CHAPTER EIGHT

MECHANISM OF FORMATION OF MAGNESITE AND DOLOMITE

NUCLEATION AND STATISTICS

Crystallization requires a solution to be supersaturated. The first to make this observation was probably Lowitz (1794), and later the observation has been confirmed by other scientists such as for example Berthollet (1803), Gay-Lussac (1813), and Schweigger (1813).

In the view of Gay-Lussac (1819) the solubility of a salt would depend solely on the temperature of the solution. Loewel (1850) could not agree with the observation of Gay-Lussac (1819) because such a saturated solution might well contain much more salt in solution: it could become *sursaturée* (= supersaturated). After observing how a saturated solution of chromium alum suddenly crystallized after being exposed to a cold night, whereas the same solution kept at room temperature for 3 months did not show any precipitation, Loewel (1850) started out on a comprehensive investigation of the phenomenon. Supersaturated solutions of some salts were very unstable: shaking their glass tubes, breaking the tubes open so that contact with the open air took place, or bringing the solutions into contact with certain surfaces was sufficient to start crystallization. But other salts gave rise to remarkably stable supersaturated solutions. For example glass tubes containing a supersaturated solution of sodium sulfate could be stored almost indefinitely, provided that the tubes remained closed. When cooling the tubes, crystallization was never taking place at exactly the temperature at which the solution was known to become saturated. Loewel (1850) described, how crystallization invariably started several degrees below that temperature.¹

Gernez (1865 A) made the observation, that as soon as a tiny crystal of sodium sulfate is added to a supersaturated solution of this salt, crystallization sets in at once. Compounds such as sodium carbonate, sodium acetate, and magnesium sulfate would show the same phenomenon. At the same time Gernez (1865 A) noted, how dust present in the air of nearly every laboratory, if not specifically excluded from the solution, also initiates crystallization. Dust in Gernez' own laboratory was analyzed and found to contain traces of sodium sulfate. But after more analyses of laboratory air Gernez (1865 B) could not detect for example any sodium acetate, sodium carbonate or sodium borate, all of which of had been used previously to prepare supersaturated solutions.

Supersaturated solutions can be prepared in several ways as Lecoq de Boisbaudran (1866) has pointed out. Cooling down a hot saturated solution is one way; a second way is to mix two ingredients, that will react and so lead to the precipitation of the desired compound; and a third method consists of the evaporation at room temperature of a saturated solution. Once prepared such a solution will be not remain supersaturated for an indefinite period of time: lowering the temperature of the solution will almost always lead to the start of crystallization. Supersaturation also ceases upon contact with an isomorphous compound, even though the exact concentration at which this takes place, may vary from one isomorph to another.² Supersaturation takes place according to Lecoq de Boisbaudran (1866) not only with hydrous salts, but also in the case of anhydrous salts. The crystallization of a supersaturated solution could be postponed almost

indefinitely, when using dust-free instruments and containers.

De Coppet (1875) noted in his experiments on the precipitation of sodium sulfate from supersaturated solutions, that there is not one definite temperature at which crystallization starts spontaneously. Instead a certain range of temperatures was always measured. The variability could be explained by De Coppet (1875) only on the basis of the "mechanical theory of heat" advanced by Clausius (1857), Naumann (1867) and Pfaundler (1867). This theory considers the molecules making up a solution as being in an incessant movement: the heat movement. Not only in the gas phase but also in the liquid state the molecules are in constant movement, but each of the molecules at its own rate. The average of all of these movements is constant for a certain temperature, but it is in fact an average of many individual movements. Therefore Naumann (1867) made a distinction between *average temperature* and *molecular (or atomic) temperature*.

The mechanical theory of heat was used by De Coppet (1875) to explain the phenomenon of supersaturation in more detail. Two different situations had to be distinguished from each other, i.e. whether or not a crystallite was present in the supersaturated solution. In the first case molecules of the dissolved solid with a low "molecular temperature" will, when touching the crystallite, adhere to it. In the second case the molecules of the dissolved solid will, because of their low "molecular temperature", meet each other in between contacts with molecules of the solvent and adhere to each other. The difficulty with which the molecules of the dissolved solid crystallize spontaneously (*la cristallisation spontanée*: De Coppet, 1875, p.281) from a supersaturated solution, would be greatly increased by "the atomic configuration" of the solid being formed. Especially the dissolution behavior of the precipitate being formed, was known to play an important role. From supersaturated solutions not the anhydrous compound, used initially to make the solution, would crystallize, but in many cases a hydrate with its solubility notably higher than that of the anhydrous form would precipitate.³

At the end of his paper De Coppet (1875) added a Note additionelle, in which his observations on the spontaneous crystallization of sodium bromide were recorded. In an attempt to obtain some quantitative information, De Coppet had followed during five months the progress of nucleation in 35 different glass tubes filled with a supersaturated solution of NaBr.2 H₂O. Each day the tubes containing crystallites were listed (and the crystallites re-dissolved) and the maximum and minimum temperature in the laboratory room were recorded. From these data De Coppet (1875) was able to calculate, how long on average the state of supersaturation per gram solution remained. What was found, was a relation with the average temperature and a possible relation with the amount of solution used. But the time it took on average for crystallization to take place in the same set of glass tubes with the same solution, differed notably from earlier measurements. Those had been made at Giessen, Germany (in the laboratory of A. Naumann), whereas the second series had been measured in De Coppet's own laboratory in Nice, France. The little glass tubes filled with supersaturated solution crystallized on average 4.5 as fast in Giessen than in Nice. De Coppet (1875) did not believe this to be mere coincidence. During the experiments in Nice the maximum temperature had been 292.3 K and the minimum temperature 280.8 K; during the experiments in Giessen the maximum temperature had been 293.0 K and the minimum temperature 282.9 K. The average temperature in Nice had been 285.7 K and 288.1 K in Giessen. It would only be logical to find, that supersaturation had been maintained longer in the glass tubes during the experiments in Giessen. But De Coppet (1875) was inclined to correlate his measurements to an observation, he had made several times before: supersaturated solutions tended to crystallize guicker, when cooling was abrupt rather than when it was gradual (De Coppet, 1872). And in fact the glass tubes had been exposed in Giessen to rapid changes in temperature during the day, whereas the experiments in Nice took place in an unheated room, opened only once a day. In other words much less "transitions" (as De Coppet, 1875 put it) had taken place in the latter situation. The diurnal variation in temperature became clear from the measurements made: it had been 6.3 K in Giessen but only 0.8 K in Nice.

Like many others before him Tammann (1898) made the observation, that crystallization always starts in only a very few, isolated points (whether crystallization takes place from a supersaturated solution or from an undercooled melt). Never the immediate and complete transition into one large crystal could be seen to occur. What took place was, that with an increasing degree of supersaturation (or undercooling) the number of nucleï would increase. In an attempt to explain the observations made, Tammann (1898) distinguished two different aspects of the process of crystallization: "the power of spontaneous crystallization" (das spontane Kristallisationsvermögen) and "the linear velocity of crystallization" (die lineare Kristallisationsgeschwindigkeit). Spontaneous crystallization would be the more important aspect of the two: it delineated the actual number of spontaneously formed centers of crystallization at a certain temperature. (It must be kept in mind, that Tammann's account was concentrated mainly on the solidification of various organic compounds from undercooled melts). The second factor, the linear velocity of crystallization, had been studied by Gernez (1882), who had found, that the velocity of crystallization was a linear function of the degree of undercooling of the melt in the case of solidification and of the degree of supersaturation in the case of crystallization from a supersaturated solution. Tammann (1898) noted in his laboratory experiments, how from certain highly undercooled melts not one type of crystal would precipitate, but instead 2 or even 3 polymorphic forms of this substance.⁴ For example compounds such as quinic acid, R-camphoric acid, santonin and chloralurethane showed the formation of 2 different nucleï, whereas compounds such as allyl thiourea, resorcinol and vanillin gave rise to 3 polymorphs upon the solidification of their undercooled melts.

