CHAPTER ONE

" DOLOMITIZATION" RECONSIDERED

WHAT DIAGENESIS ?

There has been no lack of speculation concerning the process of dolomite formation at low temperature. Early publications on the subject often contain the view, that dolomite would have been formed through the action of "magnesia-rich volcanic vapors" on pre-existing limestones (e.g., Von Buch, 1822 A; Karsten, 1848). Such volcanic vapors are not often found in the sedimentary environment. Therefore the magnesia-rich volcanic vapors of Von Buch (1822 A) and the "*dolomitisirende Gase*" of Karsten (1848) have gradually been substituted by percolating magnesia-rich solutions. Nowadays these percolating solutions seem to have many adherents, even though the actual relations between such solutions and the low-temperature nucleation of dolomite have yet to be demonstrated in reproducible laboratory experiments.

This is not the only objection against the suggested low-temperature conversion of pre-existing limestone into dolomite (= "dolomitization"). The main argument against "dolomitization" is, that the assumed chemical reaction will not take place at low temperature (around 298 K) and atmospheric pressure. **Calcium carbonate does not react with magnesium cations in solution at low temperature (around 298 K)**: no conversion of limestone into dolomite is therefore possible under conditions typical of the earth's surface. The reverse reaction does take place: a solution of calcium sulfate will change dolomite powder into calcium carbonate plus a solution of magnesium sulfate (Von Morlot, 1847 A,B,C). No reaction can be measured to take place at room temperature between calcium carbonate and magnesium sulfate or magnesium chloride in solution (Von Morlot, 1847 A,B,C; Liebe, 1855; Van Tuyl, 1916 B). Despite these basic observations the concept of "dolomitization" still persists today. It seems that the remark of Delanoüe (1854), that there is no such thing as "dolomitization", has not reached many geologists.[1] That observation is the more disappointing, because of the years gone by since Delanoüe (1854) made his remark.

Geologists often consider "dolomitization" to be one of the aspects of a process described as diagenesis. The concept of diagenesis as introduced originally by Von Gümbel (1868), was intended to describe the (metamorphic) transition of a carbonate sediment into a marble. Walther (1894) extended the definition to include a variety of wholly unrelated phenomena found in sediments, rock salt deposits and plutonic rocks as well as volcanic deposits.[2] Andrée (1911) restricted Walther's definition to apply to sediments only. In Walther's definition diagenesis would consist of "All those physical and chemical changes that influence a sediment after its sedimentation without any influence of heat or the weight of overburden" (translated from Walther, 1894, III, p.693). The concept of diagenesis will not be used in this book, because diagenesis cannot be considered to delineate a specific process operating in nature. Walther's definition sums up a variety of unrelated phenomena. What process could possibly explain at the same time compaction, phosphate deposition, anhydrite nucleation and the hardening of volcanic tuffs? Of course numerous processes may affect the sediment after its deposition, but a common factor will be hard to find in many, if not all, of these instances. At times a process of "metasomatosis" is made responsible for the formation of dolomite in sediments (e.g., Skeats, 1918 B). But then it must be realized, that in the definition of Emmons (1886) metasomatosis is essentially another name for the process of (chemical) replacement.[3]

The phenomenological approach based on the use of the concept of diagenesis has led to the postulation of perhaps as many modes of formation as there are known occurrences of dolomite. For every locality where Recent dolomite has been found some peculiarities have been chosen to suggest, that that set of circumstances, and no other, was responsible. This phenomenological approach created a diversity, which actually reflects the complexity of the local circumstances. Scientifically speaking such an approach certainly contributes to the diversification of the problem, but its significance towards a possible solution of the problem can be doubted.

MODELS OF DOLOMITIZATION

What are known as "models of dolomitization", but should be more adequately termed hydrological models, appear to have found their historic origin in the publications of Forchhammer (1849) and Bischof (1855). It was Forchhammer (1849), who had found dolomite in a layer topping in many instances the white chalk of Denmark. The bed is only a few decimeters thick and contains corals of the genus *Carophyllia* and *Oculina*. This layer has numerous outcrops in Denmark always in the same stratigraphic position, with the same fossils and nearly the same thickness. But at Faxöe Hill this formation is much thicker (some 40 to 50 m). Here the Faxöe limestone is covered by a layer of dolomite (which in turn is overlain by a thick bed of limestone made up almost entirely of bryozoa). The Faxöe Limestone[4] underneath the dolomite contains in general only 6 to 7 % $MgCO_3$ (in its pelecypoda and corals notably), and the bryozoan limestone on top of the dolomite layer contains a maximum of only 1 % $MgCO_3$. The dolomite occurs in a layer consisting of nodules; indicating according to Forchhammer (1849) its origin from springs (much like the pea stone from Carlsbad). An origin from springs was thought to be the more likely, because of the presence of a number of large, vertical tube-like cavities in the Faxöe limestone. Dissolution of the limestone by spring water was thought to be responsible for these pipes. Therefore the Faxöe Limestone as a whole must have been deposited by springs. Forchhammer (1849) attributed the origin of the dolomite nodules to a reaction between the calcium carbonate from springs and magnesium salts from sea water. The rounded form of the dolomite nodules was considered sufficient proof of the role played by spring water.[5] In order to obtain evidence for his point of view, Forchhammer (1849) performed numerous tests with spring water and sea water. When boiling for example Selters mineral water with sea water the precipitate formed was seen to contain 86.55 % $CaCO_3$ and 13.45 % $MgCO_3$.

Much like various authors before him Bischof (1855) thought, that dolomite could not have been formed by way of direct precipitation, but instead must have formed through the interaction of magnesium bicarbonate-containing solutions with limestone. After part of the calcium carbonate of a limestone had been dissolved by the bicarbonate solution, $CaCO_3$ and $MgCO_3$ would be able to follow their natural tendency and form a double carbonate.[6] Seawater was, still following Bischof, in fact such a bicarbonate solution, but it was apparently not able to change any calcium carbonate into dolomite. Despite the fact that seawater contained free CO_2 , calcareous skeletons or shells were not readily dissolved. Even the contrary seemed to be true: local, but large constructions of calcareous remains in the form of reefs were known, and as large-scale deposits known as limestones. In such limestone no evidence could be found of dissolution processes. But in sandstone such dissolution processes must have been active, because only imprints of fossils were found in most instances: the calcareous parts of those fossils must have been leached. The same phenomenon must have taken place in the case of dolomites; there too the calcareous remains had disappeared (at least in case of the dolomite found near Muggendorf, Germany described by Von Strombeck, 1831). The explanation for the phenomenon had been supplied by Apjohn (1838), Grandjean (1844) and Sandberger (1845): dolomite originates through the removal of "excess calcium carbonate" from limestones.[7] Therefore Bischof (1855) could only conclude, that during the formation of dolomite vast quantities of water must have percolated through the rock.[8] This process of dissolution was, in the interpretation of Bischof (1855), the very essence of the formation of dolomite. But whether dolomite would really form by way of replacement (*Austausch*) or by mere percolation (*Auslaugen*) could not be decided.[9] Doelter & Hoernes (1875) enlarged on Bischof's theory, and distinguished four different "hydrologic" models: 1) waters would remove calcium carbonate from magnesia-containing limestone and so lead to dolomite formation; 2) waters would remove calcium carbonate from limestone and introduce magnesium carbonate; 3) waters would introduce small amounts of magnesia, but at the same time remove more calcium carbonate; and 4) waters would introduce magnesia into the limestone, but would not remove calcium carbonate.

The percolation theory (or *Auslaugungshypothese*) seems to have received extra impetus through the work of Högbom (1894). While analyzing Pleistocene glacial tills from various locations in Sweden, Högbom (1894) observed how the percentage $CaCO_3$ decreased with an increasing distance away from the Silurian source rocks. But the percentage $MgCO_3$ remained virtually constant. In laboratory experiments, consisting of leaching samples of a marly shale with carbonated water, Högbom (1894) observed the same phenomenon of rapid removal of calcium carbonate and a virtual constant amount of magnesium carbonate.[10] Apparently the same process was acting in the world's oceans, because all 48 different analyses of deep-sea sediments listed in the Challenger Report (Murray & Renard, 1891) showed the same tendency. The great majority of the ancient dolomite rocks of course had not developed from glacial till or from marly shale, but instead must have found their origin in coral reefs. After explaining that Dana's (1872) theory of sea water as the source of the magnesium was quite untenable, Högbom (1894) postulated, that especially calcareous algae such as *Lithothamnium* were responsible for the incorporation of some 1.95 to 13.19 % $MgCO_3$ into reef limestone. The subsequent transformation of the magnesium-containing limestone into pure dolomites was clearly the result of the leaching process, removing much of the calcium carbonate.

