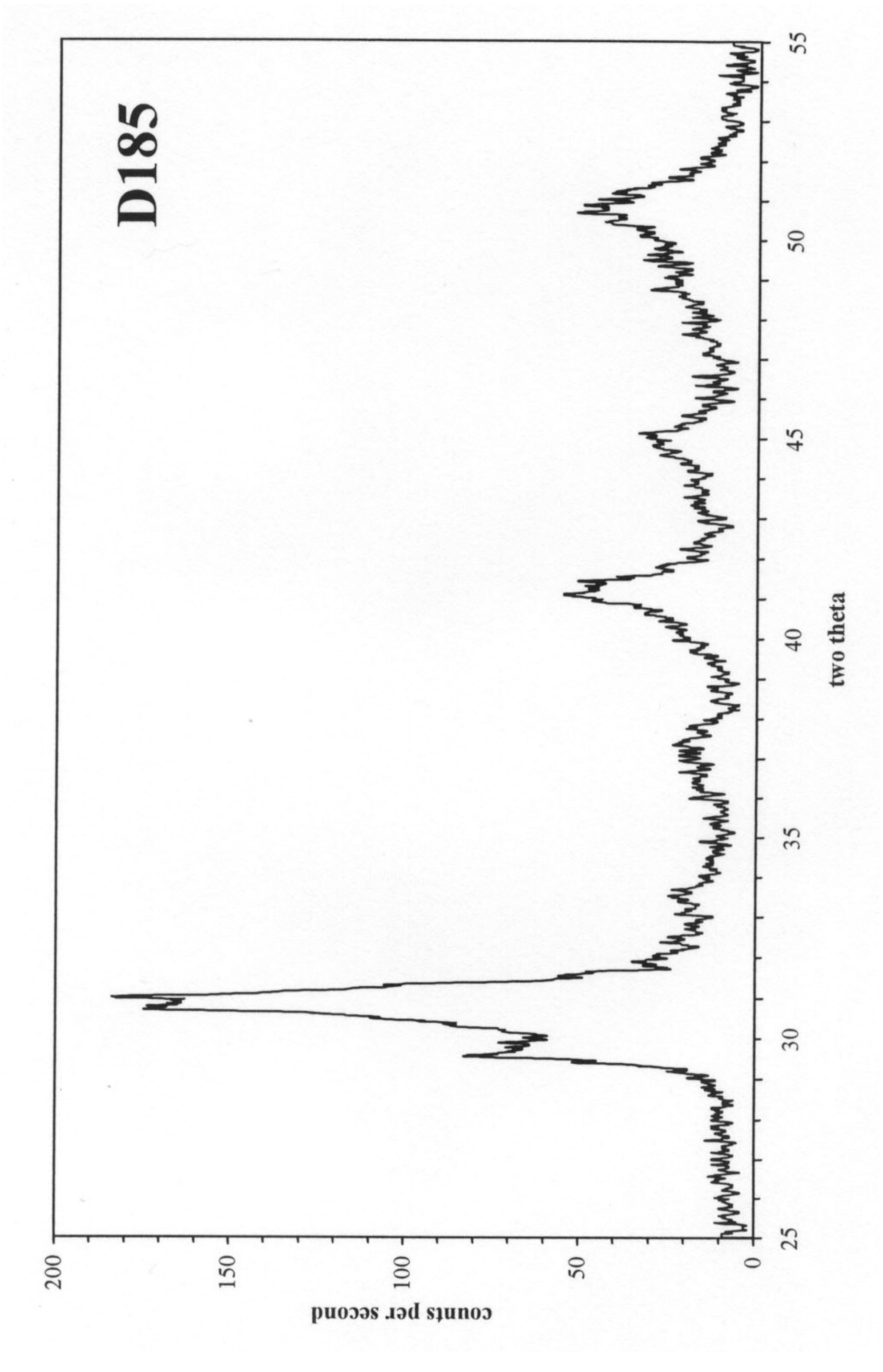

Fig.35 C – Precipitate obtained upon duplication of the experiment of Siegel (1961).

completely (taking quite some time in the case of the anhydrous sodium carbonate), all three solutions were simultaneously poured into a large glass beaker. Immediately a whitish, more or less opalescent and turbid sort of gel formed. No stirring was applied; the beaker was left undisturbed for 24 hours. After that period no gel remained, instead a white precipitate had settled on the bottom of the beaker. After filtering off, washing the contents of the filter with about 1 dm^3 of distilled water, and drying the residue at room temperature, X-ray diffraction was performed. A number of random samples all showed the presence of gypsum, along with a trace of aragonite (Fig.34 E).

Because Zeller et al. (1959) had warned their readers, that the use of magnesium *chloride* instead of magnesium *sulfate* did not lead to the low-temperature formation of dolomite, their experiment has been duplicated by me, using magnesium chloride. This test was identical to the one described above, with the exception that here 30.5 g $MgCl_2.6\ H_2O$ were used instead of magnesium sulfate. After adding the three different solutions to each other (at 290 K), a thick, white gelatinous mass formed. Only slowly a precipitate formed. After 24 hours the precipitate was filtered off, washed with distilled water (in total some 6 dm^3 water had to be used) and dried at room temperature. Subsequent X-ray diffraction of the fine-grained powder showed it to consist of aragonite together with a magnesium calcite with its main diffraction peak at 30.29 nm (Fig.35 A).

Siegel (1961) gave some additional information concerning the low-temperature formation of "proto-dolomite". The most important factor controlling the precipitation of dolomite would be the pH: optimum conditions required pH = 9.7 at 298 K. Higher temperatures and increased concentrations of the ingredients (calcium nitrate, magnesium sulfate and sodium carbonate) were found to favor ordering as well as crystallinity of the dolomite formed. The presence of the sulfate ion was essential: "The dominant mineral phase present in the precipitates was disordered dolomite, or proto-dolomite of Graf and Goldsmith (1956). Always associated with this phase was some form of calcium sulfate; γ-$CaSO_4$ was the form most commonly identified in the diffraction traces, but α-$CaSO_4.½\ H_2O$ may also have been present" (Siegel, 1961, p.141). Best results were attained by Siegel (1961), when conducting his experiments at a temperature of 373 K. But even when performing the tests at 298 K "protodolomite" would be formed, especially when using a 1 mol/dm^3 solution of calcium nitrate mixed with a 1 mol/dm^3 solution of magnesium sulfate, and adding a 2 mol/dm^3 solution of sodium carbonate.

This particular experiment, although not very different from that described by Zeller et al. (1959), was duplicated too. In 100 ml distilled water 23.6 g $Ca(NO_3)_2.4\ H_2O$ were dissolved; in another 100 ml of distilled water 24.6 g of $MgSO_4.7\ H_2O$. In 100 ml of boiling hot distilled water 21.2 g Na_2CO_3 were dissolved; after which the solution was left to cool down to room temperature (of 300 K). The calcium nitrate solution was poured into a large glass beaker and stirred by way of a magnetic stirrer. Immediately after that the magnesium sulfate solution together with the sodium carbonate solution were poured into the beaker. The pH at this moment was measured to be 8.70. As stirring was continued, a very thick, pasty mass formed, so thick that the stirring action came to a halt. The electrode of a pH meter measured at this moment pH = 8.94. The still very thick suspension was left standing for 2 hours. The precipitate was first diluted with distilled water, and only then filtered off. Some 4 dm^3 water were used to wash the precipitate on a paper filter. The filter was dried at room temperature. X-Ray diffraction of showed it to consist entirely of a magnesium calcite with its main diffraction peak at 29.44 nm (Fig.35 B).

Because Siegel (1961) had obtained his best results when conducting the experiment at a temperature of 373 K, the experiment was repeated with boiling hot solutions. All three solutions (of calcium nitrate, magnesium sulfate and sodium carbonate) were heated to 373 K,

Solutions used contained:

1/6 mol $CaCl_2.2\ H_2O$ = 24.5 g/dm^3

1/6 mol $MgCl_2.6\ H_2O$ = 33.8 g/dm^3

½ mol Na_2CO_3 anhydrous = 53.0 g/dm^3

½ mol $NaHCO_3$ = 42.0 g/dm^3

Individual mixtures contained:

A. **Mg/Ca = 3**
220 ml Na_2CO3 + $NaHCO_3$ solution
150 ml $MgCl_2$ solution
50 ml $CaCl_2$ solution

B. **Mg/Ca = 7.5**
150 ml Na_2CO_3 + $NaHCO_3$ solution
150 ml $MgCl_2$ solution
20 ml $CaCl_2$ solution

C. **Mg/Ca = 15**
150 ml Na_2CO_3 + $NaHCO_3$ solution
50 ml $MgCl_2$ solution
10 ml $CaCl_2$ solution

D. **Mg/Ca = 30**
150 ml Na_2CO_3 + $NaHCO_3$ solution
150 ml $MgCl_2$ solution
5 ml $CaCl_2$ solution

E. **Mg/Ca = 50**
250 ml Na_2CO_3 + $NaHCO_3$ solution
250 ml $MgCl_2$ solution
5 ml $CaCl_2$ solution

Table VIII – Concentrations and compositions used in duplicating the experiments of Erenburg(1961).

material obtained		standard		mineral
d(nm)	I/I_o	d(nm)	I/I_o	
81.5	52	80.8	50	N
65.9	10	-	-	
63.8	10	64.0	40	MH
61.9	10	-	-	
58.3	47	57.9	100	MH
49.7	22	49.6	30	N
44.3	12	44.6	17	MH
41.9	25	41.86	30	MH
40.6	15	40.4	2	N
35.2	12	34.8	20	N
34.00	33	33.17	30	MH
32.95	22	32.10	16	MH
32.25	27	32.07	35	N
30.85	5	30.88	10	MH
29.21	35	28.99	80	MH
28.75	40	28.63	30	N
27.09	90	26.97	75	N
24.90	100	24.73	100	N
23.74	35	23.71	30	N
23.62	33	23.50	14	MH
23.42	30	22.98	35	MH
22.07	20	23.06	16	N
21.99	17	22.12	16	N
21.46	30	21.42	18	N
21.20	40	21.11	55	N
20.25	20	20.19	25	N
19.76	30	19.94	25	MH
19.70	30	19.61	30	N
18.71	17	18.71	16	N
18.24	15	18.22	16	N
18.16	15	-	-	
17.54	30	17.50	6	N
17.31	17	-	-	
16.53	7	16.49	6	N
16.11	25	16.26	16	N
15.59	10	-	-	

Table IX - X-Ray data of precipitate obtained after duplicating one of Erenburg's(1961) experiments (MH = magnesium hydroxide carbonate; N = nesquehonite).

and kept at that temperature. Stirring took place on a magnetic stirrer combined with an electric heating element. After filtering off, washing with 500 ml distilled water and drying the precipitate at room temperature, an X-ray diffractogram was made. The precipitate formed consisted of a magnesium calcite with its main diffraction peak at 30.2 nm together with a convincing amount of a magnesium calcite with its main diffraction at 28.8 nm (Fig.35 C). No form of calcium sulfate was detected in X-ray diffraction; but the possibility cannot be excluded, that it had formed and was subsequently washed out of the precipitate.[36]

ERENBURG'S EXPERIMENTS

Not as much because Erenburg's (1961) publication appeared in the Russian language (an English translation of the *Zhurnal Struktornoi Khimii* can be found in many libraries), but mainly because of the lack of detail in his description of the procedure used, the results obtained by Erenburg are difficult to evaluate. Nevertheless an attempt was made to duplicate several of Erenburg's experiments. The abstract of the paper by Erenburg (1961) stated, that "... a series of rhombohedral mixed calcium-magnesium carbonates, containing from 17 to 50 Molar % $MgCO_3$, which do not change during prolonged keeping or when heated to 573 K, was prepared by precipitation from solutions at temperatures below 373 K under atmospheric pressure". The X-ray analyses made of these mixed Mg/Ca carbonates did not, in Erenburg's explanation, allow for the conclusion, that the crystals consisted of interlayer lattices, but rather "substitutional solid solutions" would have been formed.

The mixed Mg/Ca carbonates would form upon the slow addition of a mixed Mg- and Ca-chloride solution to a solution containing sodium carbonate as well as sodium bicarbonate. "In most of the experiments the original mixtures of molar $CaCl_2$ and $MgCl_2$ solutions (in the required proportions) were used in six-fold dilution, and mixtures (1 : 1) of molar Na_2CO_3 and $NaHCO_3$ solutions were used in two-fold dilution; the temperature of the mixture during precipitation was 323 ± 3 K" (Erenburg, 1961, p.168). Further instructions read: "The precipitates prepared as described were washed with distilled water and alcohol, filtered off with the aid of a water-jet pump, *heated gently (523 K)* and investigated by chemical and X-ray methods" (my italics). The instruction to heat to 523 K was not carried out by me: the risk of phase transformations during heating to such a high temperature is too great. Otherwise the instructions given by Erenburg (1961) were meticulously repeated. Five different mixtures were used, varying in Mg/Ca ratio from 3 to 50 (Table VIII). First the magnesium- and calcium chloride solutions were mixed and then slowly added to the solution containing both sodium carbonate and sodium bicarbonate. The mixture as such was heated to a temperature between 328 and 338 K, and was stirred for 1 hour. After that time the precipitate formed was filtered off, washed with demineralized water and dried at room temperature. In all these tests only two compounds were found: northupite ($Na_2CO_3.MgCO_3.NaCl$) and magnesium hydroxide carbonate (see Table IX). In one instance the mixed solution was left standing undisturbed for 10 days at room temperature: in that case a small amount of trona ($NaHCO_3.Na_2CO_3.2\ H_2O$) could be observed together with northupite (Fig.36 A).