Numerous experiments involving counts of the number of nucleï developed in one of the organic compounds at different degrees of undercooling, led Tammann (1898) to (amongst others) the following conclusions: 1) the number of nucleï is very small when compared to the number of molecules, that must be involved; 2) the number of the nucleï increases with an increase in the degree of undercooling; 3) the number of nucleï is very sensitive towards admixtures, whether soluble or solid; 4) the temperature at which the maximum number of nucleï occurs, will not be greatly influenced by such admixtures; 5) from highly undercooled liquids two or more polymorphs may develop; 6) at one and the same temperature two or more modifications of the compound used, may occur; and 7) in many instances the temperature of the maximum number of the nucleï of the stable form is situated below that of the less stable form, but in some cases the reverse situation was found.

In his book on crystallization Tammann (1903) made additional observations on the factors, that will influence the number of nucleï forming. In the first place Tammann had found, that if the total amount of an undercooled liquid was small, there would only be a few centers of crystallization. But the number of nucleï was not a constant one. Even when repeating the experiment with the same quantity of liquid under identical conditions, the number of nucleï formed, would vary. Othmer (1915) pointed out, that this variation in the number of nucleï must necessarily find its origin in the atomistic nature of liquids.⁵ Using the method of Tammann⁶, Othmer (1915) conducted a very large number of congelation tests, leading to the conclusion, that the variation in the number of nucleï formed (*Kernzahl*) was the larger, the smaller the number of tests. When large numbers of tests were conducted, a more precise average would be obtained. The number of nucleï appeared to fluctuate around a certain average. Little or no doubt could prevail as

279

to the nature of the observed variation around an average value: statistical variation based on mere chance would be involved. Othmer (1915) was even able to prove his theory by way of imitating his own 50 different tests by throwing 6 dices 50 times. The overall results were identical with those of the crystallization tests.

Comparable experiments have been carried out by Kornfeld (1916). Her tests were conducted specifically to investigate the possible role of statistics in nucleation processes (in the congelation of melts as well as in crystallization from solution⁷), and to check the observation made by Füchtbauer (1904), that every experiment in this field would render results different from other experiments. By virtue of the very large number of tests (one thousand), Kornfeld (1916) was able to show, that the number of nucleï formed, was indeed subject to statistical variation. The observed variations in the time at which small amounts of salol in glass tubes would crystallize were the smaller, the larger the number of tests performed. At the same time the observed statistical variation might well explain the observed differences among different authors describing the same experiment, or even differences among identical crystallization tests conducted by one and the same scientist. The values of concentration, pressure, or temperature now appeared to be but crude approximations, gross averages, when considering the atomistic phenomena, that underlie crystallization processes. Therefore it may seem, as Kornfeld (1916) put it, that under identical conditions maintained during crystallization experiments, different results are obtained. In other words the experiments by Kornfeld (1916) confirmed the initial hypothesis on the movements of individual molecules: pressure and temperature are but average values showing statistical variation, when looking at a molecular level. It was Von Smoluchowski (1916), who had pointed out such "concentration fluctuations" (Konzentrationsschwankungen)⁸ are made visible by the Brownian motion.

In 1828 Brown had reported, how finely divided pollen in water were seen to be in incessant motion. A first theoretical explanation for this phenomenon was provided by Thirion (1880), who suggested that impacts of individual water molecules must be held responsible for the characteristic irregular movements of the relatively large pollen in water. Observations with the ultramicroscope by Siedentopf & Zsigmondy (1903) provided additional evidence for this interpretation. In a mathematical analysis of the phenomenon Einstein (1905) explained, that the particles of the suspension must be obeying the same kinetic principles, that apply to the atoms and molecules of the solution itself. The fluctuating movements of the particles had to be the result of the incessant bombardment by a multitude of surrounding molecules in the solution. Einstein (1910) came to the conclusion, that because of the Brownian motion of the particles making up a solution, local differences in concentration are inevitable.⁹

STABILITY AND METASTABILITY

The original definition of metastability given by Ostwald (1893) in his textbook on general chemistry, is clearly of a thermodynamic character. Following the analogy with mechanics, the *labile* state could be defined according to Ostwald (1893) as that state of equilibrium, in which even the smallest of displacement suffices to start the system striving to a new equilibrium (for example a pyramid standing on its apex would constitute such a labile system; a pyramid in its normal position would be in the *stable* state, where its energy is at minimum). But there would be other systems, in which more than one stable state occurred: several minima in energy were separated

from each other by relative maxima. These "in between" minima were the *metastable* states. Typical for such a metastable state was the need for a supply of energy, before being able to attain the stable state.¹⁰

Later, in a paper that appeared in 1897, Ostwald applied the new concept to the process of crystallization. By way of carrying out various experiments on the solidification of phenyl salicylate ("salol", a solid with a rather low melting point at 312.7 K), Ostwald (1897) tried to unravel the mysteries of the phenomenon of undercooling. The elaborate tests led Ostwald to the conclusion, that solidification did not always take place at exactly the same temperature. Ostwald (1897) was led to the conclusion, that when cooling a liquid under its usual melting point, a certain temperature trajectory will be reached, where the introduction of amounts of the same solid (or of an isomorphous compound) will cause crystallization, but no other means could induce crystallization.¹¹ Only after cooling the liquid still further, spontaneous crystallization would commence. Below a certain temperature, markedly below the temperature known as the melting point, the process of solidification could start and not above that temperature. Ostwald (1897) summarized his investigations by formulating a general principle that has become known as *Ostwald's Rule:* upon a change of phase, whether crystallization, melting or condensation, not the most stable state will be reached, but the state next to it.¹²

Because the presence of small amounts of the same (or an isomorphous) solid inducing crystallization is characteristic of the metastable state, it is impossible to speak of a metastable state in the absence of that other solid. Much like the concept of stability, metastability appears to possess a relativistic nature.

Ostwald's student Schaum (1898) performed experiments on the solidification of benzophenon and confirmed in principle the existence of a metastable phase. A distinct boundary separating conditions under which the metastable modification forms and those conditions under which the stable modification precipitates, was found. But to his surprise Schaum (1898) had to experience, that in many instances the *stable* form of benzophenon was the first to originate (Schaum & Schoenbeck, 1902 repeated this point). The conditions required to precipitate the metastable modification of benzophenon were so exceptional, that in only few instances this metastable phase actually formed. In all other instances the stable form was the first to precipitate, and when the metastable phase did form, it quickly changed into the stable form. After performing additional laboratory experiments with phenol and salol, Schaum (1898) arrived at the conclusion, that precipitation of the stable phase instead of the metastable phase could not only be caused by the introduction of nucleï of the stable phase, but also by "certain external factors". What exactly these "external factors" were, was apparently not quite clear to Schaum (1898), since he did not elaborate. But in conclusion the observation was repeated, that within the metastable field the stable phase could very well be precipitated (as Schaum remarked, these observations were at variance with those made by Ostwald, 1897). In his 1899 paper Schaum reported to have observed the stable phase crystallizing before the metastable phase in the case of compounds such as hexachloroketodihydrobenzene, 1-menthol, 2,4-dinitro-1-chloro benzene, triphenylmethane and even sulfur (as Brauns, 1900 had discovered). In 1902 Schaum & Schoenbeck openly rejected Ostwald's definition of the metastable state, because in their view too many cases of the stable form of a particular compound crystallizing before the corresponding metastable polymorph, had become known.¹³ Crystallization of the stable phase before the metastable phase would of course be favoured by conditions counteracting the possible formation of the metastable phase (Schaum & Schoenbeck, 1902).¹⁴