It could be thought, that the theories of dolomitization mentioned are but historical examples. The contrary seems to be true. For example Högbom's (1894) theory of selective leaching of calcium carbonate has been fully confirmed by Chilingar (1956 B), who noted in laboratory experiments, that "... calcite is selectively leached out of limestones" (Chilingar, 1956 B, p.2492).

With some degree of certainty it may be concluded, that Bischof's theory of partial dissolution forms the basis of the "models of dolomitization" postulated by various 20th century authors: the "seepage refluxion model" of King (1947), Scruton (1953), Adams & Rhodes (1960) and Deffeyes et al. (1965), the "capillary concentration model" of Sherman et al. (1947)[11], the "evaporative pumping model" of Hsü & Siegenthaler (1969), the "solution cannibalization model" of Goodell & Garman (1960), the "groundwater seawater mixing model" of Hanshaw et al. (1971), the "evaporative drawdown model" of Maiklem (1971) and Kendall (1989); the "dorag dolomitization model" of Badiozamani (1973), the "geothermal springs model" of Fanning et al. (1981), the "storm recharge model" of Patterson & Kinsman (1982), the "Kohout convection model" of Simms (1984) and Saller (1984), the "tidal pumping model" of Carballo et al. (1987), the "sea water convection flow" model of Aharon et al. (1987), the "coastal mixing zone model" of Humphrey & Quinn (1989), the "eustatic pumping" model of Kaufman (1994), and the "evaporatic mixed-water dolomitization model" of Gill et al. (1995). All of these theories seem to compete in providing an explanation for the way in which seawater moves through the sediment, or how seawater mixes with rainwater. In fact all are hydrological models, and all of these lack any definite relation with the process of dolomite formation as such. The possible significance of all of these hydrological models towards the low-temperature nucleation of dolomite remains to be demonstrated in each and every instance.

HIGH-TEMPERATURE SYNTHESES

Probably the first ever synthesis of dolomite is that described by Von Morlot (1847 A). In that experiment fragments of calcite together with an amount of $MgSO_4.7\ H_2O$ were heated to 200^o R (= 523 K) in a closed glass tube. The glass tube was made to withstand the at least 15 bar pressure building up inside it during heating, by way of mounting it in a gun barrel filled with sand. The high temperature was reached by immersing the whole instrument in an oil bath, while heating. Wet chemical analyses were used by Von Morlot (1847 A) to identify the double carbonate dolomite, but in a second paper appearing that same year Von Morlot (1847 B) described to have used the dilute acid test to distinguish dolomite from other carbonates.

Favre (1849 A,B) related, how Marignac[12] had been able to synthesize dolomite from amounts of calcium carbonate and a solution of magnesium chloride. The conditions used were virtually the same as those described by Von Morlot (1847 A): the mixture was heated in a closed glass tube during 6 hours to 475 K. When heating the same mixture of $CaCO_3$ fragments with a solution of magnesium chloride during less than 6 hours, a double carbonate containing less magnesium carbonate than dolomite would be formed. A comparable high-temperature synthesis was performed by Durocher (1851): pieces of a porous limestone and magnesium chloride were heated together in a tightly closed gun barrel. The temperature reached was not measured, but Durocher (1851) stated, that the metal of the gun barrel attained a dark red color. After three hours of heating the reaction products were washed out and analyzed. Apart from unaltered limestone, magnesium chloride, calcium chloride, and a small amount of metal oxides, dolomite was found. Part of the dolomite contained iron carbonate. Durocher (1851) explained the iron carbonate to be the result of a reaction between the magnesium chloride and the iron of the gun barrel.

After remarking, that in the experiments of Von Morlot and Marignac high pressures were involved, De Sainte-Claire Deville (1858) described his own experiments, carried out at atmospheric pressure. A piece of chalk was impregnated with a solution of magnesium chloride, and heated in a platinum crucible to a temperature slightly above 373 K. That a reaction was taking place, was noted by De Sainte-Claire Deville (1858) because of the appearance of calcium chloride in the solution. But the reaction did not proceed very far: a maximum of 6 to 7 wt. % of the chalk was converted into dolomite. After washing the solution of magnesium chloride out of the piece of chalk and replacing it by a fresh one, the reaction would proceed further.

Hunt (1859) tried to repeat the experiment described by Von Morlot (1847 A) in the *Jahresberichte der Chemie* 1848 (that is to say Von Morlot's experiment with calcium carbonate plus magnesium sulfate hydrate heated during 4 hours to 473 K), but obtained mainly magnesite together with a small amount of calcium carbonate. After Hunt (1859) had repeated the experiment with the addition of some water to the mixture of calcium carbonate and magnesium sulfate hydrate, no dolomite was detected either: once more mainly magnesite with a little calcium carbonate formed. More successful were the attempts by Hunt (1859) to duplicate the experiment of Marignac (as described by Favre, 1849 A,B): after heating calcium carbonate with a solution of magnesium chloride during 8 hours to 493 K, dolomite was found (in wet chemical analysis) together with magnesite and calcium carbonate. In a different experiment

Hunt (1859) noted, how dolomite would be formed after heating calcium carbonate with magnesium carbonate tri-hydrate in a closed tube to a temperature of 448 K. Hunt (1866) synthesized dolomite by way of heating the precipitate, that formed upon adding a slight excess of sodium carbonate to a solution of equivalent amounts of calcium chloride and magnesium chloride in a sealed bronze tube to temperatures between 393 and 403 K.

Hoppe-Seyler (1875) observed dolomite formation after heating calcium carbonate powder with a magnesium bicarbonate solution in a sealed glass tube during 24 hours to 473 K. Similarly dolomite was found after heating sea water, carbon dioxide and calcium carbonate under the same conditions. Hoppe-Seyler (1875) even observed dolomite formation taking place at a temperature of 373 K: after keeping calcium carbonate and a magnesium bicarbonate solution for at least 90 hours at that temperature in sealed glass tubes, dolomite was found. After only 30 hours dolomite was detected in closed glass tubes containing calcium carbonate and a solution of magnesium sulfate heated to temperatures of 393 to 413 K. But no dolomite at all could be found by Hoppe-Seyler (1875) in experiments, in which temperatures below 373 K were used, no matter how long those experiments were continued.

Dolomite has been synthesized at a temperature of 403 K by Bourgeois & Traube (1892); in their experiment equimolal amounts of magnesium- and calcium chloride were added to a solution of KOCN, and subsequently heated in a sealed glass tube. Apart from aragonite a compound formed, which would not dissolve in acetic acid and which dissolved only very slowly in dilute hydrochloric acid. Chemical analyses showed the rhombohedra of this compound to consist of calcium- and magnesium carbonate, but too much of the latter compared to natural dolomite. Possibly a mixture of dolomite and magnesite had been formed. According to Klement (1894) a temperature of 363 to 365 K would be sufficient to create dolomite in the laboratory; his experiments consisted of boiling aragonite powder in sea water (with magnesium chloride as well as magnesium sulfate).

Kazakov et al. (1957) formed dolomite in tests, whereby a mixed Mg/Ca bicarbonate solution was heated to 423 K for 90 hours. Land (1967) synthesized dolomite in experiments conducted at 573 K. Baker & Kastner (1981) synthesized dolomite at 473 K from solutions containing magnesium chloride, calcium chloride, sodium chloride, and calcium carbonate. Baron (1958, 1960) and Baron & Favre (1958) synthesized dolomite from a solution of calcium- and magnesium chloride mixed with sodium carbonate, heated to a temperature of 523 K while under a pressure of 47 bar. Vlasova & Valashko (1971) obtained dolomite in tests, in which temperatures between 423 and 473 K were reached and pressures ranged from 1 to 600 bar. Similarly Syromyatnikov & Vorobev (1974) synthesized dolomite from mixed magnesium-calcium bicarbonate solutions at 373 K, but in their experiments CO_2 pressure as high as 500 bar was used. Although Usdowski (1967) claimed, that he had synthesized dolomite from aragonite and a concentrated solution of magnesium chloride heated to 393 K, here too pressures higher than 1 bar were involved. In his experiments Usdowski had heated closed tubes, made to withstand the pressure developed inside the tubes. Heating for example to 393 K would cause a vapor pressure inside the glass tube of 2 bar. Heating to 453 K caused an increase in pressure to values near 10 bar (Usdowski, 1967). Maunaye et al. (1981) obtained dolomite in experiments conducted at 493 K and 20 bar pressure.

In many cases a direct relation between dolomite and high temperature reactions can be deduced from field observations. In those cases the dolomite is of metamorphic origin. Especially contact metamorphism has created considerable masses of the mineral dolomite. This type of paragenesis (dolomite contacting porphyry, granite, or other plutonic rocks) was described in the very paper, which introduced the mineral. Writing on the dolomite he had found near Bolzano (N.Italy), De Dolomieu (1791) distinguished two types of occurrences. The first type of dolomite was well bedded, often horizontally bedded, and contained fossils. The second type of dolomite was more massive, denser, and showed a semi-transparency, that resembled that of marble. The second kind of dolomite was found contacting a porphyry. Later Bischof (1855) clearly distinguished between high-temperature dolomite (the result of a *plutonische Metamorphose*) and dolomite originated by way of replacement of pre-existing limestone.