The conclusion must be drawn, that most likely the "mixed Mg/Ca carbonates" described by Erenburg (1961) must have formed during the heating phase at the end of each of his experiments. In numerous experiments since those described by Hoppe-Seyler (1875) it has been shown, that the formation of dolomite can take place at temperatures around 523 K.[37] The primary phases formed, must have been northupite and magnesium hydroxide carbonate.

experiment number	**molality ($MgCl_2$ + $CaCl_2$)**	**Mg/Ca ratio**	**molality Na_2CO_3 – solution**	**pH**	**precipitate**
4	2.21 mol	5.66	1 mol	-	unknown
5	2.21	5.66	1	7.9	CH
7	2.00	5.0	1	7.3	unknown, CH
8	1.91	4.9	1	7.9	CH
14	2.00	5.9	1	7.9	CH
15	2.00	4.56	1	7.8	unknown, CH
9	1.91	4.9	0.25*	8.1	CH
2	2.12	1.14	1	-	C
6	2.00	1.0	1	6.2	C
1	2.12	1.14	0.05	-	C
3	2.21	5.56	0.05	-	A
13	2.00	5.0	0.05	6.9	A + C
10	2.00	0	0.25*	6.4	C
11	2.00	0	0.25*	6.7	C
12	2.00	0	1	6.9	C

Table X - Solutions used and precipitates obtained by Van Tassel (1962) in his attempts to duplicate the experiment of Budzinski (1961) (A = aragonite; C = calcite; CH = calcium carbonate monohydrate).

The possibility that the diffractograms of a mixture of northupite and magnesium hydroxide carbonate was confused with that of a "mixed Mg/Ca carbonate" is to be excluded, because the diffractograms are so very different.[38]

BUDZINSKI'S EXPERIMENT

In volume 28 B (Calcium) of *Gmelin's Handbuch* (Gmelin Institut, 1961) an enthusiastic account of the allegedly successful low-temperature synthesis of dolomite as performed by Budzinski (1961) can be found. First reading this review in *Gmelin's Handbuch* and then consulting Budzinski's paper as it appeared in the *Fortschritte der Mineralogie*, volume 39, must lead to some disappointment. After reading the paper the impression remains, that the claim of Budzinski will be difficult to investigate, since little or no detailed description of the successful experiment can be found there. The paper is devoted mainly to a review of various aspects of the solubility behavior of dolomite (4 out of a total of 6 pages are devoted to this matter), and Budzinski (1961) elaborated on the important contributions in this respect by the Russian investigator Janatjewa (Yanateva). Suddenly quite near the end of his paper (as if in an afterthought), Budzinski relates his successful low-temperature synthesis of dolomite. In a few sentences the whole experiment is summarized: a highly concentrated $(Mg,Ca)Cl_2$ solution, with a high Mg/Ca ratio, was mixed sodium carbonate. After a few days the gel that had formed initially, changed into a crystalline substance. Details of the procedure cannot be found in the paper.[39] No indication whatever of the temperature prevailing during the test, nor any indication as to the concentration of the sodium carbonate solution used, can be found, even though these two factors seem essential.

It is of some significance to note here, that Budzinski's experiment closely resembles that of Balló (1913), who had mixed a calcium-magnesium chloride solution with a concentrated solution of sodium carbonate (plus sodium chloride). Balló (1913) had not obtained any dolomite: gaylussite ($CaCO_3.Na_2CO_3.5\ H_2O$) had formed initially, but it had gradually been transformed into magnesium calcite plus nesquehonite.

Van Tassel (1962) undertook to duplicate the test described by Budzinski (1961). After having remarked, that in comparable tests with Mg/Ca chloride solutions mixed with alkali solutions Halla (1937) and Brooks et al. (1950) had obtained only calcium carbonate monohydrate, Van Tassel described his systematic investigation. Probably because of the lack of data on the exact procedure used by Budzinski (1961), Van Tassel performed some 15 different tests. In those experiments the molality of the mixed magnesium-calcium chloride solution was varied from test to test from 1.91 to 2.21 . The molality of the sodium carbonate solution ranged from 0.05 to 1.0 (in three experiments sodium carbonate mixed with 0.5 mol NaCl was used). The Mg/Ca ratio's of the chloride solutions varied between 0 and 5.9 (see Table X). The minerals formed were either calcium carbonate monohydrate, calcite or aragonite (in one instance the substance formed could not be identified; in two cases an unknown phase developed initially, only to change gradually into the monohydrate of $CaCO_3$). In the very test that seems to resemble the description of Budzinski (1961) most closely (i.e., test 7 of Van Tassel), a solution of 2 mol ($MgCl_2$ + $CaCl_2$) (with Mg/Ca = 5) was mixed with a 1 mol Na_2CO_3 solution. Although the initial phase could not be identified, it changed after a few days into monohydrocalcite (Van Tassel, 1962).

Horn (1969) also repeated the experiment of Budzinski (1961), by way of adding a concentrated Na_2CO_3 solution to one of 2 mol $(Mg,Ca)Cl_2$ (with Mg/Ca = 5). The precipitate formed was not dolomite according to Horn. In X-ray diffraction, in wet chemical analysis, nor

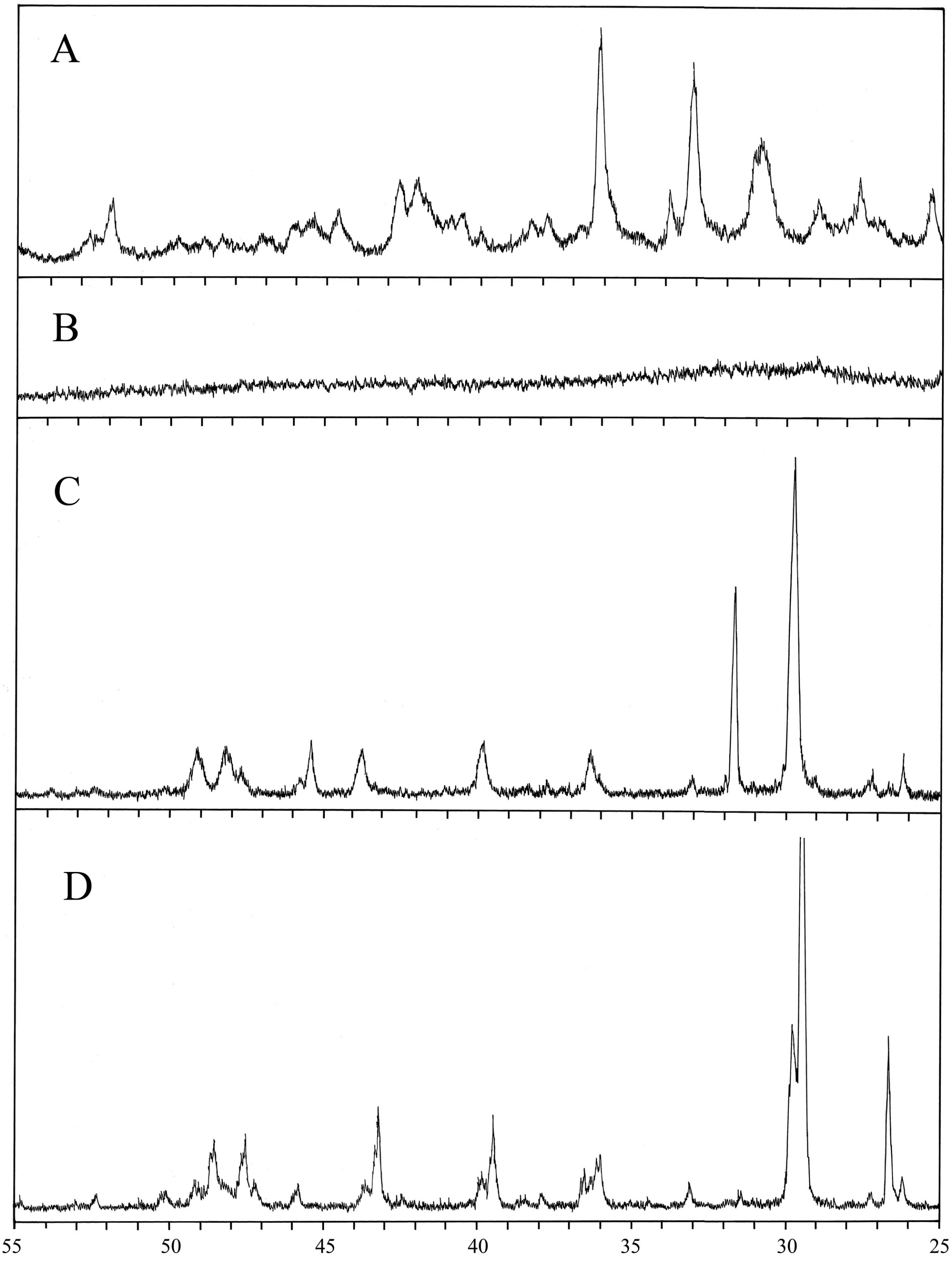

Fig.36 – Precipitates formed upon duplication of the experiments of Erenburg (1961) (= A); of Budzinski (1961) (= B), of Oppenheimer & Master (1965) (= D) and X-ray of carbonates in algal mat from Miami (= C).

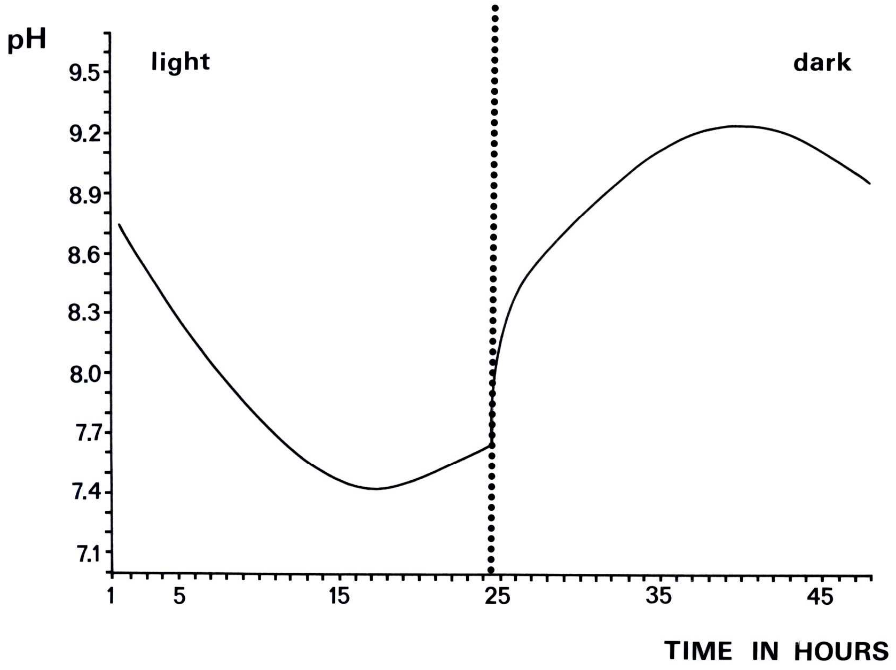

Fig.37 – Periodical change in pH in aquariums containing seawater, carbonate sediment and algal mat biotope: fluctuation in pH caused by the alternation between photosynthesis and respiration of the algae. The pH of control aquariums made sterile through the addition of mercuric chloride, remained constant at 7.8 (after Oppenheimer & Master, 1965).

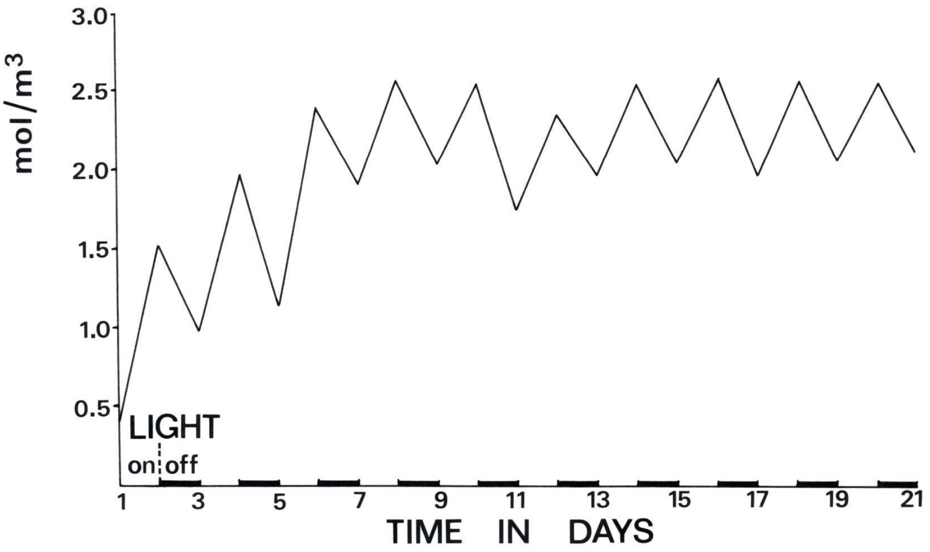

Fig.38 – Fluctuations in alkalinity of seawater aquariums containing carbonate sediment and algal mats. Much like the fluctuations in pH the periodical changes in alkalinity were brought about by the alternation between photosynthesis and respiration of the algae. Alkalinity of controls kept in the dark remained constant at 2 mol/m^3 (after Oppenheimer & Master, 1965).

in differential thermal analysis (DTA) any trace of dolomite was found. Perhaps somewhat superfluous I have tried to duplicate Budzinski's experiment as well. In 100 ml demineralized water 33.9 g $MgCl_2.6\ H_2O$ (= 1.67 mol/dm^3) and 4.9 g $CaCl_2.2\ H_2O$ (= 0.33 mol/dm^3) (Mg/Ca = 5) were dissolved. Separately 10.6 g Na_2CO_3 anhydr. was dissolved in 100 ml water. Immediately after pouring the two different solutions together, a gel formed. This gel was left standing, without stirring, for 24 hours. After that the precipitate formed was filtered off, washed with demineralized water, and dried at room temperature. X-Ray diffraction showed no diffraction peaks whatsoever: the precipitate was X-ray amorphous (Fig.36 B). This observation confirms the result of test No.7 by Van Tassel (1962), even though the described secondary change into $CaCO_3.H_2O$ could not be observed (because the precipitate had been removed from the solution).