In his book on "Kristallisieren und Schmelzen" Tammann (1903) critized Ostwald's concept

of metastability. In Tammann's explanation, metastability would be nothing less than an artefact due to the rather small quantities of molten solids used in the experiments of Ostwald. Especially when the degree of undercooling was not too large, the development of a few first nucleï would require some time, when using small quantities of a molten compound such as n-betol (= β -naphtylsalicylate-n). As a result the impression of a boundary of sorts would be created.¹⁵ At the same time Tammann (1903) pointed out, that according to Gibbs (1876/1878) the stability of a system is given by an entropy difference between the initial and final state.¹⁶ And Gibbs had been quite aware of the fact, that crystallization never was instantaneous and homogeneous. Because crystallization took place by way of a restricted number of very small nucleï, Gibbs (1876/1878) had had to introduce an additional term, the *surface energy*, into his calculations.¹⁷ But, as Tammann (1903) stressed, no method existed to measure that *surface energy*, and therefore Gibbs' concept of stability could not be used for all practical purposes.¹⁸

Criticism on Ostwald's introduction of a *metastable* state was published by De Coppet (1907). According to De Coppet, that in formulating his new theory, Ostwald (1897) had neglected the underlying atomistic notion of solutions in general and of that of supersaturated solutions in particular. This was the more astonishing, because at various occasions Ostwald had used the atomistic model. But as De Coppet (1907) remarked, Ostwald had really declared the kinetic theory incompatible with the existence of supersaturated solutions or undercooled melts during longer time intervals.¹⁹ De Coppet (1907) thought, that the kinetic theory predicted only an increasing time interval for spontaneous crystallization to take place upon the lowering of the degree of supersaturation or the degree of undercooling, but definitely not its cessation. At the same time Ostwald had claimed, how *very small* changes of temperature or concentration could effectively prevent crystallization of supersaturated solutions or undercooled melts.²⁰ De Coppet (1907) did not go as far as to deny the existence of the *metastable* state, but cited Ostwald's own statement to prove, that no sharp and sudden transition from the metastable into the labile state could exist. For there too the transition could take place by way of very small increments.

Another objection raised by Ostwald against the kinetic theory applied to the phenomena of supersaturation, dealt with the differences found when preparing supersaturated solutions from soluble salts and those of the less soluble salts. The less soluble salts dissolve to a much lesser degree in water than the more soluble salts, and conversely supersaturation would have to be reached earlier. De Coppet (1907) cited the observations made by Frankenheim (1860), illustrating that all solutions are subject at one moment or another to supersaturation and all molten compounds to undercooling. In this case too only variations in degree were to be found, illustrating in the opinion of De Coppet (1907) in a convincing manner the atomistic nature of the process. Solutions of salts which were readily showing supersaturation at a certain temperature, were often seen to occur in two (or even more) polymorphic forms at that same temperature. Solutions showing distinctly the characteristics of supersaturated solutions were, according to De Coppet (1907), almost always those of salts with two different polymorphic forms or with one or more hydrates. And in that case one of those different forms would invariably be less soluble than the other, so that the solution as a whole could be supersaturated with respect to one modification of the salt but undersaturated with respect to another. As a result the phenomenon of supersaturation was definitely *comparative*, as De Coppet (1907) put it.²¹

With emphasis De Coppet (1907) pointed out, how a solution at one and the same temperature and even at the same moment can give rise during spontaneous crystallisation to *two different crystalline phases.*²² Not Ostwald's newly introduced metastable phase, but instead the kinetic theory of spontaneous crystallization appeared to be able to explain this phenomenon. The

formation of a nucleus required, still following the line of reasoning of De Coppet (1907), 1) a number of molecules of the solid to join each other somewhere in the solution, and 2) equal molecular temperatures for these molecules. In experiments the observation had been made, that the two different crystalline phases formed during spontaneous crystallization, often showed a difference in stability. The less stable phase often changed into the more stable one, thereby releasing heat. According to the kinetic theory the average energy of the molecules making up the less stable phase, would be larger than that of the molecules of the more stable phase. Or in other words the nucleï of the less stable modification are being formed during collisions of molecules with a higher molecular temperature (i.e., kinetic energy) than that of the stable modification. And those molecules with a lower molecular temperature will participate in the nucleation of the more stable phase. As a consequence there will be a temperature interval, in which both modifications are able to nucleate.

Although De Coppet (1907) had initially stressed the role of temperature in controlling the nucleation of the less stable and/or the stable phase, in his own experiments on the nucleation of the different forms of sodium sulfate an additional, and somewhat surprising, observation was made. After concluding from his experiments, that the nucleation of Na₂SO₄.7 H₂O and Na₂SO₄.10 H₂O fully confirmed all aspects of the kinetic theory, De Coppet (1907) described how salts such as K_2CrO_4 or CuCl₂ (or an organic compound such as resorcin) could be seen to retard the nucleation of Na₂SO₄.7 H₂O from its supersaturated solutions (and so favor the nucleation of the more stable decahydrate). Without such additions the spontaneous crystallization of Na₂SO₄.10 H₂O would take place only on very rare occasions.

Three different organic compounds (resorcinol, tri-phenyl guanidine and tri-stearin) were studied by Lautz (1913) with regard to the behavior of the different stable and metastable phases. The polymorphism of resorcine had been discovered by Lehmann (1888); the spontaneous crystallization behaviour of resorcine had been investigated by Tammann (1898). Measurements of the lineare Kristallisationsgeschwindigkeit (= linear rate of crystal growth) were made by Lautz (1913) with the light microscope on two different polymorphs of resorcinol. The linear rate of crystal growth was very low: at 273 K only 0.8 to 1 mm/minute. At higher temperatures the two different polymorphs had different linear growth rates, but the two were independent of the temperature between about 288 and 353 K. In addition the linear rate of conversion (lineare Umwandlungsgeschwindigkeit) could be measured. This rate turned out to depend to a large degree on the orientation of the different crystallites towards each other. Furthermore the temperature at which the crystallites of the less stable modification had been formed, would determine the conversion rate. The fact that the linear rate of conversion would show different values at one and the same temperature, had been noted in the case of sulfur by Gernez (1884). In the case of resorcine and that of sulfur the linear rate of conversion increases rapidly with an increase in temperature above the point of conversion. Below this point the linear rate of conversion decreases with decreasing temperatures up to a maximum, after which it gradually approaches zero at still lower temperatures. As Lautz (1913) stressed, these observations made in the laboratory confirmed the theoretical explanation given by Tammann (1903) to the phenomena accompanying the transition of one modification into a more stable one. The linear rate of conversion at the very point of transition is zero in all instances. If the conversion into the more stable phase absorbs heat, an increase in temperature will increase the rate of conversion. If on the contrary the formation of the more stable modification liberates heat, an increase in temperature will inevitable slow down the rate of conversion.

BREAKING OSTWALD'S RULE

Othmer (1915) expressed his doubts concerning the suggested existence of conditions, under which spontaneous crystallization would never take place.²³ Spontaneous crystallization was known to increase with an increase in the degree of supersaturation (in the case of solutions) or the degree of undercooling (in the case of melts). But there were no indications for the assumption of the absence of spontaneous crystallization in only slightly supersaturated solutions or slightly undercooled melts. Such a field could be best described by Ostwald's definition of *metastable*, but Othmer (1915) reminded his readers, how the original definition by that time had been undermined by different, if not unrelated, applications of that concept.