REPLACEMENT

Von Buch (1822 A) investigated dolomite occurrences at numerous locations in Germany, Austria and Italy. From his field observations Von Buch (1822 A) concluded, that dolomite seldom if ever contains fossils; that it had a more porous texture than limestone; and that in the Fassa Valley of southern Tyrol the masses of dolomite were always accompanied by a black augite porphyry. This plutonic rock would have been instrumental in the conversion of the older limestone into dolomite. The dolomite rocks of the Fassa Valley would invariably contain pores and cavities lined with minute crystals, and Von Buch compared it with the same phenomenon in burnt limestone fragments from kilns described by Tennant (1799). Furthermore Von Buch (1822 A) mentioned, that pieces of dolomite had become known from the Vesuvius volcano. Taking all these observations together, Von Buch (1822 A) could only conclude, that the augite porphyry had changed the pre-existing, dark-colored limestone masses into the white masses of dolomite, and had destroyed both fossil content and bedding planes of the limestone. Having established this explanation for the formation of the dolomite in the Fassa Valley, Von Buch (1822 A) proceeded to declare this to be a universal principle. Dolomite would always be accompanied by an augite porphyry, which had caused its formation, and there where no augite porphyry was to be seen, the dolomite would still be in the stage of conversion and the augite porphyry would be hidden somewhere underground.[13]

Many geologists have followed the school of thought started by Von Buch (1822 A) and have explained the formation of dolomite in terms of a conversion of pre-existing limestone. For example Coquand (1841) stated, that dolomite in sediments had been formed through hot solutions from nearby plutonic intrusions after the deposition of calcium carbonate. The idea of magnesium "vapors" reacting with limestone was rejected by Élie de Beaumont (1854), because he had found in samples from the Fassa Valley sharp contacts between melaphyr and limestone without any sign of the supposed transformation into dolomite. Initially it had been postulated, that magnesia would enter the limestone rocks in the form of "vapors" [14] (a view advanced among others by Von Buch, 1822 A; Savi, 1830; Blum, 1843; Klipstein, 1843; Karsten, 1848 and Sismonda, 1854); but gradually the idea won more ground, that the pre-existing limestones had been converted by way of solutions of magnesium. Authors such as Provano de Collegno (1835), Von Morlot (1847 A) and Haidinger (1848) were convinced, that such solutions contained magnesium in the form of its sulfate; whereas others notably Virlet d'Aoust (1835) and Favre (1849 A,B) thought these solutions to contain especially magnesium chloride. Grandjean (1844) suggested prolonged exposure of limestone to rain water as leading to dolomite.

But there were also authors, who thought it necessary to contradict the suggested secondary change of pre-existing limestone. For example Zeuschner (1829), after visiting the same Fassa Valley dolomites of Southern Tyrol, pointed out, that the contact between dolomite and the black porphyry was not to be found at every locality where dolomite occurred. Such an association had been implied in Von Buch's (1822 A) theory. At the same time Zeuschner (1829) had found an intrusion of black porphyry into a limestone, in which instance the latter had remained unaffected by the intrusion. After analyzing a second porphyry, which had intruded into dolomite formations, Zeuschner (1829) observed, how the augite minerals of the porphyry had not been altered in a chemical sense. Such an alteration had to be expected, when assuming like Von Buch (1822 A), that the augite minerals would have supplied the magnesium necessary to change a limestone into a dolomite rock. But the main objection of Zeuschner (1829) against the "dolomitization" theory of Von Buch (1822 A) was of a chemical nature: how could calcium carbonate ever react with magnesium without leaving other traces of such a conversion? From these observations Zeuschner (1829) drew the conclusion, that dolomite had to be a precipitate from an aqueous solution: the fossils (crinoids mainly, but also some gastropods) found, were ample proof.[15] Meanwhile Von Buch (1824) had revised his theory of a high-temperature conversion caused by the contact with an augite porphyry into one he called the *Umwandlungs-Hypothese*: a secondary conversion of a pre-existing limestone must have taken place through the addition of magnesia.

Boué (1831), Bertrand-Geslin (1834), Wagner (1831, 1836), Reuss (1840), Petzhold (1843), Delanoüe (1854), Fournet (1849), and Von Gümbel (1871) all rejected the "dolomitization" concept. As a major argument against a possible secondary change, Boué (1831) cited the presence of fossils in the dolomite layers. Wagner (1831) pointed out, that Von Buch's (1822 A) own descriptions of the geology of southern Tyrol proved, that not in all instances a direct contact between dolomite and porphyry existed. After studying the dolomites of the Seisser Alm (N.Italy), Bertrand-Geslin (1834) suggested, how from the very moment of deposition these carbonate rocks had contained magnesium carbonate, and he excluded the possibility of any subsequent introduction of magnesium by way of percolating solutions.[16] Similarly Wagner (1831) concluded, that dolomite had not been deposited initially as calcium carbonate, to be changed in some later stadium into dolomite. Petzhold (1843) pointed out, that the stratigraphic relations between many dolomites and contacting limestone showed, how the formation of these dolomites could not have involved any intrusions by igneous rocks.[17] Reuss (1840) stressed the observation, that the association between dolomite and a black porphyry could not be seen in all instances. Even in Tyrol dolomite was not always accompanied by such an augite-prophyry, and several augite-porphyries were not accompanied by any dolomite at all.

After Fournet (1845) had read his paper on the regional geology of Tyrol at a meeting of the French geological society, a discussion followed, during which Virlet d'Aoust suggested an "epigenetic" origin for dolomite. Only direct precipitation could explain the well-developed bedding and fine laminations typical of many a dolomite rock. Delanoüe added to the discussion, that he had studied many dolomites in the *Alpes Ligurienes* and the Gulf of La Spezzia, and had not found any evidence in support of the *dolomitisation postérieure du calcaire*. Thin layers of dolomite intercalated in between layers of fossil-rich, well-bedded limestone would exclude any secondary conversion. Sea water would, in Delanoüe's (1854) explanation, be able to demolish in the course of a few centuries almost any limestone cliff, but it was apparently unable to change such a limestone cliff into a dolomite rock. (Much the same conclusion has been formulated by Hoppe-Seyler, 1875) The main objection against the assumed process of "dolomitization" (which, according to Delanoüe, 1854 should more adequately be described as *magnesitization*) was, that dolomite can be found in undisturbed regular layers, containing fossils and organic matter, that showed no traces whatever of any secondary change. Liebe (1855) wondered why, if for the moment one would assume the secondary conversion of limestone into dolomite, only local and rather restricted occurrences of gypsum or anhydrite were found in the neighborhood of dolomite formations. Why should this gypsum not be present in large amounts and in a homogeneous manner throughout the whole of such a dolomite formation? The formation of anhydrite from gypsum would constitute an additional problem to be solved. Von Gümbel (1871) concluded from stratigraphic relations, that dolomite was nothing but an original sediment. Dolomite could not have formed by way of the conversion of pre-existing limestone, because the contacting limestone did not show any trace of a secondary process of "metamorphism". Similarly Skeats (1905) rejected Von Buch's idea of "ascending magnesia-rich vapors" as the cause of dolomite formation as well as the suggested relation with volcanic rocks ("The early views of L. von Buch on the origin of dolomite were formed as a result of the examination of the dolomites of Tyrol, and they involved the ascent of heated magnesium-vapor from the outpourings of the Triassic volcanic rocks, which are found in association with the dolomites. Modern chemists would not agree with the chemical reactions involved in such a process, and, apart from this, the distribution of the dolomites has no causal relation to the distribution of the volcanic rocks": Skeats, 1905, p.131).

In a review on "dolomitization" theories Scheerer (1866) pointed out, that there were six different views known at that moment. The first and the oldest theory was that of the "magnesia vapors" reacting with limestone. This theory had been advanced especially by Von Buch (1822 A), but the concept had been outlined earlier by Arduino (1779) and Heim (1806). Criticism on this particular theory had been formulated by Petzhold (1843), who had demonstrated the absence of any suggested relation between the $MgCO_3$ content of limestone and the occurrence of a porphyry in the vicinity of this limestone. Similar objections had been published by Von Richthofen (1860). The second theory involved a reaction between limestone and a solution of magnesium sulfate. Authors such as Jacquemont (1824), Haidinger (1831)[18] , Provano de Collegno (1834), and Von Morlot (1847 A) had observed parageneses of dolomite and gypsum, and had suggested the possible reaction between limestone and a solution of magnesium sulfate. The third was comparable, in that it supposed a reaction between pre-existing limestone and a solution of magnesium chloride; a view advanced for example by Virlet d'Aoust (1835) and Favre (1849 A). The fourth theory of "dolomitization" was that of Frapolli (1847), who thought that dolomite formation had to be attributed to the actions of magnesium chloride vapor. The fifth subgroup of theories suggested a reaction between carbon dioxide-containing water and $MgCO_3$-containing limestone: much of the calcium carbonate of the limestone would be dissolved and the magnesium carbonate present would react to give dolomite. Authors advancing this view were for example Grandjean (1844), Studer (1844), Volger (1849), and Bischof (1855). The sixth theory was that of Nauck (1848) and Pfaff (1851): limestone would be partially dissolved by a solution of magnesium bicarbonate, and so be changed into dolomite. Most of these six different "dolomitization" theories receive little or no attention in the modern literature, with the exception of only one: the theory of Haidinger.