EXPERIMENTS BY OPPENHEIMER & MASTER

The experiments of Oppenheimer & Master (1963, 1965) essentially consist of the cultivation of pieces of an algal mat on top of a small quantity of calcareous sand. Continuous measurement of pH and Eh revealed marked changes, coinciding with the artificially introduced alternating phases of illumination and darkness. After one month of laboratory cultivation small amounts of dolomite were detected in the carbonate sediment. No dolomite formation was found in sterile control tests; no dolomite had been present in the carbonate sediment used in the experiments.

Details of the experiments have been published by Oppenheimer & Master (1965). To 1 dm^3 of artificial sea water (prepared according to the recipe of Lyman & Fleming, 1940) 1.0 g $NaNO_3$ and 50 ml of soil extract from a Florida mangrove peat were added. The solution was poured over 50 g of calcareous sand; this sand consists mainly of fine grained quartz particles of about 100 micrometer diameter, but it contained also some 7 % of calcareous fragments made of magnesium calcite. Pieces of algal mats were collected from an exposed tidal flat near the Institute of Marine Science, Miami (USA). Adhering sediment was removed by settling. The organisms involved were predominantly blue-green algae (*Oscillatoria* sp.) in combination with other microorganisms, such as algal flagellates, bacteria and fungi. In addition protozoans and even some metazoans such as nematodes were found. The sediment mixed with the artificial seawater was poured into a small plastic aquarium with a clear plastic lid. After settling of the sediment, pieces of the algal mat were added. Sterile controls were made with the same culturing medium and the same carbonate sediment, but with an addition of 0.5 % mercuric chloride (a strong poison for all microbial growth). All aquariums were then exposed to programmed light and dark periods of 24 hours duration in a laboratory room, where only artificial light existed. The 24-hour phases of dark and light were maintained during 30 days. Temperature of the water in the aquariums was a constant 297 K. Little or no evaporation could take place because of the plastic lids.

Continuous measurement of pH revealed distinct fluctuations: the pH changed from 7.4 (during the dark phases) to 9.2 (when the light was switched on) (Fig.37). A comparable fluctuation took place in alkalinity measurements: total alkalinity changed from 1.7 millimol during the periods of darkness to 2.5 millimol during illumination phases (Fig.38). Oppenheimer & Master (1965) were able to calculate, that approximately 0.05 g of $CaCO_3$ had been dissolved in each of the aquariums subjected to dark/light alternations. No changes in pH or in alkalinity were measured to take place in the sterile controls: the pH of the artificial sea water in those aquariums remained at a constant value of 7.8 , whether in the dark or in the light.

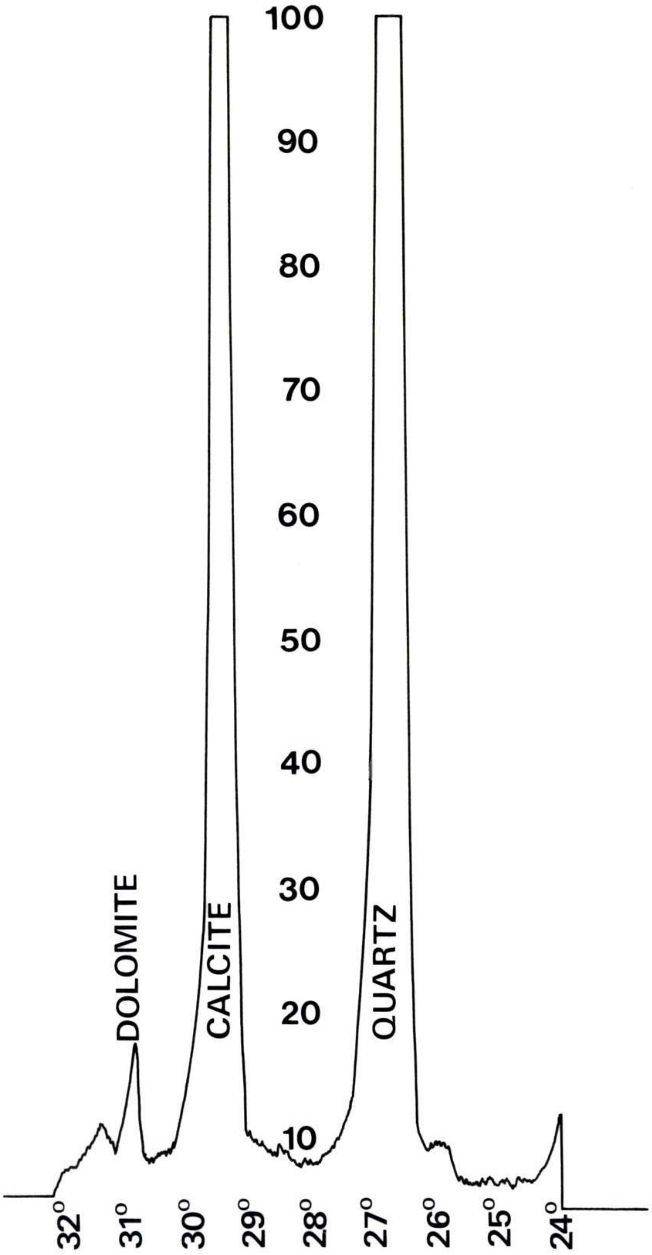

Fig.39 – X-Ray diffractogram (Cu-Kά radiation) as published by Oppenheimer & Master (1965) in evidence of their claim, that dolomite had been formed in the aquariums subject to fluctuations in pH and alkalinity.

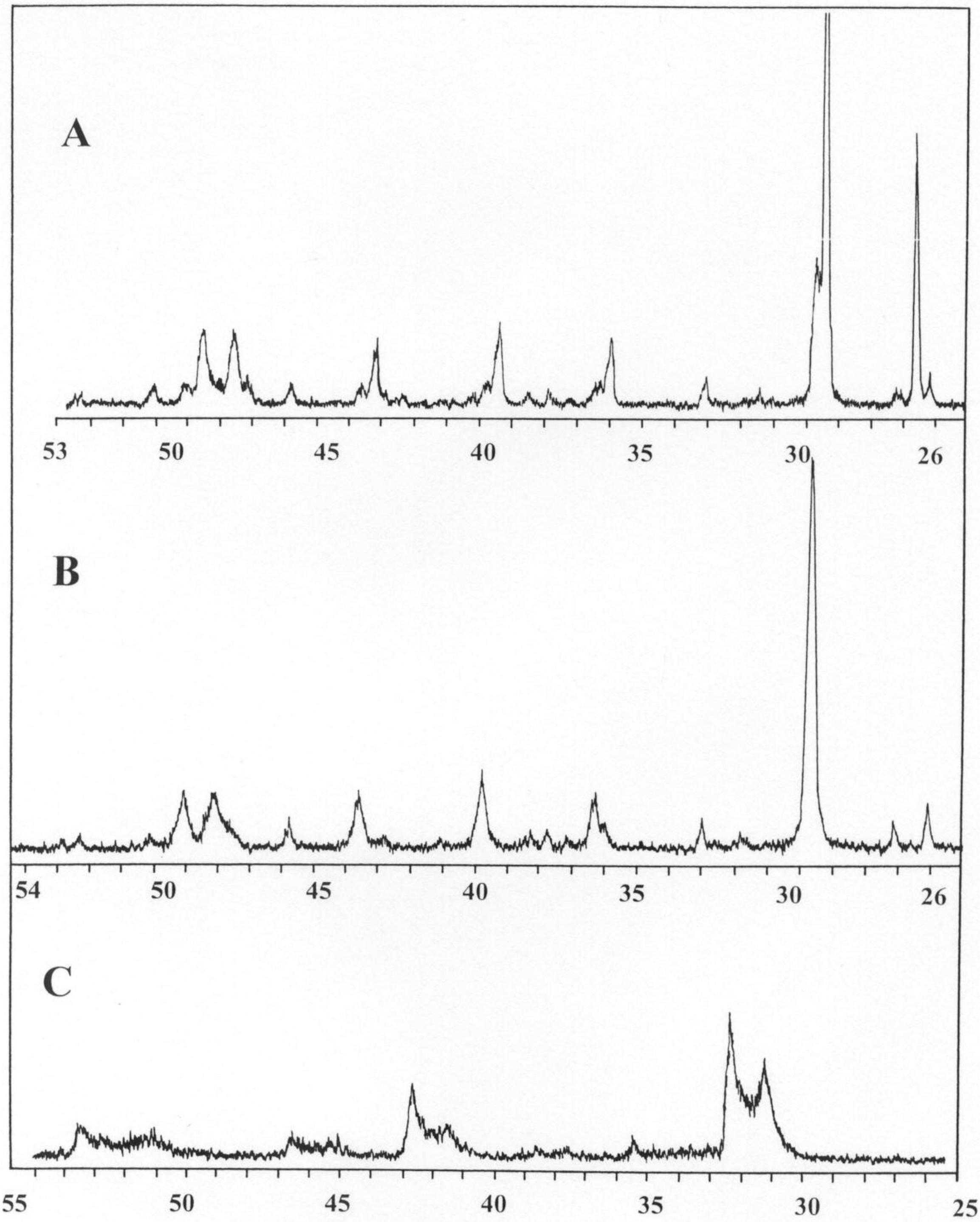

Fig.40 – Precipitates formed upon duplication of the experiments by Oppenheimer & Master (1965) (= A & B) and Liebermann (1967) (= C).

After 30 days sediment samples were taken and X-rayed. In the sediment from the aquariums subjected to alternations between light and dark phases, small amounts of dolomite were found (Fig.39). No dolomite whatever could be detected in the sediment from the sterile control aquariums.

Duplication of the experiments by Oppenheimer & Master became possible only after receiving samples of algal mats, mangrove peat and pore water samples from mangrove peat collected in the Miami area.[40] In the duplication test (D-145) artificial sea water according to Lyman & Fleming (1940) was used. To every dm^3 of this artificial sea water 50 cm^3 soil extract from a Florida mangrove peat (on the basis of sea water), 1.0 g sodium nitrate, 0.01 g $FePO_4$ and 0.1 g peptone[41] were added. Three clear plastic aquariums, each measuring 15 x 20 cm and about 5.5 cm high, were filled with 1 dm^3 of the thus prepared medium. To two aquariums 50 g each of carbonate sand from the Mediterranean Sea near Bandol[34] were added; in the third the carbonate sand was used, that had been associated with the algal mat fragments from the Miami area (crushed and sieved to measure between 250 and 125 micrometer) (A diffractogram of the latter sediment sample, taken before the start of the experiment, is reproduced here as Fig.36 C). In each of the three aquariums a small (glass-tube enclosed) heating element of 15 Watt was submerged. A variable transformer was used to attain a constant temperature in the aquarium of 298 K. Each aquarium was overlain by a glass plate, so that little or no evaporation could occur. All three aquariums were placed at about 20 cm below two medium sized fluorescent lamps (20 Watt each). The TL lamps were switched by a timer in such a way, that an alternation between light and dark in a 12-hour rhythm resulted.

After only one week it could be seen, that the algae had formed a coherent and even rubber-like layer, incorporating much of the carbonate sediment. A number of large bubbles under this layer indicated an intense production of gas. No smells of hydrogen sulfide or of ammonia could be detected, so perhaps oxygen was accumulating. After two months the experiment was stopped. The heating elements were removed, the seawater was carefully decanted, and the algal layer together with most of the carbonate sediment was removed from the aquariums. In two instances the sea water-sand mixture was transferred into large glass beakers, and quantities of distilled water were added. After thorough stirring, followed by a few minutes of settling, the supernatant was siphoned off. The same procedure was repeated, and the suspension was allowed to settle for 48 hours. After which most of the water was siphoned off and the remainder of the suspension dried at a temperature of 303 K. The carbonate sediment from the third aquarium was filtered off through a filter paper, and washed with 2 dm^3 distilled water. In this case too forced desiccation under a heat lamp at 303 K was used. All three samples were then sieved on a 125 micrometer sieve; the finest fraction was used in X-ray diffraction. In the two aquariums with carbonate sediment from the Mediterranean Sea mainly pure calcite with smaller amounts of a magnesium calcite with its main peak at 30.0 nm, were found (Figs.36 D and 40 A). The sample from the aquarium with the Miami carbonate sediment was different: it consisted mainly of magnesium calcite (main diffraction peak at 30.0 nm) with minor amounts of aragonite (Fig.40 B). [42,43]

LIEBERMANN'S EXPERIMENTS

At the outset of his paper Liebermann (1967) outlined the three basic assumptions, he had made in order to deal with the dolomite problem. In the first place the crystallization of dolomite could take place only from a true ionic solution. In this respect the often quoted

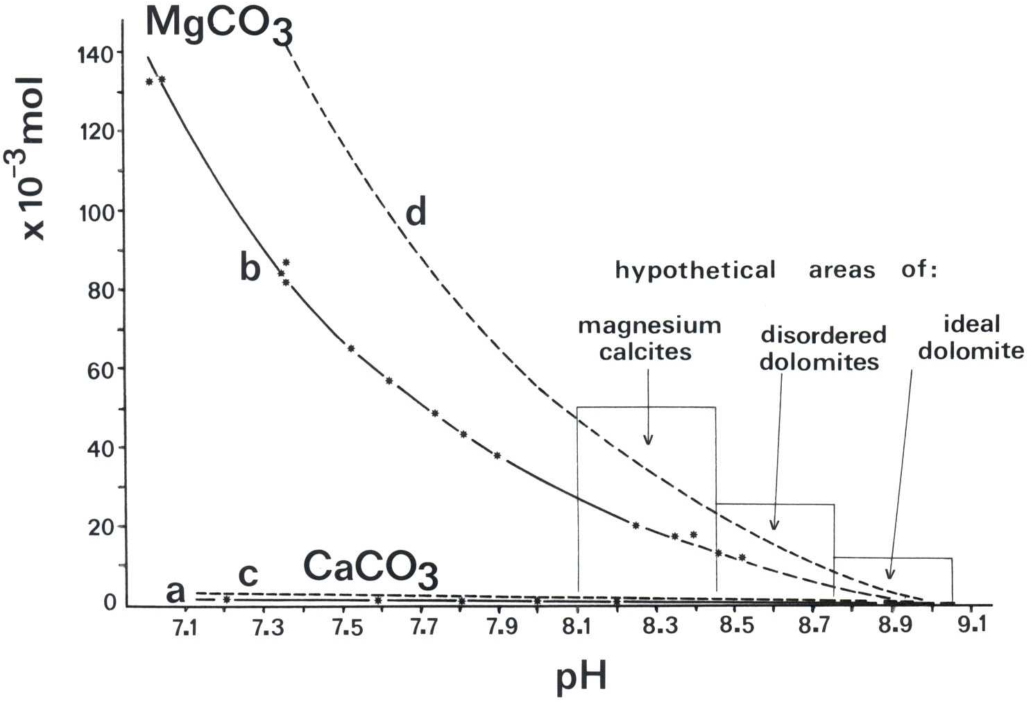

Fig.41 – Solubility curves of calcium carbonate (a) and magnesium carbonate trihydrate (b) in sea water at 25 °C, and hypothetical solubility curves for calcium carbonate (c) and magnesium carbonate trihydrate (d) in hypersaline water of 4 to 6 times the salinity of sea water, as a function of pH (after Liebermann, 1967).