Othmer (1915) had verified the observations made by Heintz (1849), Duffy (1852), Kopp (1855), and Reimer & Will (1885) on the occurrence of two different modifications of some of the tri-glycerides such as tri-myristin and tri-stearin. Cooling down for example a quantity of molten tri-myristin to room temperature, results in a mass of spherolites of the unstable modification. When heating these crystallites to a temperature of 322 K, melting takes place; but at a temperature of 328 K crystallization of the second, stable modification results. Through his own experiments Othmer (1915) confirmed the formation of both the stable and the unstable modification of these compounds: the results were found to be reproducible. The explanation for the phenomenon had to be found in the relation between the number of nucleï (Kernzahl) and the duration of undercooling. Tammann (1911) provided a theoretical explanation for the occurrence of two different solubility curves: thermodynamics would allow for a metastable and a stable phase on the basis of an atomistic model for the calculations. According to Othmer (1915) the occurrence of the unstable form was brought about by predominance of the number of nucleï of this unstable form over those of the stable modification. Predominance of nucleï of the unstable form would not have to imply the absence of any nucleï of the stable form. Especially when the linear velocity of crystallization of the unstable form would exceed that of the stable form, predominance of the unstable modification would become inevitable.²⁴

Volmer & Estermann (1921) were able to calculate that part of an amount of mercury vapor, that would not immediately change from vapor into the solid state. In Langmuir's (1913) experiments the assumption had been made, that all molecules involved in condensation phenomena would immediately and completely undergo a change of state. But Volmer & Estermann (1921) based their experiments on the observation made by Knudsen (1916), that complete condensation of mercury took place only at temperatures below 133 K. Above that temperature condensation of mercury vapor onto glass was always incomplete. Volmer & Estermann (1921) obtained quantitative data by way of measuring the diameter of an evaporating droplet of mercury with a microscope. The mercury vapor would condense in their high-vacuum set-up at a site cooled to very low temperatures; the rate of condensation could be quantified by way of resistance measurements. In the case of the condensation of mercury only 5 to 15 % of the molecules would not be adsorbed at temperatures between 210 and 178 K. When using metals such as copper or zinc, the degree of condensation was even higher. But in the case of phosphorus the phenomenon of partial condensation was much more pronounced: 50 to 60 % of the molecules would be adsorbed. And when using benzophenon only some 25 % of the molecules would be adsorbed. Therefore Volmer & Estermann (1921) were able to make the fundamental observation, that condensation (and crystallization in general) was only partial in most instances. The condensation of the vapour of for example sulfur or phosphorus into the liquid phase, even at temperatures well below the respective melting points, had often been interpreted as supplying support for Ostwald's *Stufenregel* (= Step Rule). Because the speed at which the liquid phase could be formed in these experiments was considerable larger than that for the formation of the solid phase, Volmer & Estermann (1921) had to conclude, that Ostwald's observations in fact had been founded on reaction kinetics and not on thermodynamics.

Although he did not mention Ostwald at all, Nernst (1921) was quite clear in his rejection of the "Step Rule". The only guideline for the approach of *irreversible chemical reactions* was according to Nernst (at least at that time) the principle of Thomsen (1861): reactions taking place with the smaller liberation of heat proceed in general (but not always!) faster than those in which the stable compound is being formed. Numerous examples illustrating this principle were known from organic chemistry.²⁵ (It must be added here, that Ostwald, 1902 A himself had described the whole of the process of spontaneous crystallization as an *irreversible reaction*!)

Haber's (1922) paper concerned mainly the possible change of an amorphous precipitate into a crystalline one, but it dealt at the same time in general terms with phenomena taking place during nucleation. The formation of any solid precipitate, whether amorphous or crystalline, was considered be the of by Haber (1922)to result "overstepping processes" (Überschreitungsvorgänge). Haber (1922) cited the model of Von Smoluchowski (1916) on the accumulation of several molecules into very small aggregates as caused by the statistical fluctuations resulting from the heat movement. Whether the precipitate being formed, would be amorphous crystalline. would controlled bv the precipitation or be rate of (Häufungsgeschwindigkeit) in comparison to the rate of ordering (Ordnungsgeschwindigkeit). The formation of amorphous precipitates would take place under the influence of a high rate of precipitation. Precipitation of crystalline solids was controlled, as Tammann (1903) had explained, by the process of nucleation and the linear rate of crystallization. A distinction had to be made according to Haber (1922) between the "trace melting point" (Spurenschmelzpunkt) (i.e., the temperature at which the smallest possible aggregates will not grow but melt) and the "mass melting point" (Massenschmelzpunkt). The temperature interval between these two by definition would be part of Ostwald's *metastable* state. In contrast to the explanation given by Ostwald (1897), the experiments by Othmer (1915) had shown, how the process of spontaneous nucleation would not be halted abruptly, when lowering the temperature of an undercooled melt. The curves relating the number of nucleï to the temperature in Othmer's (1915) experiments showed a distinctly symmetrical shape, each with a well-defined maximum. The ultimate cause of the observed shape of these curves had to be found according to Haber (1922) in fluctuations of free energy.²⁶ In processes of precipitation a dynamic equilibrium had to develop between the molecules in the liquid state, relentlessly moving around in an incessant heat movement, and those few molecules clustering together to form a more or less stable nucleus. The forces keeping together the solid aggregate are counteracted in the process of solidification by a definite tendency of the molecules involved, at least those at the outer layer of the aggregate, to escape again into the liquid. In this dynamic equilibrium fluctuations in free energy are capable of initiating stable nucleï with an ordered arrangement of the molecules, provided only that these fluctuations in free energy were long enough and intense enough.²⁷

Once formed the crystal nucleï in turn would influence the rate of precipitation, because of the formation of an electric double layer at the boundary between solid and solution started taking place. The resulting potential can actually be measured in electrophoresis experiments. The surface of the nucleus would, still following the explanation given by Haber (1922), have to compete with water dipoles of this double layer for the ions to be adsorbed from the solution. As explained by

Freundlich & Rona (1920) the preferential adsorption of certain ions at the interface can be quantified by the zeta potential. An adsorbed layer of water dipoles will counteract the tendency to form larger aggregates or slow down the continued growth of the nucleus. Because in general the nucleï would consist of lattices involving electrostatic bonding, crystal surfaces characterised by alternating positive and negative ions will be the slowest to grow (Haber, 1922).

Following the theoretical treatment of nucleation given by Gibbs (1876/1878), the sole explanation for metastability was found by Volmer & Weber (1926) in the capillary (or surface) forces.²⁸ But in the calculations that followed, much as Gibbs had done, Volmer & Weber (1926) excluded at beforehand any considerations on fluctuations. Therefore the theoretical model could only be applied to a spherical droplet, and as the ultimate consequence to the process of condensation only. Volmer & Weber (1926) derived from their calculations a quantitative criterion for stability: Stability is inversely proportional to the square number of supersaturation. But the calculations posed a definite lower limit: the droplet model should not approach molecular dimensions. After realizing this shortcoming, and following the example of Haber (1922), Volmer & Weber (1926) did devote their attention to the possible effects of fluctuations, and applied the calculations by Von Smoluchowski (1906, 1917) and Einstein (1905, 1910) on the kinetics of the Brownian motion. When defining *Z* as the probability of the formation of a nucleus under the influence of spontaneous fluctuations, *W* as the work required to form this nucleus, *T* the Kelvin temperature and *k* = Boltzmann's constant, then the relation

$$Z = e^{-\frac{W}{kT}}$$
(eq.37)

should exist. This approach of the nucleation process in terms of probability is, as Volmer & Weber (1926) pointed out, equivalent to the approach of Arrhenius (1889), in which a comparable relation was found between the speed of a chemical reaction and the necessary activation energy. At the same time, Volmer & Weber (1926) stressed the need to introduce the time factor into this calculation: both the mittlere Verweilzeit (average residence time) and the Wiederkehrzeit (recurrence time) had to be incorporated. In this particular case the probability for an increase in size of the droplet would equal that for a decrease, and therefore the size (better: the amplitude) of the fluctuations typical of the Brownian movement would be determined by the *Fehlergesetz* (error curve) of Gauss (1816). Because obviously enough growth of such droplets could take place as well, Volmer & Weber (1926) made the suggestion to follow the calculations on reaction rates by Christiansen & Kramers (1924). Even the comparison with the process of catalysis, as proposed by Ostwald (1902 B), could be pursued further. After listing data with the calculated values of W/k.T for droplets in water vapor at 300 K, Volmer & Weber (1926) concluded, that metastability is feigned by the strong decrease of the value of W/k.T with an increase in the degree of supersaturation. Or as Volmer (1929) formulated it: the impression of a metastable boundary is essentially caused by the rapid decline of the nucleation rate with a decrease in the degree of supersaturation.²⁹ In other words the conclusion became inevitable, that *metastability* was nothing but an artefact (and ultimately it proved Nernst, 1921 to be in the right, in that not thermodynamics but instead reaction rates are controlling the formation of the stable or the metastable phase).