It is a historical fact that Haidinger knew very well, that no reaction takes place between calcium carbonate and a solution of magnesium sulfate, unless the mixture is heated to a high temperature. Haidinger (1844 A,B) had recounted the view of Wöhler, a view shared by Mitscherlich and Gmelin, that powdered dolomite would react under conditions of low temperature and atmospheric pressure with a solution of gypsum to give calcium carbonate plus a solution of magnesium sulfate.[19] More evidence in support of this view can be found in the paper by Von Morlot (1847 A), a paper published in Haidinger's own journal: there successful high-temperature synthesis of dolomite was described, but at the same time mention was made of the fact, that at ordinary temperature the reverse reaction would take place.[20] One year later Von Morlot (1848 A) expressed the same observation even more clearly: at room temperature a solution of calcium sulfate would change dolomite into calcium carbonate plus a solution of magnesium sulfate. But the reaction between calcium carbonate and a solution of magnesium sulfate leading to dolomite plus gypsum, would require a high temperature as well as high pressure.

The suggested secondary conversion of limestone into dolomite as made by Haidinger, albeit through Von Morlot's papers, has been commented on by several authors. For example Sartorius von Walthershausen (1855) pointed out, that the suggested reaction takes place only under conditions of elevated temperature and high pressures. At room temperature (and atmospheric pressure) the reverse reaction prevails.[21] In his textbook Mitscherlich (1835), described how a solution of $CaSO_4$ will replace the Mg-cations from solid $MgCO_3$, but replacement of Ca-cations by Mg-cations from solid $CaCO_3$ does not take place. It is worth recalling, that for example Hunt (1859, p.171) noted: "Thus, according to Mitscherlich, magnesite or dolomite slowly transforms a solution of gypsum into one of sulfate of magnesia, carbonate of lime being formed at the same time. I have observed a similar reaction between dolomite and a solution of chlorid of calcium..".

LABORATORY EVIDENCE

In a multitude of laboratory experiments it has been demonstrated, that no "dolomitization" reaction will take place at room temperature and atmospheric pressure. At the same time it is quite amazing to see, how this basic observation has gradually disappeared from the literature. It is therefore necessary to recall some of the laboratory work on the supposed "dolomitization" reaction.

Foremost stands of course the observation made in a laboratory experiment by Von Morlot (1847 A), that a solution of calcium sulfate reacts at room temperature with powdered dolomite to give calcium carbonate plus a solution of magnesium sulfate.[22] While describing his successful high-temperature/high-pressure syntheses of dolomite, Von Morlot (1847 C) noted, that a minimum temperature of 200^o R (= 523 K) was required. At lower temperatures no dolomite would be formed; under those conditions the reverse reaction would predominate, and no reaction took place between calcium carbonate powder and a solution of magnesium sulfate. Liebe (1855) added pieces of limestone to magnesium chloride solutions of different strengths, and kept these for one and a half year at room temperature. Chemical analysis revealed only calcium carbonate and not a trace of dolomite.[23] The impression might exist, that if solutions of magnesium chloride or magnesium sulfate will not react with calcium carbonate to give dolomite, a solution of magnesium bicarbonate might possibly do so. This idea has been investigated in laboratory experiments by Bischof (1855): in his tests, carried out at room temperature, no such reaction appeared to take place.[24] Hoppe-Seyler (1875) conducted laboratory experiments to investigate the possible reaction between calcium carbonate powder and sea water, through which carbon dioxide was bubbled. After 4 months no reaction could be detected; no dolomite at all had been formed. According to Hoppe-Seyler (1875) the reaction between calcium carbonate and magnesium sulfate in solution required a minimum temperature of 273 K.[25] Pfaff (1894) noted in his experiments, how gypsum will actually react with magnesium carbonate in a solution at room temperature to give calcium carbonate plus magnesium sulfate.[26] Leitmeier (1915) added a concentrated magnesium bicarbonate solution to powdered calcium carbonate: even after prolonged reaction time no change whatever could be noted in the mineralogy of the calcium carbonate used. Köhler (1928) added $CaCO_3$ in the form of vaterite to a solution of magnesium sulfate saturated with carbon dioxide. After 8 days of shaking the mixture (at room temperature), chemical analyses failed to show any trace of magnesium incorporated into the calcium carbonate. Rivière (1939) placed a piece of limestone in sea water and let it react during one year at room temperature. Chemical analyses after this prolonged period of immersion showed a slight increase in magnesium content, but no dolomite at all was found. Previously Linck (1937) had remarked (after conducting hundreds of laboratory experiments on dolomite formation), that the action of magnesium chloride or magnesium sulfate solutions on calcium carbonate had never, at least at low temperatures, produced any dolomite.[27] Much the same conclusion was reached by Marlowe (1971, p.824): "... lengthy exposure to sea water alone is not sufficient to cause the formation of dolomite by replacement". Berner (1966) noted in *in situ* field observations, how the aragonite and the magnesium calcite making up the main part of modern shallow-water carbonate sediments could not be measured to change into calcite plus dolomite. ("Carbonate sediments that have been in contact only with sea water throughout their history afford no evidence for the recrystallization of metastable high-Mg calcite and aragonite to low-Mg calcite and dolomite": Berner, 1966, p.34.)

Experimental evidence often cited in support of the supposed "dolomitization" reaction seems to have been provided by De Groot (1967). Close inspection of his experiments reveals something, which is different from what is being claimed. In the experiments by De Groot distilled water in equilibrium with atmospheric carbon dioxide was being percolated over gypsum powder and into a thermoconstant vessel filled with a dolomite suspension. The reaction took place at temperatures between 298 and 333 K. Chemical analyses made during the experiments, showed in all cases a steady increase in the amount of calcium carbonate. In one experiment, conducted at a temperature of 313 K during 140 days, even relatively large amounts of $CaCO_3$ were found in X-ray diffraction of the reaction products. Contrary to the conclusions drawn by De Groot (1967), his tests illustrate the validity of the observation of Mitscherlich, Gmelin and Haidinger (1844), that a solution of calcium sulfate will change dolomite powder into calcium carbonate plus a solution of magnesium sulfate. In experiments Yanateva (1956) had confirmed this observation.

In order to test the claim of Hoppe-Seyler (1875), that solid $CaCO_3$ will not react with magnesium in the form of its sulfate or chloride, the following laboratory test has been conducted by me. To 0.5 dm^3 water 0.02 mol $CaCO_3$ (calcite powder, MERCK art. no. 2064), 0.1 mol $MgSO_4.7\ H_2O$ and 0.1 mol $MgCl_2.6\ H_2O$ (both reagent grade) were added. In order to speed up a possible "dolomitization" reaction, the solution was heated to 353 K. The solution was kept at that temperature in an electric oven. The mixture remained in a large glass beaker covered with a watch glass. Gradual loss of water was replenished from time to time with additions of water. After 6 weeks the solid material present was filtered off, washed, air dried, and X-rayed. No dolomite, nor any other anhydrous Mg/Ca carbonate, had been formed: the only solid to be detected was calcite.

The statement of Hofmann et al. (1914) was also checked. To 0.5 dm^3 water 0.02 mol $MgCO_3$ (natural magnesite from Radenthein, Austria; analyzed for purity prior to the test by X-ray diffraction), 0.1 mol $CaSO_4.2\ H_2O$ and 0.1 mol $CaCl_2.2\ H_2O$ were added. The solution was kept at 353 K for 6 weeks. In this case most of the finely ground magnesite had been changed into aragonite. In addition to some gypsum only minor amounts of magnesite remained.

From the fact that magnesium cations in solution do not react with $CaCO_3$ at low temperature and the fact, that calcium cations in solution will react with solid $MgCO_3$ has important implications. The replacement of magnesium by calcium must have its origin in the electrochemical series of Berzelius (1836):[28]

Li-Rb-K-Ca-Na-Mg-Al-Zn-Fe-Ni-Sn-Pb-H-Cu-Hg-Ag-Pt-Au.