"dolomitization reaction":

$$2\ CaCO_3 + Mg^{2+} \rightarrow CaCO_3.MgCO_3 + Ca^{2+} \qquad \text{(eq. 31)}$$

could not be correct. Liebermann's interpretation was, that dolomite formation would require magnesium in solution in two different forms: as magnesium sulfate as well as in the form of magnesium chloride. Two different reactions would take place. In the first place:

$$2\ Ca(HCO_3)_2 + MgSO_4 \rightarrow CaCO_3.MgCO_3 + CaSO_4 + 2\ CO_2 + 2\ H_2O \qquad \text{(eq.32).}$$

And in the second place:

$$2\ Ca(HCO_3)_2 + MgCl_2 \rightarrow CaCO_3.MgCO_3 + CaCl_2 + 2\ CO_2 + 2\ H_2O \qquad \text{(eq.33)}$$

The second assumption that had to be made was, that if dolomite or any other double or multiple salt is to precipitate from a solution as a solid, its solubility must be lower than the solubility of its constituents. The mineral dolomite conforms to this rule: the solubility of dolomite is much lower than that of either calcite or magnesite under the same conditions of CO_2 partial pressure and temperature.

The third assumption made, required the relative solubilities of the constituents making up the double or multiple salt, to be equal or nearly equal at the moment of co-precipitation. In the case of dolomite the solubilities of calcium carbonate and magnesium carbonate should be approximately the same at the moment of precipitation. Especially the latter aspect caught the attention of Liebermann (1967). Magnesium carbonate would be under all circumstances the more soluble of the two.[44] Removal of calcium sulfate from sea water would, in the explanation of Liebermann, lead to an increase in the solubility of calcium carbonate. Not much data on a complex medium such as seawater were available, but Liebermann was able to conclude, that upon desiccation of sea water to 110 ‰ salinity two events will be seen to take place, both contributing to a possible approach of the solubility curves of $CaCO_3$ and $MgCO_3$. At that point the solubility of magnesium carbonate would reach a maximum and would decrease from there onwards. The solubility of calcium carbonate would be increased considerably as the result of the precipitation of calcium sulfate. Although the position of a possible point of intersection could not be determined because of the mentioned lack of data, Liebermann (1967) thought that the two solubility curves might well intersect in sea water at a salinity of approximately six times that of normal sea water. The relation between the pH of pure water and the pCO_2 of the air above it, formed the basis for the conversion of the solubility curves for $CaCO_3$ and $MgCO_3$ (originally expressed in millimol versus pCO_2) into curves giving the solubility as a function of the pH of the solution. In Liebermann's Fig. 4 (reproduced here as Fig.41) these solubility's in terms of pH were used for normal sea water as well as for a brine with some 4 to 6 times normal salinity (at 298 K).

On the basis of these three basic assumptions Liebermann (1967) described the possible formation of dolomite as a two-step process: the first step requires the dissolution of calcium carbonate deposits by hypersaline sea water; the second step would be the simultaneous precipitation ("co-precipitation") of calcium carbonate and magnesium carbonate. The dissolution of $CaCO_3$ is enhanced by low temperatures, by an increase in pCO_2 , and by an acidic pH of the solution. The co-precipitation of $CaCO_3$ with $MgCO_3$ would be brought about by low pCO_2 values, by high temperatures, or by alkaline pH values. The first set of conditions would prevail during the winter season or during the night; the second set predominated during the summer season or during the daytime. In addition day/night changes in the photosynthetic activity of chlorophyll-containing plants or even in bacterial activity, would lead to the required periodical alternations between two different sets of conditions.

After establishing this theoretical framework, Liebermann (1967) described a number of experiments to produce dolomite under conditions characteristic of "coastal areas with restricted water circulation during periods of aridity". "The necessary acceleration of the natural process of dolomite formation was achieved by a strict regulation of the two alternating steps...": Liebermann (1967, p.243). In the experiments artificial seawater was used. The pH of the artificial sea water was adjusted with sodium carbonate to make pH = 8.0; in some of the experiments addition of ammonia was used to adjust the pH. Dissolution of the calcium carbonate was favored by cooling to temperatures between 278 and 283 K, while at the same time carbon dioxide would be bubbled through during 6 hours (in later experiments 12 hours). The second phase consisted of heating to 316 K. Variations with respect to salinity, gypsum content, the pH, partial pressure of carbon dioxide, temperature of the solution and duration of the experiment were investigated. In one of his experiments Liebermann (1967) found an extremely small amount of what he called an ordered dolomite. That particular test (Exp.No. 57) had been started with artificial sea water concentrated six times the standard salinity, to which a small amount of calcium carbonate had been added; the solution contained no calcium sulfate, and its pH had been adjusted with ammonia to an initial value of 7.5 . After the first phase of carbon dioxide bubbling through, the pH had changed to about 5.3 . It changed back to 7.9 after the second phase of heating to 316 K. Duration of the first phase was 12 hours; the second took 60 hours. The two-step procedure was repeated 14 times. Upon completion of Liebermann's test No. 57 a small amount of dolomite was detected in X-ray diffraction. "The amount of it produced after fourteen cycles was insufficient to prove this point, but sufficient to show that the initiation of the main reflection (104) at 2.88 Å, which is characteristic of ideal dolomites" : Liebermann (1967, p.244).

Duplication was tried, despite the fact that Liebermann (1967) had not described exactly how much calcium carbonate had been used in his Experiment No.57. All that could be discerned in the text was "... the calculated amount of calcium carbonate". But the referred calculations were not given either. Therefore I have tried to estimate this amount from the solubility curve of calcium carbonate versus salinity (Liebermann's Fig. 3). At a salinity of six times that of normal sea water about 2 milliMol $CaCO_3$ seem to dissolve (it must be admitted, that this estimation on the basis of Liebermann's Fig.3 is not very exact).

Artificial brine was made of 53.66 g NaCl, 6.42 g $MgCl_2.6\ H_2O$, 4.48 g $MgSO_4.7\ H_2O$ and 1.52 g KCl (all of p.A. quality) added to 332 ml distilled water. To the brine 0.20 g $CaCO_3$ (p.A. quality) were added, and carbon dioxide gas (industrial grade) was bubbled through the solution in a 500 ml conical flask during about 12 hours. All of the calcium carbonate had been dissolved after that time. With a few drops of a dilute NH_4OH solution (p.A. quality) the brine was titrated until pH = 8.5 had been reached. The conical flask was placed on an electric heating element and with the aid of a variable transformer the solution was kept at a virtually constant temperature of 298 ± 2 K. Almost immediately the solution became turbid, and a flocky precipitate was seen to form (which remained afloat). This phase of gradual CO_2 (and NH_3 ?) escape was continued for the next 60 hours. The second cycle started with bubbling carbon dioxide through the solution during 12 hours. The precipitate that been formed initially, disappeared: the solution became quite clear again. The pH was measured at this moment as 5.85. After the addition of dilute ammonia solution pH = 8.24 was attained. Once again the solution was placed on the heating element and kept at 298 K during the following 60 hours. (During the bubbling through of CO_2 the solution reached room temperature, which during the time of this experiment varied slowly in day/night rhythm from 291 to 294 K). The same

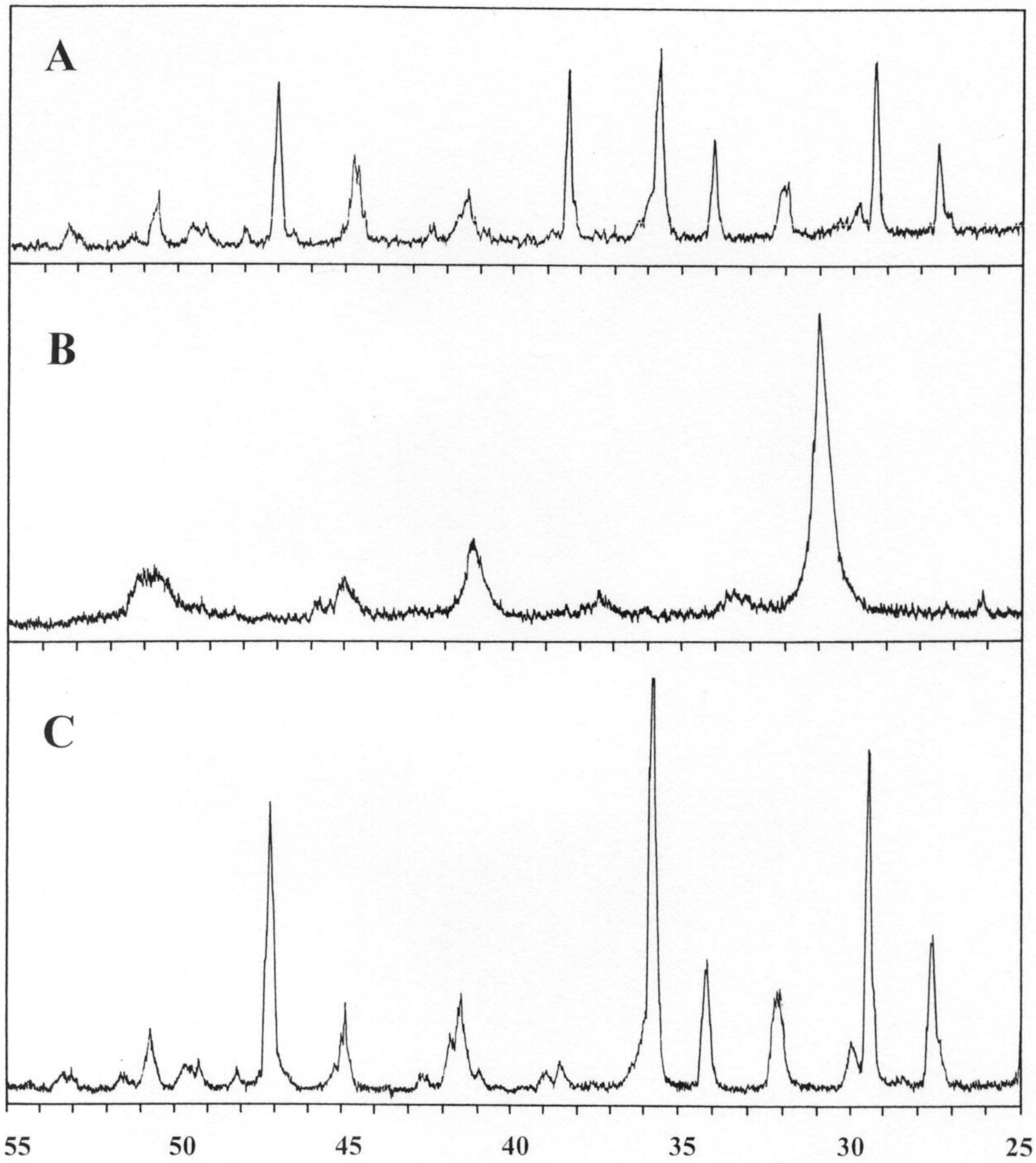

Fig.42 – Precipitates formed upon duplication of the experiments by Glover & Sippel (1967) (= A & B) and Donahue & Donahue (1968) (= C).

procedure was subsequently repeated twelve times. The pH obtained after additions of ammonia was not every time the same: in one instance it was for example 8.25 and in another it was 8.06 . But the maximum pH was 8.50 and the minimum was 8.0 . Because of the slight difference between the solution's temperature and the room temperature at the time of this experiment, little water evaporated from the flask. Through the repeated additions of the dilute ammonia solution, the volume in the conical flask even increased: at the end of this experiment the conical flask contained about 450 ml solution. In the last stages of the experiment salts would no longer precipitate in large amounts, as had been the case in the earlier stages. After 14 alternations the experiment was concluded with a final stage, involving bubbling carbon dioxide through the solution during 24 hours. The precipitate was scraped from the bottom of the glass of the conical flask, filtered off through paper and washed with about 2 dm^3 of distilled water. The filter was dried at room temperature. X-Ray diffraction applied to the sample showed the formation of a magnesium calcite with its main diffraction peak at 28.7 nm (Fig.40 C). None of the superstructure reflections typical of dolomite could be discerned.