The calculations on the probability of nucleation by Volmer & Weber (1926) could not explain all aspects of the process either. The equation given above predicts a steady increase of the stability with an increase in the degree of undercooling (or supersaturation). However Tammann's

(1898) experiments had shown the number of nucleï to increase, but only up to a certain maximum value. After that point a further increase in the degree of undercooling or supersaturation leads to less and less nucleï. Apparently the theory advanced by Volmer & Weber (1926) still needed extension. And this was found in the noted dependence of the energy required for the construction of a new *Netzebene* (lattice plane) on the orientation of the lattice plane itself. During nucleation the start of each new lattice layer poses a kind of barrier, but such a barrier can easily be overcome by a slight excess in the degree of supersaturation.

Evidence in support of the re-interpretation of Ostwald's *Step Rule* for the nucleation of polymorphic modifications has been supplied by Stranski & Totomanow (1933). The theory of two-dimensional nucleation of Volmer & Weber (1926) and Volmer (1929), more in particular the equation for the probability of the formation of a nucleus, leads to two distinct curves for the number of nucleï, each with a clear maximum, provided the calculations are based on a difference in specific surface energy. This fact had been overlooked by Volmer & Weber (1926), and therefore the calculated curves of Stranski & Totomanow (1933) show the maxima found earlier by Tammann (1903).

According to Volmer (1929) nucleation should be considered to be part of the process of crystal growth. But nucleation is a relatively rare event, because it requires fluctuations in concentration (Dichteschwankungen). The importance of fluctuations in free energy towards the process of nucleation has been stressed particularly by Volmer (1939). After recalling, that it had been Ostwald himself, who had outlined how fluctuations in p, T, or x would lead to nucleation in supersaturated solutions near the metastable boundary (see note 20), Volmer (1939) discussed in detail the role of such fluctuations. The degree in which locally the value of for example concentration would differ from the average of the solution, controls in fact the formation of a nucleus.³⁰ In other words not the overall average given by most instruments used in physical chemistry, but the amplitude of the fluctuations in free energy determines the process of nucleation.³¹ Calculations by Volmer & Weber (1926) showed, how condensation from supersaturated vapour requires an "activation energy" to be supplied in order to form droplets, that will not momentarily disappear again. But the parallel with droplets is difficult to maintain, since nucleation from solutions gives rise to crystallites, which do not show an instantaneous equilibrium with the surrounding solution. The nucleation of solids is essentially different from the process of condensation, in that nucleation is a step-wise process taking place layer-by-layer (Volmer & Estermann, 1921; Volmer, 1921, 1922). The start of each new layer poses an energy barrier, which can be overcome only through pronounced *fluctuations in free energy*³² (Stranski, 1928, 1932, 1950; Stranski & Kaischew, 1935). But even so the energy barrier to be overcome for the initial nucleus to form, is by far larger than that at the start of a new layer.³³

REVERSIBLE OR IRREVERSIBLE ?

In every textbook on thermodynamics one or more sentences, perhaps even two or three whole pages, will be devoted to irreversible processes. Inevitably one will be able to read, that "... all natural processes are irreversible". But what is the meaning of that statement? What are the consequences of this observation for the formation of magnesite and dolomite?

In the very first sentence of his first publication Planck (1879) stressed the ultimate meaning of the Second Law of thermodynamics: invariably processes take place in nature in a certain

direction, so that a return to a former state will be made impossible. Clausius' (1865) definition of *Entropie* was capable of expressing all such natural processes in a mathematical equation.³⁴ Initially Clausius had devoted his attention to cyclic processes only, but later also natural (i.e., irreversible) processes were studied. The calculations were to be applied to all processes taking place in nature (in which a process as such was defined as the change from an initial situation into some different end situation). Two kinds of processes were to be distinguished: those in which the initial situation present at the outset could be fully restored, and those in which complete restoration was not possible. The distinction between these two fundamentally different processes therefore depends solely on the nature of the initial and the final situation.

In his dissertation Planck (1879) defined an irreversible process as: "a process, in which nature prefers the final situation above the initial situation". Many of Planck's contemporaries used the term irreversible to describe a process, that cannot (under no circumstance whatever) be reversed. In the view of Planck (1879) even an irreversible process can be made to return to its initial state in a thermodynamic sense, but that would leave its traces on the surroundings of the system. As a good example of an irreversible process Planck (1900) considered the emission and the absorption of heat (or electromagnetic radiation in general). After applying the Second Law to electrodynamic phenomena, Planck(1900) found an entropy increase, because only one specific frequency of radiation can be absorbed from a wide range of frequencies emitted by a "black box" source. (In this manner not only the observations of Thomson, 1852 on dissipation were explained, but at the same time the principle underlying quantum theory was outlined by Planck, 1900.) The application of thermodynamics to chemistry had been founded on the cyclic processes of Carnot (1824), studied preferentially by Clausius (1876), Gibbs (1876/1878) and Von Helmholtz (1882).³⁵

For example Von Helmholtz (1882) had stressed the point, that in his view the concept of free energy (i.e., that part of the energy, that is "free" to be used in for example chemical reactions) implied, that the reaction should be reversible.³⁶

In the explanation of Planck (1904) entropy is by far the most important parameter of a thermodynamic system, and not temperature. The "mechanistical" approach to thermodynamics typical of for example the work of Von Helmholtz (1882) required for its calculations a "heat equilibrium". But Planck(1904) objected, that only from the point of view of the irreversible processes such a heat equilibrium (when entropy is at its maximum) can be understood. For as the Second Law implies, a system will always possess a specific value for its entropy, but only a system in a stationary state can be assigned a specific temperature.

As Planck (1904) pointed out, the most important consideration in selecting the way, in which to calculate entropy should be its usefulness in determining entropies not for probable states, but for the less likely states of a system. In this sense Gibbs' (1902) approach ceased to be of significance: conditions of non-equilibrium were not considered by Gibbs. As Planck (1904) stressed, only Boltzmann's (1877) definition of entropy can be applied to systems lacking equilibrium as well as to irreversible reactions. The generality of the definition of entropy by Gibbs had been obtained at the expense of a quite restricted physical meaning (not in the least because in Gibbs' account no distinction was made between the nature of individual particles). For reversible reactions the Gibbs approach can be used, but for irreversible processes in which the entropy concept finds its ultimate cause, Boltzmann's (1877) definition offers the most useful approach.

Verschaffelt (1936) stated, that reversible processes are always created artificially, and that by contrast natural processes are invariably irreversible. This aspect of human intervention responsible for the creation of reversible phenomena has been stressed by Sommerfeld (1956, p.19): "... reversible processes are not, in fact, processes at all, they are sequences of states of equilibrium.

The processes which we encounter in real life are always irreversible processes, processes during which disturbed equilibria are being equalized." Such infinitely slow (or quasistatic) changes in an overall state of equilibrium would be characterized by the fact, that the system's capacity for performing work could be used to the full, and that no energy whatsoever would be irreversibly lost (in other words would be dissipated). The only reliable criterion for a process to be called reversible, would be that "... during its course there are no lasting changes of any sort in the surroundings if the process is allowed to go forward and then backward to the original state" (Sommerfeld, 1956, p.19). Starting from this definition of a reversible process, it must be easy to define an irreversible process. Collie (1982) explained, that the term irreversible does not necessarily mean, that the change of state A into state B cannot, by no means whatever, be reversed into a change from state B into state A. Irreversibility would mean, that "... the conditions which obtain when the change is going forward are different from the conditions when it is going backwards" (Collie, 1982, p.180).