Berzelius (1836) pointed out, that the underlying principles of the electrochemical series dated back to Volta (1800) and especially Davy (1807, 1808), who had successfully used the electricity from Voltaïc cells in chemical reactions.[29] From these electrochemical experiments Davy drew the conclusion, that all inorganic chemical reactions find their origin in electric phenomena.[30] Experiments by Becquerel (1827, 1829) had shown the role of electricity in even the smallest of chemical reactions. Later developments led to instruments to measure the amounts of electricity involved, and thus it has become possible to measure accurately electro-

Li	- 3.01	Volt
Rb	- 2.98	
Cs	- 2.92	
K	- 2.92	
Ba	- 2.92	
Sr	- 2.89	
Ca	- 2.84	
Na	- 2.71	
Mg	- 2.38	
Ti	- 1.75	
Be	- 1.70	
Al	- 1.66	
V	- 1.5	
Mn	- 1.05	
Zn	- 0.76	
Ga	- 0.52	
Fe^{2+}	- 0.44	
Cd	- 0.40	
Co^{2+}	- 0.27	
Sn^{2+}	- 0.14	
Pb^{2+}	- 0.13	
H	0.000	
Cu^{2+}	+ 0.34	
Ag^+	+ 0.80	

Table I - Electrode potentials of metals in water (from Bockris & Reddy, 1970).

chemical potentials in units Volt (Table I).

Replacement taking place for example in the reaction AB + C → AC + B is according to Berzelius (1836) the result of a greater chemical affinity of C towards A, and this chemical affinity had its origin in electrochemical phenomena.[31] Reactions of the type

$$Ba^{2+} + CaSO_4 \rightarrow Ca^{2+} + BaSO_4 \qquad \text{(equation 1)}$$

are caused by this difference in affinity based on electrochemistry: the standard electrode potential of barium (- 2.92 Volt: Bockris & Reddy, 1970) is higher than that of calcium (- 2.84 Volt: Bockris & Reddy, 1970). The standard electrode potential of calcium (- 2.84 Volt) is higher than that of magnesium (- 2.38 Volt: Bockris & Reddy, 1970). The electrochemical series (or "replacement series" or "lyotropic series") shows that the low-temperature replacement of calcium by magnesium is not possible. On the contrary magnesium will be replaced by calcium (calcium being the more electropositive element).

HUNTITE AND NORSETHITE

In recent years the dolomite problem has been enlarged with two side-ways: one will have to consider the possibility of a process of "huntitization" and a process of "norsethitization".[32]

The mineral huntite, $CaCO_3.3\ MgCO_3$, has been described by Faust (1953) from the dolomite/magnesite deposits at Currant Creek, Nevada (USA). Although this particular deposit is of hydrothermal origin, Faust was convinced that the new mineral had been deposited by ".. cool waters in cavities and vugs". Numerous authors have since described huntite from comparable parageneses, where huntite would have formed from surface waters in the weathering zone of carbonate rocks. Examples include Koblencz & Němecz (1953), Baron et al. (1957), Skinner (1958), Golovanov (1959), Veen & Arndt (1973), Cole & Lancucki (1975), and Ivanov & Palgueva (1976). Huntite from caves was described among others by Pobeguin (1960), Paděra & Povondra (1964), Thrailkill (1971), and Fischbeck (1976). Huntite has been found in sabkha's by Kinsman (1967), Perthuisot (1971, 1974), and Schneider (1975). In ephemeral lakes the mineral occurs as well: reports by Irion (1970) and Irion & Müller (1968) document such occurrences.

There can be no doubt, that huntite, much like dolomite, can be formed even at low temperatures within a relatively short period of time: Cassedanne & Cassedanne (1963) found in a mine huntite, which could not have been older than 20 years. Syntheses of huntite have become known from the hydrothermal tests of Biedl & Preisinger (1962). In those experiments huntite formed at temperatures between 373 and 403 K and under CO_2 pressures of 3.2 to 18 bar. The alleged low-temperature syntheses of huntite by Davies et al. (1977) are difficult to reproduce, even difficult to evaluate. In those experiments nesquehonite reacted with carbonate sediments immersed in hypersaline brine in the presence of an abundant microbial population. The reaction time was 10 months; the temperature during the test was room temperature (between 293 and 303 K). The claim of Davies and co-workers that huntite (along with dolomite, hydromagnesite, calcite, and monohydrocalcite) formed because of the high concentration of the carbonate anion groups, was not substantiated with experimental evidence. The highly complex and ill-defined nature of their system must have contributed much in this respect.

The structure of the mineral huntite has been analyzed by Graf & Bradley (1962). On the basis of powder diffraction photographs the conclusion was drawn, that huntite should be considered to belong to the orthorhombic R 3 2 space group. The rhombohedral unit cell, that resembles the cleavage rhombohedron of calcite and contains 1 calcium atom, 3 magnesium atoms, and 4 carbonate groups, with *a* = 60.75 nm and α = 102^o 56' . An alternative interpretation on the basis of a hexagonal symmetry led to a unit cell with 3 calcium atoms, 9 magnesium atoms, and 12 carbonate groups. Much like dolomite the mineral huntite consists of an ordered array of layers, populated exclusively with either one of the two different kinds of cations or with carbonate anion groups only. The alternation between these three different layers follows essentially the direction of the c-axis, but the lattice is complicated to some extent by the tilting of a number of the CO_3-groups (Graf & Bradley, 1962).

Another similarity between huntite and dolomite can be found in the dissolution behavior. Attempts to measure the solubility of huntite turned out to be problematical. Halla & Van Tassel (1968) stated that the dissolution of huntite in water involves an irreversible reaction.

A possible parallel between the low-temperature formation of dolomite and that of norsethite, $BaMg(CO_3)_2$, has been suggested by Lippmann (1967, 1973), Morrow & Ricketts (1986) and Böttcher (2000). The structure of dolomite would be "comparable" to that of norsethite, and the latter contained magnesium carbonate in an anhydrous form just like dolomite. At closer look however it is difficult to see, why the structures of dolomite and norsethite would be "comparable". In fact the dolomite lattice belongs to space group R 3 - C^2_{3i} (Wyckoff & Merwin, 1924) and the lattice of norsethite to space group R 3 2 - D^7_3 (Mrose et al., 1961). "*The analogy between norsethite and dolomite breaks down because Ba and Mg sites in the two minerals are very different. In norsethite Mg is octahedrally coordinated as in dolomite, but Ba is surrounded by 12 oxygens. Mg cannot fill the dodecahedral-Ba site and Ba cannot substitute into the octahedral-Mg sites*": Althoff (1977, p.778).

However there are certain parallels between dolomite and norsethite. Like dolomite, norsethite can be found in metamorphic carbonates (for example near Rosh Pinah, Southwest Africa: Steyn & Watson, 1967) and in sedimentary carbonates, that must have originated under low-temperature conditions (such as the Green River Formation carbonates: Milton & Fahey, 1960). A second parallel is perhaps that norsethite, much like dolomite, does not form by way of replacement ("barium carbonate may be left in contact with magnesium chloride solutions .. for more than a year without appreciable changes taking place": Lippmann, 1968, p.35). Because the reaction

$$2\,BaCO_3 + Mg^{2+} \rightarrow BaMg(CO_3)_2 + Ba^{2+} \qquad \text{(eq. 2)}$$

is not likely to take place at low temperatures (i.e., below 373 K), Lippmann (1973) concluded, that the analogous "dolomitization" reaction

$$2\,CaCO_3 + Mg^{2+} \rightarrow CaMg(CO_3)_2 + Ca^{2+} \qquad \text{(eq. 3)}$$

will not take place at low temperatures either.[33]

SOLID STATE DIFFUSION

The experimental evidence cited in the previous section makes it difficult to understand, how under low-temperature conditions a chemical reaction would take place between calcium carbonate and magnesium in solution. Because of this lack of factual evidence in support of such a reaction, some theories on "dolomitization" tend to describe the suggested reaction in terms of a very slow process of solid state diffusion. Such an idea was propounded initially by

Graf & Goldsmith (1956), who postulated, that magnesium calcite and "protodolomite" could be changed into dolomite by way of "... cation rearrangement by dry, solid-state diffusion within small crystalline units" (Graf & Goldsmith, 1956, p.174). Various authors have since taken up this suggestion. For example Baron (1960) suggested that the process of ordering of an initially formed anhydrous $MgCO_3$-$CaCO_3$ solid solution would take place by "*diffusion intracristalline*". Other authors have thought it necessary to restrict the extent of solid state diffusion to the outer few molecular layers of a dolomite crystal. In fact Peterson et al. (1966) postulated that diffusion would take place in a disordered surface layer of only one or two unit cells thickness. Because such an ultra-thin layer is beyond the resolution limits of X-ray techniques or even electron microscopy, it would effectively withdraw itself from observation (and verification for that matter).