A second duplication was required in this case, because Liebermann (1967) in some of his tests had used ammonia to adjust the pH and a concentrated solution of sodium carbonate in others. As a consequence I have had to make another duplication of Liebermann's experiment No. 57. The same amounts of salts were dissolved in 332 ml of distilled water, and again 0.2 g$CaCO_3$ (p.A. quality) was added. During 12 hours carbon dioxide was bubbled through the solution. This time the pH of the solution was adjusted with a concentrated solution of sodium carbonate until pH = 8.0 was reached. The flask was placed on an electric heating element, and heated to 308 K. In the course of the experiment more and more material precipitated on the bottom of the conical flask. Bubbling through of carbon dioxide became increasingly difficult, because time and again the little glass tube used for this purpose became clogged up. As a result only 11 different alternations could be carried out this time. Most of the precipitate formed, disappeared however upon filtering off and washing with some 6 dm^3 distilled water. After drying at room temperature, X-ray diffraction showed the remaining precipitate to consist of a magnesium calcite with its main diffraction peak at 28.8 nm together with an amount of nesquehonite.

EXPERIMENTS BY GLOVER & SIPPEL

Although most of the paper by Glover & Sippel (1967) is devoted to descriptions of low-temperature syntheses of magnesium calcites, it also contains a claim on the successful synthesis of dolomite. In their experiment 85 A Glover & Sippel outlined the preparation at room temperature of a magnesium calcite with a composition identical to that of dolomite. In 150 cm^3 of demineralized water 100 g $MgCl_2.6\ H_2O$ had to be dissolved, and this solution should be poured into one containing 7.5 g $NaHCO_3$ [45] in 150 cm^3 water, followed by the addition of 2.23 g $CaCl_2.2\ H_2O$ and 40 g NaCl to the same mixed solution. Subsequent chemical analysis of the precipitate showed it to contain 49.9 wt.% CaO and 47.3 wt.% MgO , or 0.502 mol $CaCO_3$ and 0.466 mol $MgCO_3$. Titration on magnesium indicated, that 48.7 mol % $MgCO_3$ was present.

It has been claimed by Glover & Sippel (1967), that the preparation of magnesium calcites with a composition resembling that of dolomite, would be reproducible (within certain limits). At the same time Glover & Sippel warned their readers, that "...the lack of equilibrium" would make duplication to a problem. For example changes would take place, when leaving a precipitate in contact with the mother liquor. "Preparations like No. 85 A may recrystallize in contact with the precipitating solution to give small amounts of aragonite and, for the higher Mg to Ca ratios, magnesium carbonates such as nesquehonite over a period of months": Glover & Sippel (1967, p.612).

Duplication of the experiments by Glover & Sippel (1967) has been described by Ohde & Kitano (1978). In numerous experiments the role of the concentrations of calcium chloride (1 to 50 mMol/dm^3), of magnesium chloride (0 to 2.1 mMol/dm^3) and of sodium hydrogen carbonate (0.10 , 0.18 or 0.30 mMol/dm^3) were investigated. Temperature was 298 K in all experiments and only the atmospheric pressure was involved. The formation of "protodolomite" (that is to say, a magnesium calcite with as much as 47 mol % $MgCO_3$ as determined in X-ray diffraction) required at a concentration of 0.18 mol/dm^3 of $NaHCO_3$ a concentration of at least 50 mMol/dm^3 $CaCl_2.2\ H_2O$ plus 2.14 mol/dm^3 $MgCl_2.6\ H_2O$. (Compare the concentrations of 50 mMol/dm^3 calcium chloride, 1.63 mol/dm^3 magnesium chloride and 0.29 mol/dm^3 $NaHCO_3$ used by Glover & Sippel, 1967 in their experiment 85 A.)

"The rate of formation and the crystallinity of the high magnesian calcite depend on every detail of the preparation, especially on the manner of mixing and the surface to volume ratio of the solution": Glover & Sippel (1967, p.605). Despite this explicit warning several attempts have been made by me to obtain magnesium calcites "... with a composition resembling that of dolomite". The magnesium chloride solution was poured into the solution of sodium hydrogen carbonate immediately followed by the calcium chloride solution. The resulting solution was stirred during one hour. The turbid solution was filtered off; the precipitate washed with 0.5 dm^3 of demineralized water, and dried at room temperature. Only nesquehonite formed, as was noted in X-ray diffraction. The solution that had seeped through the filter paper was left standing for 6 days at room temperature. The precipitate then formed was adhering firmly to the wall of the glass beaker; after discarding the solution, it had to be scraped off. This precipitate too consisted entirely of nesquehonite (Fig.42 A).

A second attempt was markedly more successful. This time the first precipitate was sampled after 15 days of reaction time. The carbonate adhering to the beaker was found to be nesquehonite. The solution was poured in another glass beaker. After another 20 days the solution was poured into a new glass beaker, and the second precipitate was analyzed. In addition to nesquehonite two other carbonates were found: calcite and sodium hydrogen carbonate. The third phase of the experiment took as long as 4 months. The precipitate formed after that time consisted entirely of what has become known as "protodolomite", but what really is a magnesium calcite with its main diffraction peak at 28.8 nm (Fig.42 B).

The formation of $MgCO_3.3\ H_2O$ as the first precipitate found when performing the experiment of Glover & Sippel (1967), may seem somewhat surprising at first sight. But then it must be realized, that Von Knorre (1903) had observed the same precipitate after mixing a solution of magnesium sulfate with one containing both Na_2CO_3 and $NaHCO_3$ (at room temperature). The same observation has been made by Menzel & Brückner (1930), who noted that no immediate reaction takes place, when mixing a solution of magnesium chloride or magnesium sulfate with one containing $NaHCO_3$ or $KHCO_3$. Especially when using higher concentrations, the mixture obtained would not be stable. When standing for a longer time, or more clearly when stirred, small bubbles of carbon dioxide would emerge and $MgCO_3.3\ H_2O$ (or $MgCO_3.5\ H_2O$ at low temperatures) would precipitate. According to Menzel & Brückner (1930) the reaction involved took place in two steps:

$$Mg^{2+} + 2\ HCO_3^- \rightarrow Mg^{2+} + H_2CO_3 + CO_3^{2-} \rightarrow MgCO_3.3\ H_2O + H_2O + CO_2 \qquad \text{(eq. 34)}$$

[In other words the slow escape of carbon dioxide leads to the continued hydrolysis of the

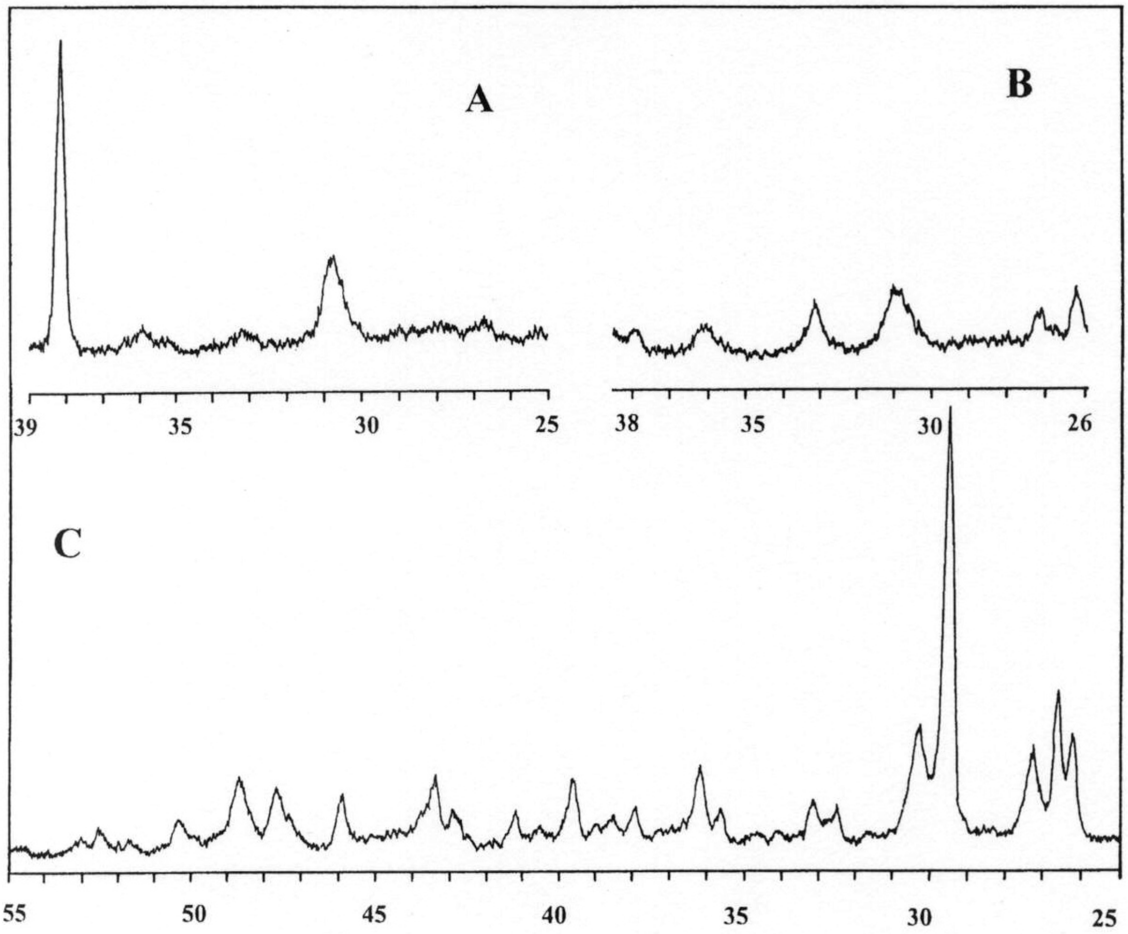

Fig.43 – A: Magnesium hydroxide carbonate after 2 hours of heating at 473 K; B: precipitate obtained upon duplication of the experiment of Donahue & Donahue (1968) after 2 hours of heating at 473 K; and C: precipitate obtained upon duplication of the experiment of McCunn (1975).

bicarbonate ion into carbonate, according to:

$$2\,HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_2CO_3\ (= CO_2 + H_2O). \qquad \text{(eq. 35)]}$$

Because experiment 85 A of Glover & Sippel (1967) was found to be reproducible, it can be used for a number of additional purposes; for example to demonstrate the active role of urea (plus urease) in accelerating the precipitation of "protodolomite". When repeating test 85 A of Glover & Sippel in the manner indicated, but adding 10 g urea plus 0.25 g urease, "protodolomite" will be formed after 37 days instead of after 4 months (my experiment D-132). Ultimately it was possible to obtain "protodolomite" in only 3 days time, when conducting experiment 158 of Glover & Sippel (1967) at 308 K and adding before its start 2 g urea[46] (my experiment D-191).

Yet another interesting possibility opened up by the experiments of Glover & Sippel (1967) concerns the relation between the exact position of the X-ray diffraction lines and the chemistry of the magnesium calcites. In my first duplication experiment a magnesium calcite had been formed with its main diffraction peak at 29.2 nm. When using the conversion diagram of Füchtbauer & Goldschmidt (1965), this particular dolomite would contain 65 mol % $CaCO_3$ and 35 mol % $MgCO_3$. The sample was subsequently subjected to (wet) chemical analysis. From the titrations the following composition was calculated: 28.95 % Ca = 51.70 wt.% $CaCO_3$ = 51.70 mol % $CaCO_3$ and 16.74 % MgO = 35.02 wt.% $MgCO_3$ = 41.7 mol $MgCO_3$. A comparable discrepancy between X-ray analysis and wet chemical analysis had been noted by Glover & Sippel (1967). Analysis of a magnesium calcite formed in their experiment 85 A with the aid of X-ray diffraction showed it to contain 45 mol % $MgCO_3$, but in wet chemical analysis 48.7 mol % $MgCO_3$ was measured by Glover & Sippel.

EXPERIMENT BY DONAHUE & DONAHUE

A claim on successful synthesis of dolomite at relatively low temperature (310 K) and under atmospheric pressure has been put forth by Donahue & Donahue (1968). In their view it was necessary to imitate in one way or another the marine supratidal environment. Instead of seawater a mixed magnesium/calcium bicarbonate solution was used. Desiccation of this solution was not static, but took place at intervals. Repeated additions of 50 cm^3 each of the bicarbonate solution were made into a glass beaker kept at a constant temperature of 310 ± 1 K. The mixed bicarbonate solution was saturated with both magnesium carbonate and calcium carbonate. A new addition was made only after complete desiccation of the previous quantity. Intermittent desiccation was continued until a quantity of carbonates sufficient for X-ray diffraction had accumulated. Donahue & Donahue reported, that calcite, magnesite, and dolomite had been formed.