When following this definition of irreversible processes by Collie (1982), the application of thermodynamics to the low-temperature nucleation of magnesite and dolomite becomes clear. For application of equilibrium thermodynamics only leads to serious difficulties. Many authors must have wondered about statements such as "... the oceans are supersaturated with respect to dolomite, and calcite or aragonite on the floor of the ocean should react with the sea water to form dolomite" (Garrels et al., 1960, pp.414-415) and ".... the only stable mineral under reasonable surface or near-surface geologic conditions is magnesite" (Christ & Hostetler, 1970, p.450). Calculations of the solubility products of magnesite and dolomite have been made up to now in most instances on the basis of the assumption of equilibrium. But in a variety of laboratory experiments it has been shown, that the conditions during the dissolution of magnesite or dolomite in carbonated water are fundamentally different from the conditions required for the nucleation of these minerals under conditions of low temperature & atmospheric pressure.

The dolomite lattice consists of a periodical alternation between calcite and magnesite monolayers, and therefore a process of "sorting out" on an atomic scale will have to operate during its low-temperature nucleation. As Graf & Goldsmith (1956, p.184) put it: "The difficulty with which dolomite is crystallized at low temperatures, as evidenced by experimental data, is considered as a consequence of the necessity of attaining an ordered Ca-Mg configuration." Compared with the more or less random array typical of magnesium calcites, a definite degree of atomic ordering will be required according to Graf & Goldsmith (1956). But the necessary increase of order (or lowering of entropy) cannot take place at room temperature, when using classical thermodynamics with its inherent assumption of equilibrium. It is possible though, to increase order in an open system at the expense of a change somewhere else (as Planck put it). But such an approach is necessarily based on the statistical mechanics typical of the kinetic theory. Or as Einstein (1907) concluded, classical thermodynamics "... is not exact enough" ("*nur angenähert richtig*") to allow for the fluctuations characteristic of Boltzmann's kinetic theory.

In 1913 Planck claimed, that the very source of irreversibility in the case of the heat radiation is to be found in the emission of free electrons upon the absorption of radiation energy. After absorption has taken place, a new situation will have been created with respect to the vibrations of all oscillators involved; the intensities of all frequencies of radiation being emitted, will be different from that absorbed. But for the system as a whole (i.e., for both emitter and absorber) the total entropy would have increased. If we would consider only the absorber, it follows inevitably, that there the entropy will have been lowered. Planck has never made such a distinction (in fact a subdivision of the system under consideration). In this respect Boltzmann (1897) was

much more outspoken: in his view the general observation, formalized into the theorem known as the Second Law, had been deduced for systems situated at the earth's surface at the present moment and suddenly being isolated from the rest of the events on earth. For those situations the prediction that isolated systems will inevitably reach a state of thermal equilibrium, had been found to possess a probability, which bordered onto certainty. And the probability for such an isolated system to displace itself from thermal equilibrium, would have become highly improbable.

In his definition of an irreversible process Von Smoluchowski (1915) made a distinction between the *Beobachtungszeit* and the *Wiederkehrzeit*: reversible is a process, in which an initial configuration shows a short recurrence time (Wiederkehrzeit) compared to the duration of the observation (Beobachtungszeit). Irreversible is a process with a relatively long recurrence time compared to the duration of the observation.³⁷ Von Smoluchowski (1915) did not hesitate to define two different realms of application for the second law of thermodynamics.³⁸ After giving a number of examples for the calculation of the recurrence time for diffusion of oxygen into nitrogen gas, Von Smoluchowski (1915) was able to draw conclusions regarding the reversibility of this reaction. During observation times within human standards the dimensions of the system were decisive: on the atomic and ultramicroscopic scale the reaction had all chacteristics of a reversible reaction, but when looking on a scale of centimeters or decimeters (as in most laboratory experiments) the reaction definitely looked irreversible. And from the calculations it could be deduced, that the dividing line was roughly a frequency given by the inverse of the square root of the number of particles. This estimate could be used in the absence of any exact information on the recurrence time of the system. In one of his last papers on thermodynamics Planck (1926), much like Born (1921) before him, discussed the new formulation of the Second Law given by Carathéodory (1909).³⁹ Planck (1926) recalled, how Von Helmholtz (1884) had stated, that there is no real need for a cyclic process nor any need for an ideal gas, when delineating the basis of the Second Law. But in the view of Planck (1926) the version of the Second Law given by Carathéodory (1909) was somewhat too general; it implied the conversion of heat into work, taking place without any compensation. In Planck's explanation the reverse of this statement would also have to be true, and therefore the conversion of work into heat may as well take place without any compensation. And even the denial of both statements (the two different sorts of conversion are not to take place at all) should be possible, when following Carathéodory's own words. After giving a more precise definition of a reversible and an irreversible process⁴⁰, a very pointed version of the Second Law was given: the generation of heat through friction is irreversible ("Die Wärmerzeugung durch Reibung is irreversibel": Planck, 1926, p. 456). And after a number of additional considerations Planck (1926) was able to re-formulate this new version into: every process in nature takes place in such a way, that the sum of the entropy-values of all components will be increased; only in the rare exception of a reversible process the sum of all entropy-values remains constant.⁴¹

But there is another, even more fundamental, observation made by Carathéodory (1909), that was not mentioned by Planck (1926). At the end of his paper Carathéodory (1909) draws a conclusion, that seems to have escaped attention in general. In almost all thermodynamic considerations the concept of temperature is used. Because temperature defines the movement of individual particles (atoms or molecules), it cannot be considered to be an independent, a primary quantity. The usual concept of *a temperature* presupposes equilibrium (as Planck, 1904 had noted). In the case of radiation being emitted and being absorbed, unexpected contradictions result, when continuing the equilibrium assumption. An adequate description of a system involving heat radiation and absorption, would in the words of Carathéodory (1909) have to include all of the individual material points making up such a system.

At present there is no real need to follow the rejection by Carathéodory (1909) of the much too general *temperature* concept, because as Von Laue (1917) stipulated, all considerations on fluctuations should include such an amount of atoms or molecules, that the concepts of concentration and of temperature can be used at all. But the serious objections by Carathéodory (1909) inevitably lead to a clearer understanding of the relations between fluctuations and the energy barrier, described by Ostwald (1893) to exist between the metastable and the stable state. At the same time the true meaning of the distinction made by Arrhenius (1889) between a "normal" and an "active" molecule (only the latter is capable of a chemical reaction), can be understood. For it is obvious, that only the "active" molecules with a kinetic energy higher than the average are

capable of overcoming the energy barrier separating the metastable from the stable state. At least during the initial stage of nucleation (to be distinguished from the subsequent stage of growth) periodical changes in the collision number (*Stosszahl*) of Boltzmann (1896) will counteract the differences in the nucleation rates and the rates of growth of the metastable and the stable phase. In other words fluctuations are essential in nucleating the (at least) two different phases, the metastable phase and the stable phase. Not as much an increase of the *average temperature* (although that too may be quite effective) leads to measurable amounts of the stable phase, but fluctuations in the distribution of kinetic energy over the numerous particles in the system under consideration.