Experiments have been described, that seemed to provide support for the theory of "dolomitization" by way of solid state diffusion. Baron (1960) prepared a quantity of magnesium calcite by mixing 50 cm^3 of a 0.5 N calcium chloride solution with 50 cm^3 of a 0.5 N magnesium chloride solution and adding 50 cm^3 of a 1 N sodium carbonate solution at a temperature of 423 K. At the start of the experiment an amount of carbon dioxide ice had been added, and the pCO_2 had reached an initial value of 4.9 bar. The reaction took place during 5 minutes in a closed pressure vessel, and during the heating phase a maximum pressure of 14.7 bar was reached. After X-raying Baron (1960), divided the magnesium calcite formed into two equal amounts. The first was used as a dry powder (after filtering off and washing the precipitate); the second half was mixed again with the initial salt solution. After adding another quantity of carbon dioxide ice, the two samples were enclosed again in the pressure vessel, and heated during 4 hours at a temperature of 423 K. X-Ray diffraction applied to the two different samples, showed according to Baron (1960), that the presence or absence of the salt solution had not at all influenced the conversion of magnesium calcite into dolomite.[34]

In the syntheses of Graf & Goldsmith (1956) temperatures of 763 K and more were used. At such high temperatures cation ordering can take place, because of the increase in kinetic energy of the ions ("... at elevated temperatures ionic mobility is great enough for cation ordering to take place": Graf & Goldsmith, 1956, p.174). This also forms the reason, why the claim of Kulp et al. (1951), who had measured "detectable ionic substitution" among the cations in mixed Ca-Fe-Mn carbonates, seems to be justified: in their experiments the carbonates were heated to temperatures of at least 1323 K. At low temperatures (around 298 K) the two different cations of dolomite do not possess sufficient kinetic energy for solid state diffusion and "spontaneous" processes of cation ordering. Measurements with radioactive isotopes confirm this observation. In fact the ionic mobility of cations in the calcite lattice at room temperature is so low, that it cannot even be measured at that temperature. Brätter et al. (1972) were able to estimate the ionic mobility of calcium cations in calcite. Using Ca^{45} and Na^{22} as tracers, the Ca^{2+} self-diffusion coefficient and the Na^+ diffusion coefficient could be established at elevated temperatures. Calcite crystals were heated in a CO_2 atmosphere to 1073 K. At that temperature the diffusion rate of Ca^{45} could be measured. Other calcite crystals were heated and exposed to quantities of the sodium isotope, and diffusion rates of Na^{22} could be established after cooling down and leaching successive layers of the crystal parallel to the labeled reaction face. Even after heating to 1073 K, actual measurements were difficult to make because of the low rates of diffusion. Nevertheless Brätter and co-authors have estimated, that the self-diffusion rate of calcium cations in calcite was less than 5×10^{-16} $cm^2.sec^{-1}$, and that the diffusion rate of sodium cations into the calcite lattice would be less than 10^{-52} $cm^2.sec^{-1}$. Accepting these findings opens the possibility to estimate the time, which would be required to "dolomitize" a small crystal of calcite. Even a very small volume of calcite, say 10^{-4} cm^3 , would require for its 99 % conversion into dolomite at least 10^5 years according to Brätter et al. (1972). Modern dolomite younger than 100,000 years therefore provides evidence against any suggested process of alteration by way of solid state diffusion. "The idea of cation replacement as the main mechanism for dolomite seems improbable... "(Brätter et al., 1972, p.53).

Adsorption of magnesium and calcium ions from artificial seawater onto polished surfaces of calcite has been quantified in scanning Auger microanalysis by Mucci et al. (1985). In those analyses no indication could be found for the existence of solid state reactions between the bulk of the (magnesium calcite) crystal and its outermost adsorbed layers. In the experiments by Fisler & Cygan (1999) the diffusion of calcium and magnesium cations into calcite has been measured by way of Mg^{25} and Ca^{44} tracers at temperatures between 823 and 1073 K. Diffusion coefficients of calcium cations in calcite of 5×10^{-17} $m^2.sec^{-1}$ at a temperature of 823 K to 245×10^{-17} $m^2.sec^{-1}$ at 923 K were measured. At the same time diffusion coefficients for magnesium cations in calcite of 39.8×10^{-17} $m^2.sec^{-1}$ at 823 K to 12.6×10^{-4} $m^2.sec^{-1}$ at 1073 K (Fisler & Cygan, 1999).

The measurements by Brätter et al. (1972), Mucci et al. (1985) and Fisler & Cygan (1999) appear to confirm in a way the earlier observations of Lahav & Bolt (1964), who had measured the self-diffusion coefficients of Ca^{45} added in the form of calcium chloride to suspensions of calcite or dolomite. The calcite and dolomite were ground to a grain size smaller than 5 micron. For calcium cations in solution in contact with calcite powder, a self-diffusion coefficient of 8×10^{-20} $cm^2.sec^{-1}$ was found. For calcium cations in solution in contact with ground dolomite, a value of about 10^{-20} $cm^2.sec^{-1}$ was measured. Such extremely low values for diffusion coefficients effectively preclude any active role for the process of solid state diffusion in the low-temperature formation of dolomite. Hence the conclusion of Graf & Goldsmith (1956, p.185): "The virtual absence of dry diffusion in carbonates at earth-surface temperatures is shown by the persistence of metastable magnesian calcites in fossils as old as Eocene (Chave, 1954 B) that were embedded in relatively impervious shales." Much like Brätter et al. (1972) before them, the diffusion experiments led Fisler & Cygan (1999) to the conclusion that dolomite formation at low temperatures (around 303 K) can not take place by way of cation diffusion. Instead dolomite formation might well involve "solution and precipitation" (Fisler & Cygan, 1999, p.1398).

More observations that contradict the suggested role of solid state diffusion have become known from isotope studies. On the basis of measurements of the exchange between isotope-labeled carbon dioxide and calcite at a temperature of 576 K Haul et al. (1953) concluded, that no diffusion into the crystal takes place. Only an extremely thin outer layer of the crystal, in fact only one monolayer of calcite, would be involved in exchange processes. Using the same technique of isotopic exchange, Haul & Stein (1955) measured a diffusion coefficient of CO_2 into calcite of 5×10^{-17} $cm^2.sec^{-1}$ at a temperature of 973 K. Anderson (1969), using isotopes as tracers, demonstrated that diffusion of oxygen or carbon does not take place in carbonates at room temperature. From their measurement on the distribution of C^{13} and C^{14} isotopes in the modern dolomite formed in the rivers of the Coast Range of California, Barnes & O'Neil (1971) concluded that dolomite is a primary precipitate and that dolomite could not have been formed by way of an incorporation of magnesium cations into pre-existing calcium carbonate. Similarly Benson & Matthews (1971) concluded, after studying the Mg^{2+} distribution in carbonate cements of the Pleistocene rocks of Barbados, that even after 700,000 years no trace of solid state diffusion could be detected with the electron microscope. Dynamic computer simulations of the possible absorption of magnesium cations from solution onto a calcite surface, and their possible incorporation into the bulk of the calcite crystal, led De Leeuw & Parker (2001) to conclude that once the magnesium cations are incorporated in the surface layer, they will remain there instead of diffusing into the bulk crystal.

The multitude of isotopic measurements made on dolomite for age determinations can be considered to supply as many pieces of evidence against any suggested secondary conversion of carbonates after their deposition. It is the absence of any measurable degree of solid state diffusion, which accounts for the preservation of the delicate differences in calcium, magnesium, carbon, and oxygen isotopes in the sedimentary environments. Even after millions of years that followed upon their deposition, the anhydrous Mg/Ca carbonates appear to have maintained the isotopic composition of the very moment of nucleation. No secondary changes appear to have affected these carbonates and their ultimate components, the atoms and the molecules.

MICROTEXTURES

More evidence against the "dolomitization" reaction comes from investigations on the ultrastructure of dolomite crystals. By way of thinning dolomite to extremely thin foils and using these foils in transmission electron microscopy, Reeder & Wenk (1979) revealed the existence of a regular microtexture in dolomite ("tweed texture"), consisting of a more or less regular pattern of dark/light contrasts resembling to a certain degree the appearance of spinodal decomposition[35] microstructures. The wavelength of the modulation varies from sample to sample, but ranges commonly from 75 to 200 Å. Blake et al. (1982) confirmed the occurrence of this particular microtexture in dolomite. Comparable modulated textures had been detected previously in a number of alloys, including Cu-Au, Nb-O, Ni-V (Van Landuyt, 1964) and Cu-Be (Tanner, 1966). The dolomite samples studied by Reeder & Wenk (1979) were calcium-rich (containing 3 to 6 mol % excess $CaCO_3$), and ranged in age from Lower Paleozoicum to Quaternary. After applying various techniques of electron diffraction and optical modeling, Reeder (1981) came to the conclusion that this microtexture of dolomite must have been caused by fluctuations in the basal spacing of the lattice. But later Reeder & Prosky (1986) became convinced that the pattern was caused by different orientations within different growth sectors of a crystal. Additional support for this view came from measurement of the modulation's long dimension, which was invariably found to be parallel to the growth normal (Reksten, 1990). Growth zones were also present in electron microscopy of (Ca-rich) dolomites in the form of a fine growth banding (which is always perpendicular to the orientation of the modulated structures). Such growth zoning is irregular in its dimensions: it may range from 75 Å to as much as 1 μm. Dislocations in (Ca-rich) dolomite are quite common according to Reeder (1992). The orientation of these growth dislocations is usually parallel to the trace of the modulated structure and perpendicular to the fine growth zoning.