The experiment by Donahue & Donahue (1968), not in the least because it is so simple, has been duplicated by me. In a large plastic bottle 5 dm^3 of demineralized water were saturated first with carbon dioxide, then 10 g $CaCO_3$ [16] and 40 g magnesium hydroxide carbonate[17] were added. After several days of contact (and stirring from time to time), excess solid was filtered off, and a sample of the liquid was taken for chemical analysis. A small amount of hydrochloric acid added to the sample made sure, that no precipitation would take place. Subsequent analysis showed the bicarbonate solution to contain 0.84 g $CaCO_3$ and 5.6 g $MgCO_3$ per dm^3. The mixed bicarbonate solution was then used in a set-up involving

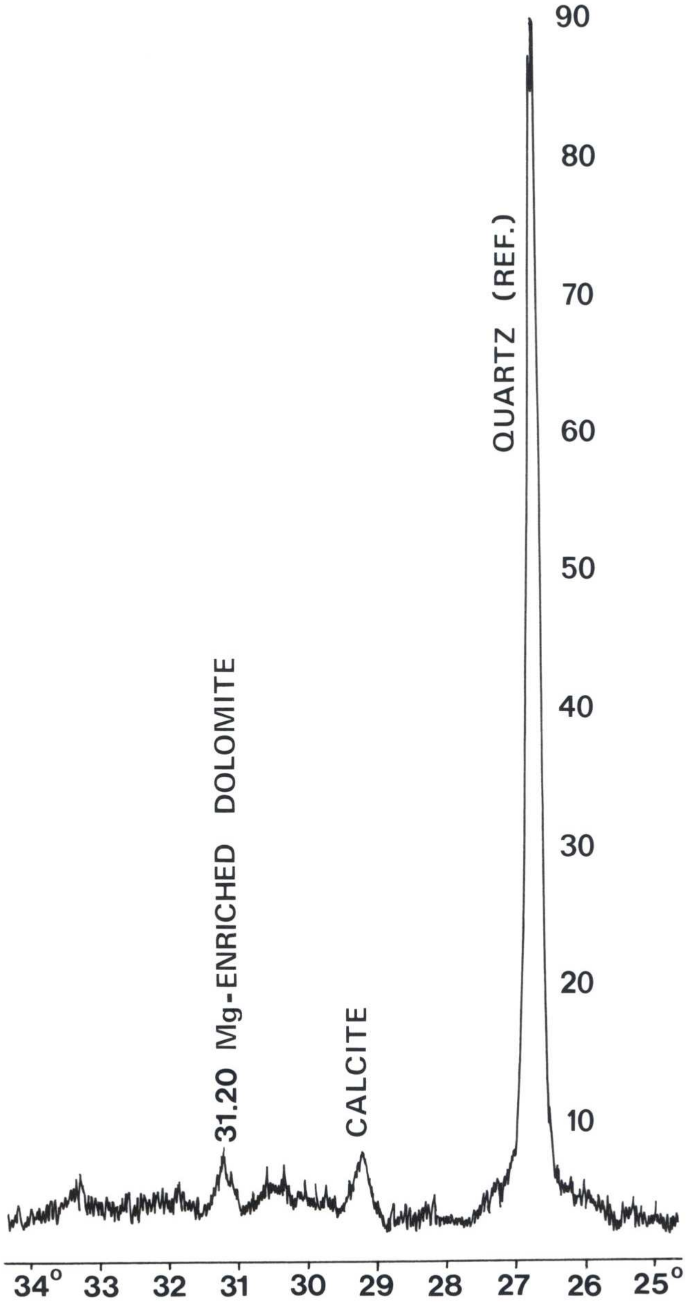

Fig.44 – X-Ray diffractogram showing, that in the experiment by McCunn (1975) a small quantity of a "…Mg-enriched dolomite" (main peak at 31.2° in Cu-$K_{\acute{\alpha}}$ radiation) had been formed (after McCunn, 1975).

intermittant desiccation at a constant temperature of 310 ± 0.5 K. Every time 50 cm^3 of the bicarbonate solution would be poured into a large Petri dish kept at that temperature. Only after complete desiccation a new addition was made. In total 20 different additions were made. X-Ray diffraction of the powdered precipitate showed only nesquehonite to be present. In view of the fact that no form whatever of (Mg-containing) calcium carbonate could be detected in the sample subjected to X-ray analysis, selective leaching was used to remove some of the nesquehonite. The precipitate was treated several times with water saturated with carbon dioxide. X-Ray diffraction was repeated using a sample from the mixture obtained after dissolving about one half of the initial amount of the precipitate. The result was, that in addition to nesquehonite the main diffraction peak of calcite could be detected (Fig.42 C).

A second attempt has been made to duplicate the experiment of Donahue & Donahue (1968). In this second test a laboratory pump was used to pump 10 cm^3 of a mixed Mg/Ca bicarbonate solution once per hour into a glass beaker. Actual pumping took about 4 minutes; during the remainder of each hour the added amount of solution would desiccate. The pumping sequence was controlled by an electromagnetic time switch. The glass beaker was kept at a constant temperature of 318 K. The solution contained 0.12 g $CaCO_3$ (calcite powder) and 0.68 g magnesium hydroxide carbonate dissolved with excess carbon dioxide in 2.5 dm^3 of demineralized water. After 2 weeks the material accumulated in the beaker was sufficient to allow for X-ray diffraction: aragonite, magnesium hydroxide carbonate and possibly some dolomite had been formed. As stated before, it is rather difficult to detect any dolomite in a mixture, which also contains magnesium hydroxide carbonate. Acid treatment was out of the question: the risk of loosing the very small sample could not be taken. Therefore an attempt was made to use thermal decomposition as a means of distinction. The magnesium hydroxide carbonate will readily change, when heated to for example 473 K, but dolomite heated to that temperature will remain unaffected.[47] After heating quantities of the pure compound magnesium hydroxide carbonate and a quantity of the carbonate mixture from this last experiment for 2 hours at 473 K, a clear distinction could be made indeed. The magnesium hydroxide carbonate was seen to develop a new, distinct peak at 38.2° (in Cu-K_α radiation) and no such peak developed in the carbonate mixture of experiment D-5 (Fig.43 A & B). Therefore it can be concluded, that in experiment D-5 dolomite had been formed at a temperature of 318 K.

McCUNN'S EXPERIMENTS

Successful synthesis of dolomite as a sedimentary mineral has also been claimed by McCunn (1974, 1975).[48] Although his experiment is rather complex, it seems that a mixture of solid Mg/Ca carbonates reacted with CO_2-rich water and that the resulting bicarbonate solution was subjected to interrupted desiccation: after each phase of desiccation the dried mixture was replenished with water.

The exact recipe as given by McCunn (1975) will be repeated here. One part of a mixture containing equal amounts by weight of $CaSO_4.2\ H_2O$ and $MgSO_4.7\ H_2O$, was mixed with two parts of $NaHCO_3$. Seawater was added and the three solids reacted with it during several days. McCunn reported, that X-ray diffraction applied at this stage, showed the formation of aragonite, magnesium calcite, nesquehonite and magnesium hydroxide carbonate. The mixture was washed several times with distilled water, filtered off and dried. Amounts of organic material (fish flour and bran) were added along with sodium chloride. The thus obtained mixture was kept under at least 5 cm of water for one month; after that time the mixture was allowed to desiccate completely. Next and final step in the procedure involved an infrared (heat) lamp above the mixture, in order to attain complete desiccation after each renewed addition of water. In McCunn's experiment the system was subject to fluctuations between wet and dry: after each phase of desiccation the dried up mixture was replenished with rain water (or tap water made slightly acidic with decaying plant remains[49]). "Repeat the wetting and drying episodes bi-daily. The process will create a rock flour or pulverulant type carbonate sediment. In approximately 4 months you should have a goodly percentage of dolomite" (McCunn, 1975). The addition of organic matter was found to be a necessity. The use of slightly acidic water was observed to lead to the best results. The wetting and drying should take place in alternating phases: "The material was completely dried between each period of wetting. The wetting and drying episodes produced a pulverulent fine-grained tan to gray carbonate mud. After a period of approximately 90 days the material was reacted in dilute acetic acid (5 %) ... A fine brown powder resulted ... This material was X-rayed and proved to be dolomite" (McCunn, 1975).

In a second experiment McCunn (1975) confirmed his earlier findings; although his second experiment had been modified somewhat with respect to the first. Pelecypod shells were placed in seawater, to which organic matter had been added. Magnesium sulfate, gypsum and sodium bicarbonate were introduced and the mixture was allowed to react for several days. Numerous minute aragonite needles were seen to be covering the pelecypode shells after the reaction had taken place. During the following 9 months the mixture was left standing, undisturbed except for the addition of slightly acidic water as soon as the solution had disappeared from the mixture of solids. The carbonate material formed during this period was found to contain dolomite. From the diffractogram provided by McCunn (reproduced here as Fig.44) it can be seen, that the (rather small) main peak of the mixed Mg/Ca carbonate formed is located at 31.2 ^{o} (in Cu-K$_{\alpha}$ radiation). McCunn (1975) interpreted this observation, as evidence of the formation of dolomite with 53 mol % $MgCO_3$ ("Mg-enriched dolomite").

The first experiment of McCunn (1975) has been duplicated by me. It started with mixing 10 g $CaSO_4.2\ H_2O$ with 10 g $MgSO_4.7\ H_2O$ and 40 g $NaHCO_3$. Added to the mixture was 1 dm^3 of artificial sea water (as per Lyman & Fleming, 1940)[35]; the whole was left to react during one week. Filtering was followed by washing the precipitate with 2 dm^3 distilled water. After drying at room temperature, the precipitate was weighed (7.82 g) and X-rayed. Aragonite, calcite and magnesium calcite had been formed. The next step consisted of mixing the precipitate with 10 g bran plus 50 g fresh fish (whiting), and adding 0.5 dm^3 distilled water. During one month the organic compounds gradually decayed in the presence of the mixture of carbonates. After that the remaining organic material was sieved off, and the carbonate powder dried again at room temperature. X-Ray analysis at this stadium showed the presence of calcite, magnesium calcite and aragonite. The final phase of the experiment took 4 months, and it involved adding once every 12 hours some 15 cm^3 of tap water, made slightly acidic with decaying plant material (first peppermint leaves, later spinach). The water would stream into a Petri dish of about 15 cm diameter, which slowly rotated underneath a heat lamp. This infrared lamp kept the temperature in the Petri dish at 298 to 303 K, and thus secured the complete desiccation of the solution in the Petri dish each time before a new addition was made (through an electromagnetic valve controlled by a time switch). The precipitate obtained after 4 months reaction time was collected, washed by repeated settling in distilled water and dried at room temperature. As can be seen in Fig.43 C the precipitate consisted of two different magnesium calcites (one with its main diffraction peak at 30.28 nm and a second with a markedly smaller main peak at 29.5 nm). In addition small amounts of aragonite and alpha quartz (the latter is probably a contamination introduced with the plant material) were present.

EXPERIMENTS BY MIRSAL & ZANKL

Having postulated an entirely new approach towards carbonate geochemistry, based on the possible actions of transition metal chelates on calcium and magnesium, Mirsal & Zankl (1985) described a number of laboratory tests in which, it was claimed, dolomite had been formed at room temperature. Successful synthesis involved 500 cm^3 of artificial sea water prepared mainly according to Lyman & Fleming (1940) (with Mg/Ca = 5.28), but to which more NaCl had been added to reach a salinity of 55 ‰. To this amount of artificial sea water 5 cm^3 of a chelate solution containing 51 . 10^{-4} g $FeCl_2$ and 36 . 10^{-4} g oxalic acid was added, followed by 0.5 g ascorbic acid (as a reducing agent), and ultimately 40 cm^3 of a 0.1 mol Na_2CO_3 solution were added as well. The thus prepared mixture was left standing at room temperature (293 to 298 K) during 10 days. "X-Ray diffraction analysis of the formed precipitate revealed a composition ranging from high magnesium calcite to dolomite-similar phases with some order peaks. The so formed crystals are mostly very minute (less than 5 µm) and have a chemical composition (by channel analyzer: ORTEC) resembling the ideal composition of dolomites (1 : 1 ratio)": Mirsal & Zankl (1985, pp.373-374). Although the claim on successful low-temperature synthesis of dolomite was cautiously worded, Mirsal & Zankl did not hesitate to head the section, which dealt with said synthesis, with "Precipitation of dolomite from seawater and related brines - experimental results". The following text was added to a scanning electron photomicrograph, showing rhomb-like crystals: "Dolomite rhombohedra precipitated from artificial sea water using chelate solution containing $FeCl_2$ and oxalic acid" (Mirsal & Zankl, 1985, p.373).

Because the possibility to form dolomite in only ten days time was of considerable interest to me, and only a small number of relatively well defined chemicals was required, I have taken the trouble to duplicate the tests of Mirsal & Zankl (1985) (see also Deelman, 1988). As a first step the artificial sea water according to Lyman & Fleming (1940) was prepared by way of weighing 23.47 g NaCl , 4.98 g $MgCl_2.6\ H_2O$, 3.91 g Na_2SO_4 , 1.10 g $CaCl_2.2\ H_2O$, 0.66 g KCl and 0.19 g $NaHCO_3$ and adding distilled water to make 1 dm^3 . In order to attain the required salinity of 55 ‰ an additional 31.53 g NaCl were mixed into the solution. Although not mentioned by Mirsal & Zankl (1985), another addition has to be made. The Mg/Ca ratio of this artificial sea water is not 5.28 ; because 4.98 g magnesium chloride and 1.10 g calcium chloride had been used, and no other forms of magnesium or calcium salts were involved, the Mg/Ca ratio actually is 3.27 . Calculation shows, that an extra 3.06 g $MgCl_2.6\ H_2O$ is needed to make the Mg/Ca ratio = 5.28 .