Once reconciled with the absence of equilibrium in a classical sense, the nature of the reactions becomes relatively easy to understand. For in the very paper that has established the existence of chemical equilibria, Guldberg & Waage (1867) considered an equilibrium to be made up by two different reactions, and as soon as the two different "reaction forces" would have become equal, equilibrium would be attained. The notion of reaction rates (to replace the "reaction forces" of Guldberg & Waage, 1867) has been contributed by Van 't Hoff (1884) and taken up by Arrhenius(1889). Equilibrium requires the rates of the forward reaction and that of the reverse reaction to become equal. But a different line of reasoning must be taken, when considering a system, in which for example two different polymorphs may nucleate. Given a difference in the reaction rates for each of the polymorphs, the fastest rate will invariably predominate. The same reasoning can be applied to two different phases (i.e., two entirely different compounds!), which may form in one and the same system such as for example the precipitation of either magnesium hydroxide carbonate or magnesite from the very same solution. As found in my experiments, the reaction rate for the low-temperature nucleation of magnesite is notably smaller than that of magnesium hydroxide carbonate. Only through an intervention in the form of fluctuations in pH the larger reaction rate for the precipitation of magnesium hydroxide carbonate can be overcome. But this mechanism cannot be understood in terms of equilibrium; at least two different precipitation reactions must be considered. And when trying to obtain the product of the second reaction, the first reaction will have to be stopped or slowed down. In this sense the criticism of Nernst (1921) on Ostwald's Step Rule must be understood: as predicted by Nernst the different reaction rates characteristic for what was described by Ostwald as the metastable phase and the stable phase, provide the better insight.

Originally Van 't Hoff (1884), in his *Études de dynamique chimique*, had assigned two different reaction rates for an equilibrium to take place; reaction rate k_1 for the reaction

$$A + B \rightarrow D + E$$
 (reaction I) (eq.38)

And reaction rate k_2 for its reverse

$$D + E \rightarrow A + B$$
 (eq.39).

In the case of the formation of a different phase from the same initial ingredients, a second reaction takes place, with two additional reaction rates:

$$A + B \rightarrow F + G$$
 (reaction II) (eq.40)

with reaction rate k₃ and

$$F + G \rightarrow A + B$$
 (eq.41)

with reaction rate k4.

This second reaction between A and B gives rise not to the metastable phases D (or E), but to the stable phase F (or G). In other words: in the case of irreversible reactions $K = k_2/k_1$ cannot be considered to represent an "equilibrium constant", but only as the quotient between two different reaction rates (hence the new name of **RATE QUOTIENT**: Deelman, 2001). The two different reactions delineated above in general will possess differences between the two different solubility constant $K_{\alpha} = k_2/k_1$ and $K_{\beta} = k_4/k_3$. If solubility constant K_{α} is larger than K_{β} , reaction I will predominate over reaction II. As soon as conditions of dissolution prevail over the usual conditions of precipitation, reaction I is favoured over reaction II and a large part of the reaction products D and E will disappear again. Because reaction II is slower, dissolution takes place to a lesser degree and as a result some of the reaction products F and G remain behind. After repeating these different steps, that is the usual precipitation interval alternating with an interval of dissolution, more and more of the reaction products F and G will accumulate. The alternations between precipitation and dissolution favor the formation of the stable phase instead of the metastable phase because of the inherent differences between precipitation and dissolution rates.

The fact that the low-temperature nucleation of magnesite or dolomite does not take place by way of a reversible process, explains the apparent anomalies on the number of phases present in carbonate sediment. For as Tammann (1924) stated, in the absence of an equilibrium the wellknown "Phase Rule" of Gibbs (1876/1878) cannot be applied. Earlier Bakhuis Roozeboom (1891) had observed, that when salts which are isomorphous and form a double salt, this double salt is obviously in equilibrium with only one particular composition of the contacting solution. For all other compositions no equilibrium exists. Seifert (1937) reiterated, that the "Phase Rule" cannot be applied to what he called anomalous mixed crystals. Similarly metal alloys possessing not only a disordered state, but a superlattice as well, necessarily contradict the Gibbs "Phase Rule" as Nix & Shockley (1938) stressed. Metastable assemblages such as for example aragonite, magnesium calcite plus dolomite obviously contradict the "Phase Rule". Or as P. K. Weyl (cited in Brätter et al., 1972, p.50) put it: "Every handful of carbonate sediments clearly violates the phase rule, for where thermodynamics teaches that there should be only one or at most two carbonate phases, an abundance of different carbonate minerals is found."

FORMATION OF MAGNESITE

In general magnesium hydroxide carbonate or a hydrated carbonate of magnesium precipitates under conditions of room temperature & atmospheric pressure. Similarly magnesium chloride, magnesium sulfate, and magnesium nitrate usually form hydrates. Magnesium is not the

only cation, which shows difficulty in its dehydration reaction in aqueous solution. Calcium cations exhibit a comparable behavior. Hexahydrated calcium carbonate and calcium carbonate monohydrate are known to occur under conditions, that are not at all extreme. But CaCO₃.6 H_2O and CaCO₃. H_2O are metastable, and tend to convert to anhydrous calcium carbonate. The spontaneous conversion of MgCO₃.3 H_2O into magnesite, because the hydrate would be unstable with regard to magnesite, has been claimed by Rosza (1926). Observations published by Gloss (1938) and D'Ans & Gloss (1938) on the formation of magnesite from MgCO₃.3 H_2O in a tensimeter experiment do illustrate the possibility for this reaction to take place at 307 K.

Quantification of the degree of hydration of ions is possible through a variety of more or less indirect physical-chemical techniques. Since each of these techniques measures a somewhat different aspect of the cation/water dipole interaction, most of the published hydration numbers depend to a large degree on the technique used (Bockris, 1949). The difficulties can be largely avoided, when using methods capable of *direct* quantification of the number of water dipoles surrounding each cation in solution. Instrumental techniques such as nuclear magnetic resonance spectroscopy, X-ray diffraction of solutions, ultraviolet spectroscopy and isotopic dilution techniques provide information on the primary hydration of cations (Burgess, 1978). X-Ray diffraction of a flowing solution coupled with computer analysis of the signal, was used for example by Bol et al. (1970). The method showed, that most divalent cations possess a well-defined shell of 6 water molecules in primary hydration⁴² (Bol et al., 1970; Burgess, 1978). Small cations such as Be²⁺ and Li⁺ have a primary hydration number of 4, and some of the larger cations have a coordination number of 8 or 10. These primary hydration numbers are not influenced by the concentration or the temperature of the solution (Burgess, 1978). According to Bol et al. (1970) the cation/water dipole distances involved in primary hydration are in good agreement with those measured in crystalline hydrates of the type $M(H_2O)_6^{2+}$. At the same time X-ray analysis provided an explanation for the observed differences among the hydration numbers measured with the older techniques. In many of those methods (for example in measurements of viscosity, conductivity, settling rate, compressibility, cryoscopy or dialysis) the sum of the primary and the secondary hydration numbers (or the sum of primary hydration and part of the secondary hydration) were being measured. In the case of magnesium cations Bol et al. (1970) were able to distinguish, through the use of X-ray diffraction, 6 water molecules in primary hydration and 12 water molecules in secondary hydration. Additional measurements with the same technique have shown, that not only magnesium and calcium cations are hydrated in aqueous solution; for example Li, Na, K, Rb, Cs, Be and Sr exhibit the same phenomenon.

There can be no doubt, that magnesium cations are surrounded by water dipoles in solution; but calcium cations exhibit the same phenomenon, although possibly to a somewhat lesser extent. Therefore the conclusion seems inevitable, that the hydration of magnesium cations can not be made responsible for the kinetic barriers blocking the low-temperature nucleation of magnesite and dolomite. Perhaps the problem is not restricted to magnesium and calcium cations. The problem might be more fundamental, and related to the nucleation of anhydrous salts from aqueous solutions in general. Although magnesite does not by itself dissolve in large amounts in water and needs dissolved carbon dioxide to do so, the precipitate formed in this case is the hydrate.