Finding microtextures in Paleozoic dolomites, that had been buried to considerable depths during lithification, as well as finding it in Recent dolomites, that have never been subjected to any form of burial, excludes any possibility of secondary changes. No changes involving solid state diffusion appear to have affected these dolomites. “Compositional zoning in crystals many million years old suggests that mass transfer on a scale as small as 10 μ (or less) is effectively precluded by slow diffusion rate”: Reeder (1981, p.155).

Additional evidence comes from magnetization measurements on ultra-fine grained (0.05 to 0.1 micrometer) biogenic magnetite found in Quaternary dolomites. Most probably through bacterial activity magnetite/maghemite crystallites of about 4,000 to 100,000 nm diameter were deposited at the sedimentary interface (Stolz et al., 1990). Individual grains retain the magnetic polarity of the moment of formation, even after recrystallization of the original aragonite into magnesium calcite or even after "recrystallization" into dolomite (McNeill, 1990). As McNeill & Aissaoui (1991) put it: no process of recrystallization had apparently been able to change the geomagnetic orientation of the magnetite particles in "dolomitized" carbonates.

DISCUSSION

Consistent failure met in attempts to synthesize dolomite at room temperature, must have initiated a more or less general conviction, that dolomite does not form at low temperatures.[36] Extrapolation and interpretation of the more successful high-temperature syntheses created the idea, that "... a very slow process of replacement" would be involved. This process of replacement would be so slow, that it could not be observed or measured. Notwithstanding the speculative character of the suggested process, numerous authors appear to have taken up the suggestion.

That a certain chemical reaction actually takes place requires proof in the form of a test, usually conducted in a laboratory set-up. Trivial as the observation may seem, it touches nevertheless the very core of the discussion on the possible existence of any "dolomitization" reaction. It will be clear, that a possible chemical reaction cannot be postulated merely on the basis of observations made on sedimentary rocks in the field or in thin-sections. Even so geologists have been using this phenomenological approach as their only tool. The fallacy of this approach can be demonstrated with little difficulty. For example Van Tuyl (1916 A) explained, that the so-called mottled limestone (limestone containing patches enriched in dolomite) showed "... an incipient stage in the process of dolomitization". Van Tuyl's conclusion, that therefore many dolomites must have passed through a comparable stage in the reaction between the magnesium of sea water and the carbonate sediment, could not be maintained after scrutinizing additional evidence. It was Van Tuyl himself who, in a second paper published in 1916, offered several arguments against any secondary process of "dolomitization". For example: 1) zoned crystals, with alternating sequences of calcite and dolomite, illustrating that simultaneous precipitation of the two minerals was possible. 2) Carbonates that did not consist entirely of dolomite, showed how the accumulation of dolomite crystals followed primary sedimentary features instead of following secondary features such as cracks or joints. 3) The mottling of mottled limestone was not uniform, which would have been the result of a chemical reaction between a more or less homogeneous carbonate sediment and seawater. 4) Grain-to-grain relations near dolomite crystals indicated, that the dolomite crystals must have formed before the sediment became lithified. 5) The widespread occurrence of virtually uniform dolomite deposits proves, that dolomite must have been formed by "... an agent capable of operating uniformly over wide areas". 6) Many dolomite strata were directly overlain by pure limestone, which did not contain any dolomite, proving that the process of dolomite formation had been concluded before the overlying limestone layers were deposited.

The zoned dolomite crystals mentioned by Van Tuyl (1916 B) exhibit a series of concentric alternations between dolomite and another mineral such as calcite, hematite, siderite or even quartz. Zoned dolomite crystals have one aspect in common: the different zones follow the outline of the rhombohedron faces. One of the earliest accounts mentioning zoned dolomite crystals, is that by Skeats (1903), who had worked on cores from the Funafuti Atoll. Zoned dolomite crystals have been described (or depicted) by among others Cullis (1904), Cayeux (1935), Shearman et al. (1961), Evamy (1963), Deininger (1964), Murray (1964), Friedman & Sanders (1967), Goldberg (1967), Perconing (1968), Katz (1968), Abou-Khadrah & Khaled (1978), Reeder & Prosky (1986), Buelter & Guillmette (1988), Cander et al. (1988), Gregg (1988), Holail et al. (1988), El-Sayed et al. (1991), and Humphrey (2000). Not replacement, but primary precipitation is the most likely cause for the inherent alternation between dolomite and the other minerals: "The texture of the calcian and ferroan dolomite zones and their crystallographic orientation ... show that they represent growth stages of the dolomite crystals" (Katz, 1971, p.45). The zoned dolomite crystals studied by Katz (1971) must have been deposited in a very shallow marine environment, which was exposed periodically to the atmosphere. Evidence for that particular conclusion came from petrographic examination, from the observed sedimentary structures in this formation, and from palaeontological analyses. Richter (1974 B) described zoned dolomite crystals from Devonian limestone in the Eifel Mountains (Germany), and came to the conclusion, that variations in the magnesium ion concentration of the sea water had been responsible for the phenomenon.

Although Van Tuyl (1916 A,B) interpreted his field- and thin-section observations in a conscientious manner, examples to the contrary are known as well. What to think of a statement like "The structure is exactly like what would result if beds closely resembling Oolitic strata were changed into a crystalline rock by the replacement of half the lime by magnesia" (Sorby, 1879, p.85). Because Sorby (1879) failed to explain what mechanism had caused the conversion of pre-existing limestone into dolomite, it can never have been clear at beforehand, why the resulting rock looked as it did look. What Sorby (1879) described, presumably unintentionally, is of course a perfect circle reasoning.[37]

In their paper on the "*Growth of dolomite crystals*" Peterson et al. (1963) postulated an extremely thin layer of virtually molecular dimensions on the outer side of each dolomite crystallite to be instrumental in the creation of the ordered dolomite lattice. This thin layer itself was thought to be quite disordered, virtually amorphous, but it would be capable of introducing a certain form of molecular rearrangement responsible for the required ordering. Such a view is reminiscent of the more general theory of Madelung (1919), who had postulated, that all ionic crystals would possess an extremely thin outer layer with less ordering than the bulk of the crystal, because ions near the surface lack the regular interactions of the bonding forces within the lattice. There is of course no point in denying the actual observations made by Peterson et al. (1963); observations that were made while leaching in successive fractions crystals of Recent dolomite found in the Deep Springs Lake, California, but the interpretation of their results is open to doubt. The calcium-rich outer rims described by Peterson and co-authors may well mark the cessation of dolomite formation ("It should be mentioned that this Ca-rich rind, rather than indicating accretion of Ca and later diffusion of Mg inward, may only indicate that the final water in contact with the crystal was Ca-rich": Weaver & Beck, 1977, p.133).

Having realized the shortcomings of the phenomenological approach, a different approach must be considered. This new approach should center round the question "What conclusions are to be drawn from finding a certain chemical compound in nature, while at the same time this compound can be synthesized in the laboratory only at high temperatures?" One possible solution might be to deny the low temperatures prevailing in the sedimentary environment. In certain instances authors have used even this explanation. For example Favre (1849 B) thought, that the conditions under which Von Morlot (1847 A) had been able to synthesize dolomite (a temperature of at least 473 K and pressures of more than 15 bar) were very reasonable indeed. Water temperatures of 473 K and more could easily be created during submarine volcanic eruptions. And the required minimum pressure of 15 bar indicated, according to Favre (1849 B), that a water depth of at least 150 meter would be needed. Under those conditions a normal limestone, that had been deposited originally in warm and shallow sea water (as witnessed by its fossil content), could be changed into dolomite.[38] Nevertheless close inspection of the sedimentary environment, and especially those areas where modern dolomite has been found, will undoubtedly show, that temperatures above 473 K and pressures of more than 15 bar are perhaps unrealistic. Similarly unrealistic are those explanations of dolomite formation, which require high pressures of carbon dioxide, even though in laboratory tests dolomite can be synthesized in that manner.