To 500 cm^3 of this modified artificial sea water the following reagents were added, in the order as given: a) 5 cm^3 of a chelate solution with 1 g iron (Fe^{2+}) chloride and 0.72 g oxalic acid in 1 dm^3 of distilled water, b) 0.5 g ascorbic acid[50] and c) 40 cm^3 of a solution of 10.59 g Na_2CO_3 in 1 dm^3 of distilled water. The clear solution thus prepared was left for 10 days in a glass beaker at room temperature (which during the experiment slowly fluctuated in day/night rhythm between 292 and 297 K). After this period a very small amount of precipitate had accumulated on the bottom of the glass beaker. After scratching it off, and filtering it with excess distilled water, the paper filter was dried at room temperature. The amount of the precipitate was so small, that X-ray diffractometry had to be excluded, and recourse had to be taken to Guinier photographs for identification. Lines at 87, 62, 44, 39.1 , 36.8 , 35.9 , 33.8 , 31.7 , 30.9 , 28.1 , 27.8 , 24.3 , 24.1 , 23.7 , 23.4 , 22.8 , 22.4 , 22.1 , 21.8 , 21.2 , 20.3 , 19.9 , 19.6 , 19.0 , 18.4 , 17.9 , 17.5 and 17.4 nm were measured. The strongest three lines, in order of decreasing relative intensity, were 62, 27.8 and 44 nm. Using the International Centre for

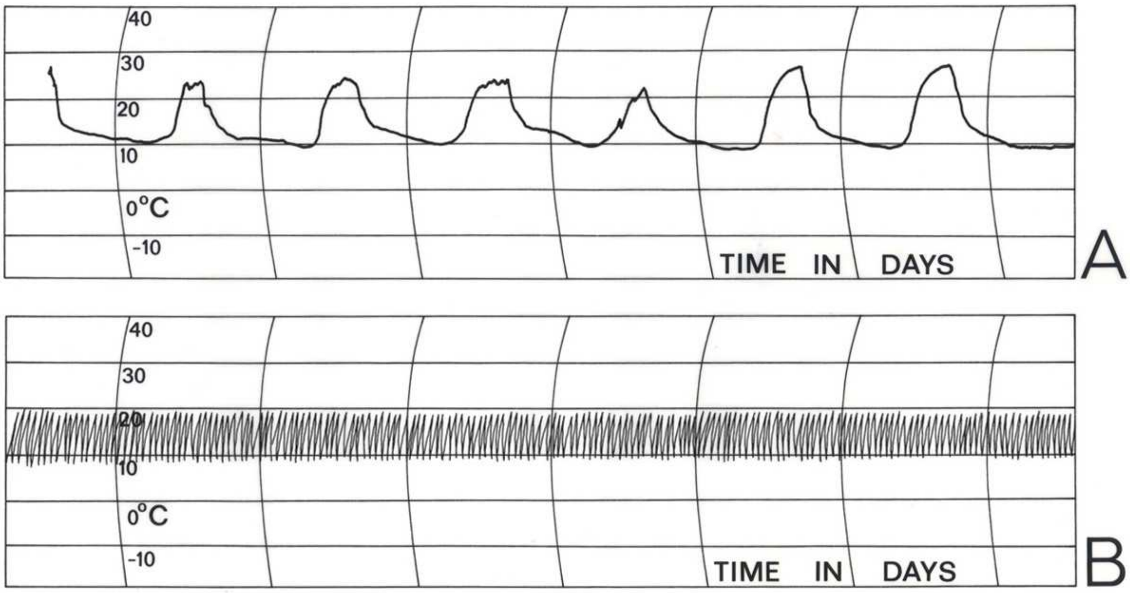

Fig.45 – Day/night changes in temperature (A) and ½-hour changes in temperature caused by an electric heating element controlled by a time-switch (B).

Diffraction Data file, the precipitate could be identified as calcium oxalate dihydrate (compare JCPDS card 17-541).

In order to test the suggestion of Mirsal & Zankl (1985, p.367), that "... traces of transition metals together with organic matter ... play a central role in carbonate production", the described experiment was also duplicated without any iron chloride, oxalic acid, or ascorbic acid. To 500 cm^3 of the modified artificial sea water 40 cm^3 of a solution containing 10.59 g Na_2CO_3 anhydr. in 1 dm^3 of distilled water, were added. This test was carried out under the same conditions of temperature as the previous experiment, and during the same time. Considerably more material accumulated this time at the bottom of the glass beaker, and a Guinier photograph (made after washing the precipitate with excess water and drying the filter paper at room temperature) showed it to consist entirely of aragonite.

The possibility should be considered, that I did not obtain the same precipitates as Mirsal & Zankl (1985) claimed to have found, because duplication had not involved the same circumstances or because the chemicals used were different. But it was quite difficult to follow the description of Mirsal & Zankl (1985) to the letter: the very description of their experiment No. 7 is insufficient to allow for duplication. In particular it was not mentioned, whether the iron (II) chloride and the oxalic acid contained any crystal water or not. Because the quantities of these two substances were expressed in gram and not in moles, the distinction between the hydrated and the anhydrous form is essential. To overcome this difficulty, two more experiments had to be carried out. In my third test 5 cm^3 of a solution with 0.84 g oxalic acid dihydrate (the amount needed when supposing, that Mirsal & Zankl had used an anhydrous oxalic acid instead of $C_2H_2O_2.2\ H_2O$) plus 1 g $FeCl_2.4\ H_2O$ in 1 dm^3 of distilled water were added to 500 cm^3 of the modified artificial sea water described by Mirsal & Zankl (with Mg/Ca = 5.28). Then 0.5 g L(+)-ascorbic acid was added, the mixture was stirred for a short while, and as the last step 40 cm^3 of a solution containing 10.59 g Na_2CO_3 anhydr. in 1 dm^3 were added. After stirring again, the glass beaker was left standing for 10 days at room temperature. After 10 days the precipitate formed was washed, filtered off, and dried at room temperature. X-Ray diffraction revealed it to consist of aragonite. Although iron (II) chloride is not commonly available in its anhydrous state, a fourth experiment was necessary, because it was not clear whether Mirsal & Zankl (1985) had used anhydrous $FeCl_2$ or its hydrated form. This particular test was identical with the first one described, except that 1.60 g $FeCl_2.4\ H_2O$ were used instead of the indicated 1.0 g. The compound that precipitated from this solution was calcium oxalate dihydrate.

In their reaction on my duplications Mirsal & Zankl (1988) explained, that their experiment No.7 had in fact suffered from a number of set-backs. For one thing the yield of the experiment had always been very low, so that recourse had to be taken to energy dispersive X-ray spectroscopy as the only method of analysis. At the same time experiment No.7 had suffered from a lack of reproducibility: closed vessels always rendered aragonite, but open vessels did give the results as described. Furthermore the use of oxalic acid, an essential element of experiment No.7 , would lead to the formation of oxalate. After leaving experiment No.7 behind as a station passed, Mirsal & Zankl (1988) described two new experiments yielding "... X-ray identifiable dolomite". Because in both experiments dolomite crystals were used "... to catalyze the process" as they put it, I have refrained from any attempt to duplicate those experiments.

DEELMAN'S EXPERIMENTS

As recorded in my 1975 paper on "*Dolomite synthesis and crystal growth*" crystallites showing in X-ray diffraction a small, but recognizable peak at 31^o (in Cu-K$_\alpha$ radiation), had been formed in a mixed bicarbonate solution subjected to slow, periodically interrupted desiccation. The main precipitate consisted of aragonite, but in X-ray diffraction a very small amount of dolomite was detected. In scanning electron microscopy individual crystallites of the dolomite were clearly recognized. The solution used had been made with 0.4 g calcium carbonate[16] plus 0.4 g magnesium hydroxide carbonate[17] dissolved in 1 dm^3 demineralized water. The glass beaker from which the few dolomite rhombs had been collected, had been standing in a window sill for about 2 weeks (covered by a watch glass). During the experiment the day / night changes in temperature had been traced by a recording thermometer (Fig.45 A).

Immediately after writing the short *Research Note* for the journal *Geology*, attempts were made to increase the amount of dolomite formed. The line of reasoning was initially, that because fluctuations seemed to be involved, a higher frequency of these would increase the amount of dolomite. In the next experiments the desiccation of mixed Mg/Ca bicarbonate solutions was brought about by a 15 Watt glass-encased heating element (of the immersion-type used in aquariums), periodically switched on and off in a 1/2 hour rhythm (Fig.45 B). But X-ray diffraction of the precipitates formed, were not really convincing. As a consequence I concluded, that the main problem remained (i.e., how to increase the amount of dolomite).

From the very outset I was convinced, that *fluctuations* played an essential role. There were two convincing arguments at the time. In the first place the observation made by Müller et al. (1972), who had recorded, that "stationary" lakes do not contain dolomite, whereas "dynamic" lakes do contain the mineral. A dynamic lake shows distinct (seasonal) changes in amount and in chemistry of the accumulated water, whereas static lakes do not show such changes. Although Müller et al. (1972) had made the observation as such, they had refrained from drawing any conclusion relating dolomite formation to such dynamic conditions. Instead Müller et al. (1972) made a distinction between "primary" and "secondary (or diagenetic)" carbonates, and stressed especially the possible role of the Mg/Ca ratio of the solution ("...diagenetic carbonate minerals are found in ... environments with elevated Mg/Ca *and* high-Mg calcite as a primary mineral": Müller et al., 1972, p.161).

There was a second, and in my view an even more convincing argument in favor of an active role of *fluctuations*. That was the observation made in studies on crystal growth on the energy barriers at the start of each new layer. Therefore I went on to use periodical changes in temperature to precipitate dolomite (in my view energy and temperature are closely related if not identical). With the aid of time switches of one kind or another various sorts of heating elements would be switched on and off at for example 1/2 hour intervals. But it did not work; increased amounts of dolomite could not be detected. In quite a number of subsequent experiments no dolomite at all was found.

Encouragement came (several years later) in an unexpected manner. In one of my experiments conducted in 1982 amounts of the mineral *northupite* $Na_2CO_3.MgCO_3.NaCl$ had been formed. And when repeating the experiment without NaCl, the mineral *eitelite* $Na_2CO_3.MgCO_3$ formed. Up to 1982 eitelite had been synthesized only at temperatures of at least 333 K. In my experiments eitelite formed at 298 K. At the same time the essential role of fluctuations was demonstrated. Eitelite was synthesized by way of periodical additions of small amounts of a magnesium bicarbonate solution to either solid sodium carbonate or to sodium hydrogen carbonate. Once per half hour for example 2 cm^3 of the magnesium bicarbonate

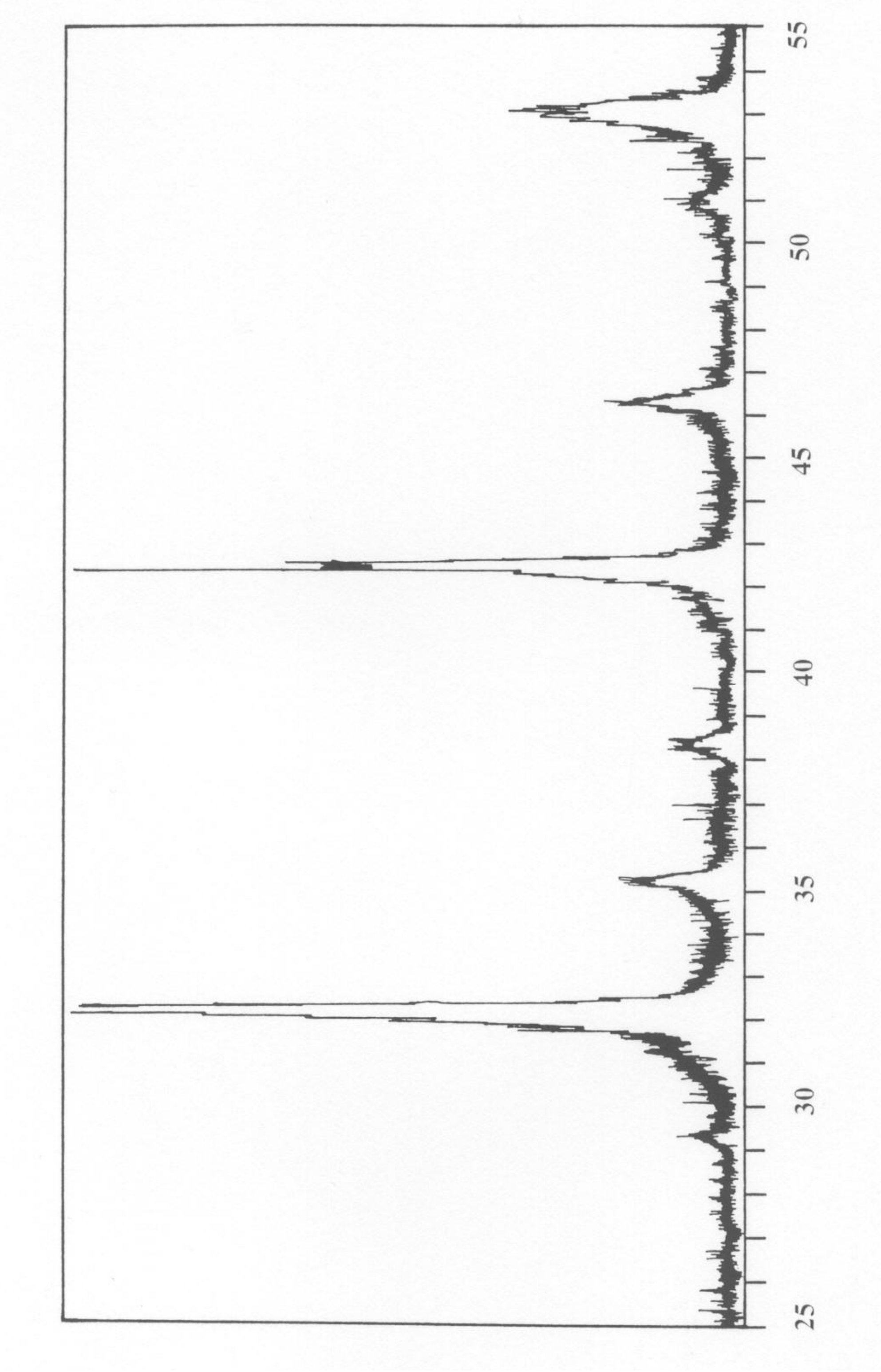

Fig.46 – Magnesite obtained upon duplication of Liebermann's (1967) experiment number 57 at a temperature of 313 K (my experiment M-223).

experiment no.	temperature (K)	base	precipitate
D-163	316	NH_4OH	D + M
D-164	298	NH_4OH	D
D-190	298	Na_2CO_3	N + MgC
D-211	313	NH_4OH	C + D + M
D-217	313	Na_2CO_3	H
M-211	333	NH_4OH	M
M-223	313	NH_4OH	M
M-224	333	NH_4OH	HU
M-226	303	NH_4OH	MgC + HU
M-227	333	NH_4OH	M
D-228	313	NH_4OH	A + MgC + M

Table XI - Precipitates formed after duplicating experiment No. 57 of Liebermann (1967). A = Aragonite; C = calcite; D = dolomite; H = magnesium hydroxide carbonate; HU = huntite; MgC = magnesium calcite; M = magnesite; N = nesquehonite.

solution (of 0.2 g magnesium hydroxide dissolved in 1 dm^3 water with the aid of CO_2 bubbled through it) would stream onto a tray with either Na_2CO_3 or $NaHCO_3$ spread on it. During the rest of each 30 min interval the solution would be forced to desiccate by way of a heat lamp.