A third possibility to explain the presence of dolomite in the sedimentary environment would be to introduce a new hypothesis, which would eliminate the initial contradiction. For example the hypothesis that dolomite will not be formed as dolomite, but that some (as yet unknown) secondary change of initial products such as calcite or aragonite, leads to the formation of dolomite. Apart from the philosophical observation, that a problem can never be solved by the introduction of a new one, justified objections can be raised against such a "dolomitization" reaction. Such objections find their origin in a number of laboratory experiments. The absence of the suggested reaction between solid calcium carbonate (whether calcite, aragonite or vaterite) and magnesium ions in solution has been established as early as 1847 by Von Morlot,[39] and additional evidence has been given in this chapter. It has been shown, that at low temperature only the reverse of the suggested "Haidinger reaction" takes place: dolomite in contact with a solution of gypsum converts into calcium carbonate plus magnesium sulfate in solution.[40]

Whatever theoretical approach is chosen, the problem was, and still is, much the same: no reproducible low-temperature syntheses of dolomite were known (up to 1999, that is). Despite this lack of actual evidence numerous authors have since repeated the suggestion, that dolomite can be formed only in a reaction between calcium carbonate and magnesium in solution. There is no point in citing all those journal papers, books, symposia volumes and dissertations, where this "dolomitization" theory has been repeated over and over again. Very few exceptions have become known. One of those very few was published by Johnston (1854).[41] But such exceptions have never received any great interest.

A curious diversification has meanwhile taken place: as early as 1875 the suggestion has been made, that because of the diversity of the various locations where dolomite had been found, a comparable diversity would exist concerning the very mode of formation of dolomite.[42]

However various objections against this suggestion have become known. For example Klement (1895) pointed out, that the assumed secondary conversion of a limestone rock requires it to be quite porous. The resulting dolomite had to re-crystallize again in order to become a more or less compact rock. In addition the large amounts of dissolved calcium carbonate had to have been deposited somewhere else, but in what form? Could all of these processes have taken place without leaving any such traces? In this respect Daly (1907, pp.109-110) stated: "... if we accept the leaching hypothesis or the hypothesis that dolomite is the result of metamorphic processes by which magnesium comes to replace calcium in ordinary limestone, we meet with very grave difficulties, long ago stated and never overcome. The rapid alternation of clean-cut beds of pure or nearly pure calcium carbonate with other clean-cut beds of magnesian limestone or dolomite is a fact hardly to be reconciled with these metamorphic theories. The metamorphism is, by these theories, accomplished through the activities of circulating underground waters; yet it seems impossible that such wholesale metamorphism could leave the original bedding so well marked". Nahnsen (1913) argued, mainly on morphological grounds, that the dolomite described by him, had been formed during the sedimentation of neighboring limestone. From a large number of chemical analyses Salisbury & Beck (1914) concluded, that magnesium had been present from the very moment of deposition of certain dolomite-containing limestone and that it could not have been introduced at some later stage. From experiments involving dye adsorption (staining) on dolomite, Steidtmann (1917) concluded, that few if any dolomites would have been formed by way of replacement of limestone. As convincing evidence Steidtmann mentioned the textural relations between dolomite crystals and such secondary phenomena as faults and fissures. It certainly is surprising to find, that Steidtmann rejected the idea of "dolomitization by recrystallization". From the fact that many magnesium calcites of organic origin had survived the ages, Steidtmann concluded, that dolomite could not have been formed under the influences of any secondary changes from pre-existing limestone.

In the absence of any process of "dolomitization" the relation between porosity and dolomite has to be explained in a different manner. After pointing out the economic importance of "local dolomitization porosity", Landes (1946) claimed the local porosity of many dolomites to be the result of excess dissolution over precipitation. Originally it had been Élie de Beaumont (1836), who had suggested, that the conversion of calcium carbonate into dolomite would have to be accompanied by a volume contraction of about 12 %. But Lindgren (1912) pointed out, how most geological replacements take place volume by volume and not molecule for molecule. By far the most convincing argument against "porosity through dolomitization" has been advanced by Murray (1930): the suggested conversion creating porosity has never been demonstrated to take place.

Of the more recent publications that by Taft & Harbaugh (1964) deserves special mention. The suggestion that aragonite and magnesium calcite would gradually react with seawater to form dolomite has been critically investigated by those two authors. In their field study Taft & Harbaugh noted, that there is no evidence to support the suggested transformation. No significant changes in neither aragonite nor magnesium calcite, which had been in contact with sea water for the last few thousand years, could be measured. When sediments consisting of calcium carbonate remain in contact with seawater (or saline pore water) for millions of years, no systematic increase in the percentage dolomite in those sediments can be detected (as Delanoüe, 1854 had observed). After studying 844 different samples of post-Jurassic marine sediments from the Deep Sea Drilling Project for its dolomite content, Lumsden (1985) could discern no large-scale increase in dolomite with increasing age for individual sites. Increasing percentages of dolomite down hole could have provided evidence in support of "dolomitization" theories.

There are still more objections to be made: one of the additional objections is to be found in the supposed "de-dolomitization"[43] reaction, as described for example by Teall (1903)[44], Jourdy (1914), Brückner (1941), Chilingar (1956 A), Shearman et al. (1961), Braddock & Bowles (1963), Evamy (1963, 1967), Schmidt (1965), Friedman & Sanders (1967)[45], Sass (1967), Goldberg (1967), Katz (1968, 1971), Folkman (1969), Braun & Friedman (1970), Schofield & Nelson (1978), Frank (1981), Back et al. (1983), Budai et al. (1984), Thériault & Hutcheon (1987), Dockal (1988) and Ayora et al. (1998). The process was explained in some detail by Evamy (1967, p.1204), who stated that "... dedolomitization is the reverse process of dolomitization", and that the reaction would be brought about by solutions with high Ca/Mg ratio's, which would be "... reacting with dolomite to form calcium carbonate". Symptomatically it was necessary to change the mineralogical name for $CaCO_3$ and it was "... termed "dedolomite" for convenience" (Evamy, 1967, p.1204). Not all geologists appeared to appreciate this sort of convenience: at least Smit & Swett (1969) protested, that the term "dedolomite" would be inconsistent with standard nomenclature, and added that the suggested term was ambiguous and misleading with respect to the chemical reaction, that it was thought to represent. Braddock & Bowles (1963) interpreted their field observations in terms of the low-temperature conversion of dolomite into calcite as the result of the reaction with calcium sulfate solutions. But many authors have chosen a different path, and persisted in using the term "de-dolomitization". An obvious consequence of such preference is, that one will have to recognize the process of "re-dolomitization" as well (as did for example Johannes, 1970; Clark, 1980, and Füchtbauer, 1980): *et ad absurdum*.

One of the last possibilities to explain the "dolomite problem" would consist of admitting, that no chemical reaction between $CaCO_3$ and magnesium in solution can be measured in the laboratory[46], followed by the postulation, that such a reaction does take place, but so slowly, that it withdraws itself from observation. The "time factor" is often invoked in want of adequate explanations. But then any process that is so slow, that it cannot be measured with modern instruments, is non-existent with respect to the means of observation available. In this sense too "dolomitization" is non-existent. Laboratory experiments by various authors in which radioactive tracers were used, show that no process of solid state diffusion can be made responsible for the low-temperature formation of dolomite. The reason behind this lack of reactivity in the solid state can be understood, when realizing the kind of forces that are involved. In clear contrast to metals, ionic crystals possess (at least) two different types of ions: anions and cations. The strong electrostatic attraction between anions and cations virtually prohibits a situation, in which a cation would be contacting other cations. Such a situation would result upon solid state diffusion. The possible extent of solid state diffusion in ionic crystals is therefore very limited: "In ionic crystals ... disorder has an extremely high energy, since the wrongly placed ion is surrounded by ions of like sign and is therefore subject to strong repulsive electrical forces. The energy, in fact, is so high that this effect occurs very rarely and plays no part in diffusion in ionic crystals": Girifalco (1964, p.82). Other authors were even more outspoken in their rejection of solid state diffusion in ionic crystals at low temperatures. For example Shewmon (1963, p.138) stated frankly, that solid state diffusion in ionic crystals by way of movement of individual ions "... is out of the question". The principal difference between metals and ionic crystals with respect to diffusion can be illustrated with numerous measurements. To give only a few examples (from Barrer, 1951, p.275): the diffusion coefficient for the migration of Au through Pb is 4.9×10^{-1} $cm^2.sec^{-1}$; that for the movement of Pt in Au is 1.24×10^{-3} $cm^2.sec^{-1}$; for the diffusion of Cu in Ag it is 5.9×10^{-5} $cm^2.sec^{-1}$; and for the diffusion of Cd in Cu this coefficient is 3.5×10^{-9} $cm^2.sec^{-1}$. With these four examples of diffusion of a metal into another metal the self-diffusion coefficient of calcium into calcite should be compared. According to Brätter et al. (1972) it is 5×10^{-16} $cm^2.sec^{-1}$. It will be clear, that this value is of a totally different order of magnitude than that of metals. The numerical data illustrate once more, that solid state diffusion invoked to explain the low-temperature formation of dolomite "... is out of the question".[47]