Verification of the essential role of fluctuations in the low-temperature nucleation of eitelite took place by way of a *static control* experiment. The dynamic test involved 2 cm^3 of a saturated $NaHCO_3$ solution streaming once per half hour into a tray with 2 g magnesium hydroxide carbonate. This small amount of solution would desiccate under the heat lamp at 298 K during the rest of each 30 min interval. The static control for this particular experiment involved adding 2 g magnesium hydroxide carbonate to a saturated $NaHCO_3$ solution in one action in a glass beaker at 298 K. After 9 days X-ray diffraction showed, how in the dynamic experiment eitelite, trona and $NaHCO_3$ had been formed. In the static control no eitelite at all could be detected and only the original ingredients (sodium hydrogen carbonate plus magnesium hydroxide carbonate) were present (Deelman, 1984).

The low-temperature syntheses of eitelite illustrate how in fact the dehydration of magnesium cations obviously has nothing to do with the nucleation of anhydrous magnesium carbonate. Of course the question remained, how the low-temperature synthesis of eitelite correlates with that of dolomite. Although the two minerals can be found in close association (for example in the Green River Formation in Wyoming and Colorado, USA), the two are not exactly identical. During the years that followed, I became more and more convinced of the close relation between low temperature nucleation of dolomite and that of magnesite. For when looking in detail, there really is no problem at all with the nucleation of $CaCO_3$ in the sedimentary environment. But problems arise as soon as the nucleation of $MgCO_3$ or that of $CaCO_3.MgCO_3$ are considered. And in my view the nucleation of anhydrous magnesium carbonate might well constitute the minor problem of the two. Therefore I started to concentrate on the various aspects of the physical chemistry of magnesium cations in aqueous solution. Apart from the hydration of magnesium cations (which was no longer an issue for me), there is the phenomenon of hydrolysis (which in fact must be responsible for the precipitation of magnesium hydroxide carbonate instead of magnesium carbonate or magnesium carbonate hydrate). Therefore a next series of experiments was devoted to attempts to prevent the hydrolysis of magnesium cations. Because hydroxyl ions are powerful oxidizers, I concluded, that reducing conditions must counteract the presence of hydroxyl ions. And there are in fact numerous indications, that dolomite or magnesite might well have formed under reducing conditions. Various experiments based on this hypothesis were carried out. But even when using the most powerful reducing agent (hydrogen gas in solution) no dolomite or magnesite would form in my laboratory experiments. Nor would the presence of H_2S gas (another powerful reducing agent) in solution lead to the nucleation of magnesite.

It must have been around this time, that I decided to try and duplicate all of the known claims on the low temperature formation of dolomite (and magnesite). For the experiments with H_2S gas had in fact been described much earlier by Pfaff (1894). And the experiments with slowly desiccating Mg/Ca bicarbonate solutions are of course originally the experiments of Scheerer (1866). Even the experiments by Lalou (1957), involving bacterial sulfate reduction in a marine medium, were duplicated by me. In the course of the years that followed, I have duplicated almost all of the experiments by others on magnesite or dolomite, yet one of the few that remained to be done was that by Liebermann (1967).[51] The only reason why I had hesitated to start duplicating those experiments, was that measurement of pH was involved. Because I did not have any means to measure pH at my disposal except for indicator paper strips, I had to borrow a pH meter. Therefore the experiments of Liebermann were the last ones to be duplicated. After a few more experiments the chapter on *Dolomite syntheses* of my

experiment no.	temperature (K)	variation	precipitate
D-213	313	without NaCl	C + N
D-214	313	without NaCl, KCl	A, MgC + D
D-215	311	without NaCl, KCl, $MgCl_2$	gypsum
D-216	313	without NaCl, KCl , $MgSO_4$	A
D-219	313	titration until pH = 7	C, MgC + D + E (?)
D-222	312	plus urea	D (!)
D-223	303	plus urea, plus gypsum	A
D-224	313	plus urea, plus $CaCl_2$	A + C (trace)

Table XII - Variations on experiment No. 57 of Liebermann (1967). A = Aragonite; C = calcite; D = dolomite; E = eitelite; MgC = magnesium calcite; N = nesquehonite.

planned publication was ready.

The results were truly amazing. In my first attempt to duplicate Liebermann's Exp.No.57 (my experiment D-163) clearly dolomite and possibly magnesite had been formed at a temperature of 316 K. But as it turned out, I seem not to have realized these facts fully at that time. For it took several more months for me to realize the success in duplicating Liebermann's experiment. In the meantime I was much too busy with other concepts and preconceived ideas to seriously start considering my own results. By following the wrong leads, by testing almost all other concepts, it became August 1996 before embarking seriously on duplicating Liebermann's experiment. By that time, after having discarded virtually all of the existing physical-chemical theory on the nucleation of magnesite and dolomite, I was free at last to embrace the practical results regardless of any assumed theoretical background. In other words I had finally decided to rely solely on laboratory evidence and I was no longer inclined to believe any theoretical consideration at all.

After that time almost any duplication of Liebermann's experiment No.57 was successful. For example in my experiment D-211 dolomite, magnesite and calcite were found in X-ray diffraction after duplicating Liebermann's Exp. No.57 at 313 K. Pure magnesite was found in experiments M-211 (333 K), M-223 (313 K; see Fig.46), M-224 (333 K), and M-227 (333 K). But when conducting the same experiment at 313 K again, the magnesite would be accompanied by aragonite and magnesium calcite (my experiment M-313). No magnesite was found when doing the same test at 303 K: after the usual time of 42 days magnesium calcite and huntite were found in X-ray diffraction (see also Table XI).

Because in his paper Liebermann (1967) stated to have used ammonia or sodium carbonate in the titrations, several duplications were carried out by me using a solution of sodium carbonate instead of ammonia. But in those cases the stable phases (dolomite, magnesite, huntite) did not appear. For example in my experiment D-190 (conducted at 298 K) nesquehonite and magnesium calcite resulted; and in D-217 (313 K) only magnesium hydroxide carbonate.

The artificial brine used by Liebermann (1967) is made up of only a few salts, and therefore it is rather simple to investigate the possible role of each individual salt. When duplicating Liebermann's Exp. No.57 at 313 K without NaCl (titrations with ammonia) the result is calcite plus nesquehonite (my experiment D-213). When leaving out NaCl and KCl at 313 K (D-214) the precipitate consists of aragonite, magnesium calcite plus dolomite. Leaving out NaCl, KCl, and $MgCl_2$ at 311 K (D-215) leads to the precipitation of gypsum only. And when duplicating Liebermann's Exp. No.58 without NaCl, KCl, and $MgSO_4$ at 313 (D-219) the precipitate formed consists of aragonite (see also Table XII).

More variations can be invented, for example performing all titrations up to pH = 7.0 instead of pH = 8.0 . The result in that case (performed at 313 K) was a mixture of calcite, magnesium calcite, dolomite and possibly eitelite. The addition of urea to the artificial brine used in my duplications of Liebermann's experiment was but another variation. Apparently urea catalyses the formation of perfect dolomite (as for example in experiment D-222 at 312 K). However when adding not only urea but gypsum as well (D-223 conducted at 303 K), only aragonite forms. And when using urea plus calcium chloride (D-224 at 313 K) the result is aragonite along with a trace of calcite.

Definite conclusions are difficult to formulate at present, not in the least because *terra incognita* was explored. On the basis of physical-chemical considerations the suggested role of the Mg/Ca ratio and/or the salinity of the solution, must be doubted (Deelman, 1975 B). Although not particularly clear at a first look, there may well exist a relation between mineralogy of the precipitates and temperature during the escape-of-CO_2-phase. But this is merely a first impression, and a multitude of additional laboratory experiments can only bring certitude. Instead of carrying out all those experiments (which would take years), I decided to publish the initial results in my 1999 paper and to continue writing the present publication. Through this publication the novel knowledge contained in it, can be spread world wide in the most effective way.

STATIC CONTROLS

Of course it would be possible to argue, that because fluctuations are virtually omnipresent, such fluctuations can never be made responsible for dolomite formation. However there are convincing arguments against this point of view, especially in the form of static control experiments. When repeating a particular experiment without the artificially introduced fluctuations, and not finding for example dolomite, the only conclusion can be that these fluctuations do play an active role.

Here experiments on the low-temperature formation of magnesite with and without fluctuations will be discussed. Not in the least because any discussion on dolomite formation has been thoroughly confused through the introduction of the names “neodolomite” and “protodolomite” for what really are magnesium calcites with high percentages of magnesium carbonate. No such confusion pertains to the low-temperature formation of magnesite. At the same time these static control experiments are essential to dolomite formation, because in my low-temperature syntheses magnesite formation was preceded by dolomite formation.

In Liebermann’s experiments (1967) intervals of precipitation alternate 14 times with intervals of dissolution. The dissolution is brought about by bubbling carbon dioxide through the solution during 12 hours. Precipitation will be attained through titration with ammonia until pH = 8.0 has been reached followed by 60 hours of heating the solution to a constant temperature (of for example 313 K). Because the quantity of carbon dioxide dissolved each time into the solution had not been measured, there was no possibility to use Liebermann’s syntheses as a basis for a static control experiment. It will not come as a complete surprise to find, that when adding all of the ammonia used in the 14 different titrations typical of the Liebermann experiment in one action into the salt solution, no magnesite forms. What really precipitates is magnesium hydroxide carbonate.

As stated before, ammonia played an essential role in my duplications of Liebermann’s experiments. For when using sodium hydroxide instead of ammonium hydroxide for the titrations, no magnesium at all would form. Therefore it seemed only logical to study more in detail the possible significance of ammonia. What was found consisted of details of an industrial process used to make sodium carbonate: the Solvay ammonia soda process. As for example Hou (1942) mentions, various magnesium salts precipitate during the “ammoniation stage” of the saturated sodium chloride brines used. Among these magnesium salts also magnesium carbonate in the form of magnesite (Hou, 1942). In a patent claim Waeser (1923/1926) stated, that the reaction

$$MgCl_2 + 2\,NH_3 + CO_2 + H_2O = MgCO_3 + 2\ NH_4Cl \qquad \text{(eq. 36)}$$

would become reversible at temperatures above 303 K. This rather simple reaction would adequately explain the role of ammonia in the low-temperature nucleation of magnesite, and can be used to design a static control.

The first static control experiment consisted of dissolving 0.1 mol $MgCl_2.6\ H_2O$ in 0.5 liter demineralized water. The solution was saturated with carbon dioxide by bubbling CO_2 (industrial grade) during 48 hours (at 293 K). The closed glass bottle containing the carbonated solution was equilibrated at a temperature of 318 ± 1 K, much like a closed glass bottle containing 28 gr of a 25 % NH_4OH solution (p.A.) in 0.5 liter water. The amount of ammonia should be sufficient to convert all of the magnesium chloride into magnesium carbonate. Immediately after adding the ammonia solution in one action into the magnesium chloride solution, a precipitate formed. After filtering off and washing with demineralized water, the filter paper was dried at room temperature. Because the filter paper remained wet, additional re-suspension, filtration and washing was needed. Only then a dry precipitate could be obtained for X-ray diffraction. The precipitate from this experiment was found to consists of $Mg(OH)_2$.

In my next experiment 0.2 mol ammonium carbamate $NH_4CO_2NH_2$ (p.A.) was dissolved in 0.5 liter water. In another 0.5 liter water 0.1 mol $MgCl_2.6\ H_2O$ were dissolved. Both solutions were first equilibrated at a temperature of 318 K, and after that poured in one action into a large glass beaker. It took some 2 hours before a precipitate formed; after filtering off, washing and drying at room temperature X-ray diffraction was used for identification. The precipipitate was seen to consist of $MgCO_3.3\ H_2O$ (nesquehonite).

The third experiment involved the reverse reaction of the reaction mentioned by Waeser, that is to say the possible reaction between magnesium carbonate and ammonium chloride. To 0.5 mol demineralized water 0.5 mol NH_4Cl (p.A.) kept at a temperature of 333 K during the whole of the experiment, 0.6809 gr of a finely powdered, pure sample of natural magnesite from Radenthein (Austria) was added. After reacting for 14 days the remaining precipitate was filtered off, washed, dried and X-rayed. The precipitate still consisted of magnesite, but it weighed only 0.4839 gr. In other words 29 % of the initial amount of magnesite had been dissolved (as magnesium chloride). Taking the results of all three experiments together, it may be concluded that the claim made by Waeser (1923 / 1926) that the reaction mentioned by him would become reversible at temperatures above 303 K can not maintained. At a temperature of 333 K the reaction between magnesite and ammonium chloride takes place at a measurable rate. But the most important conclusion must be, that in static experiments lacking any fluctuations in free energy (p, T, x), no magnesite will be formed.