Any suggestions concerning the possible role of the hydration of the magnesium cation in preventing the low-temperature nucleation of magnesite of course have been made obsolete by the laboratory synthesis of anhydrous MgCO₃ at temperatures of 313 to 333 K and under atmospheric pressure (Deelman, 1999). Those syntheses were based on the duplication of Exp. No.57 of Liebermann (1967). Upon duplication of Liebermann's Exp. No.57 at 298 K (and using ammonia

for the titrations) a magnesium calcite with its main diffraction peak at 28.7 nm (lacking the superstructure reflection typical of dolomite) had formed. But when conducting exactly the same experiment at 333 K (my experiment M-211) magnesite together with magnesium hydroxide carbonate was found in X-ray diffraction. After leaching this precipitate during 12 hours in water saturated with CO_2 , pure magnesite remained.

When conducting the same experiment at 313 K at first calcite, dolomite and magnesite formed. (Here the 0.2 g CaCO_3 used in every experiment precipitated as carbonate; the fate of the calcium carbonate in for example tests M-211 and M-223 remains unknown for the present moment.) Curiously enough the paragenesis of magnesite plus magnesium hydroxide carbonate was found again in a second duplication of Liebermann's experiment No.57 at 313 K. In contrast to the suggestion made by Liebermann (1967), the use of a sodium carbonate solution instead of a solution of ammonia does not lead to the formation of any magnesite. For when using a concentrated solution of sodium carbonate in the titrations at 313 K the result is a precipitate of magnesium hydroxide carbonate.

Some thoughts must be devoted to the role of salinity on the low-temperature nucleation of magnesite. In Liebermann's Exp. No.57 the salt content of the solution was six times higher than that of normal seawater. When relying entirely on this observation, it would underline the significance of finding magnesite in (highly) saline environments (e.g., the observations by Alderman & Von der Borch, 1961; Skinner, 1963; Kinsman, 1967; Irion, 1970; and Gac et al., 1977). The mechanism of *Breaking Ostwald's Rule* (Deelman, 2001) may well turn out to work largely independent of factors such as salinity. At present this is merely a conviction, not proven in laboratory experiments. Therefore it is not possible at this time to explain all of the known occurrences of modern magnesite. In particular magnesite associated with weathering serpentine or olivine rocks appears to form independent of any saline solutions, much like the modern magnesite from caves.

It has been claimed by Ostwald (1893, 1897), that there may well exist more than one metastable phase. In the case of the low-temperature nucleation of magnesite, minerals such as nesquehonite, lansfordite, artinite and magnesium hydroxide carbonate (formerly "hydromagnesite") can be considered to be metastable. For Langmuir (1965) has pointed out, how only magnesite is stable compared to the four metastable phases mentioned. The fundamental reason behind Langmuir's (1965) observation can be found in measurements of the (Gibbs) free energies in aqueous solutions at room temperature and under atmospheric pressure (except for the measurements made on magnesite). Even though in the described low-temperature syntheses of magnesite, magnesium hydroxide carbonate invariably formed as the metastable phase, additional experiments may well reveal the possible role of nesquehonite, lansfordite or artinite as the metastable phase. And only after such additional experiments any definite answer can be given to the question, in how far the theories on the "secondary" change of primary minerals such as nesquehonite, lansfordite or magnesium hydroxide carbonate into magnesite, were based on actual facts. In the meantime it is of considerable significance to note, that authors such as Vitalj (1953), Graf et al. (1961), and Alderman & Von der Borch (1963) have found magnesite in Recent deposits invariably together with magnesium hydroxide carbonate.

The fact that possibly the formation of dolomite may precede that of magnesite has been established in high temperature experiments by Klement (1895). Observations suggesting the same process, have been published by Redlich (1909 A), Clar (1931), Friedrich (1951, 1959, 1963), Angel & Trojer (1953, 1955), and Johannes (1966, 1967). Several times calcite together with dolomite formed initially in my duplications of Liebermann's (1967) Exp.No. 57 at room

temperature and atmospheric pressure. But during subsequent dissolution phases these two carbonates disappeared and instead magnesite plus magnesium hydroxide carbonate originated.

Does the observation made in my laboratory experiments on the initial precipitation of one or more metastable phases to be dissolved subsequently during recurring phases of dissolution, followed by the growth of the stable phase, provide the much-sought-after evidence in support of "a reaction series" ⁴³? Strictly speaking: no, of course not. For the postulated change of aragonite into Mg-calcite, of Mg-calcite into Ca dolomite, of Ca dolomite into ordered dolomite was based on the supposed "dolomitization reaction" postulated by Von Morlot (1847 A, B). At the same time it must be noted, that Alderman & Von der Borch (1963), who had initially suggested the existence of this "reaction series", did observe the occurrence of periodicity at that particular site ("The first three stages, up to calcian dolomite, can take place, we believe, during the aqueous phase of the annual cycle": Alderman & Von der Borch, 1963, p.466). But when considering the low-temperature nucleation of anhydrous Mg/Ca carbonates from sea water, not as much the "increasing age of its environment" is responsible, but in fact the dynamics of this environment in terms of fluctuations of sufficient amplitude and required frequency.

Two different "dolomite associations" (1: dolomite & Mg-calcite and 2: dolomite & magnesite) have been described by Von der Borch (1965). These two different assemblages are in fact two stages in the dynamic development of an initial metastable mineral assemblage changing into a stable one. Being a dynamic process, the reaching of a certain stage will necessarily depend on the amplitude and the frequency of the fluctuations at that particular location. Therefore it is not at all certain, whether a local assemblage of dolomite plus Mg-calcite will ever be changed into pure dolomite or into dolomite plus magnesite or into pure magnesite. The crucial role of the frequency and the amplitude of the fluctuations in pH have been recognized in theory and experiments, but will need confirmation from *in situ* measurements.

Despite the term "reaction series" little evidence has meanwhile been published to support the suggested conversion of dolomite into magnesite. In the case of the low-temperature formation of dolomite numerous papers with evidence on the dissolution of an earlier (apparently metastable) phase, have been published. Therefore one might wonder, why not as much evidence in support of the dissolution of dolomite or huntite and its replacement by magnesite, was found. The reason is simple. In the case of dolomite the metastable phase to be dissolved, consists of a form of calcium carbonate. The skeletal remains of a large number of fossil organisms are made up originally from calcium carbonate (aragonite, calcite, vaterite, or even magnesium calcite). Because the ultrastructure of most of such hard parts is well known, any process of dissolution is easily detected by microscopic analysis. The reason why no modern organisms building their skeletons of magnesite are known, can only be guessed. Perhaps the solubility of magnesium carbonate is so high, that precipitation from seawater would take place at very high salinities. Only a few halophytic micro-organisms are capable of living in such an environment. Curiously enough the only fossils reported up to now from Paleozoic magnesite deposits are micro-organisms: algae found by Valdiya (1968), and Paleobasidiospores found by Brunel et al. (1984) and Chayé d'Albissin (1985, 1988). Earlier De Llarena (1950) had reported on finding organic material in magnesite deposits, as well as in contacting dolomite layers with an abundance of marine fossils in it.

Valdiya (1968) studied the (Ordovician) magnesite deposits of the Kali and Alaknanda Valleys (Himalaya Mountains, India), and noticed a close relation with contacting stromatolitecontaining dolomites. In the magnesite well-preserved algal structures were found. Therefore Valdiya (1968) suggested the formation of both magnesite and dolomite to have taken place in a

295

sedimentary environment, possibly aided by algal growth. At the same time Valdiya (1968, p.924) stated, how "... the earlier-formed carbonates, were converted into carbonate-assemblages of higher magnesium content, including magnesite." And "It is suggested that algae played a significant and active role in creating an environment conductive to the evolution of such assemblages of Mg-rich carbonates ..." (Valdiya, 1968, p.924). This conclusion of Valdiya (1968) may well hold true, but probably not in the sense as suggested, in that the algae would have been responsible for the creation of fluctuations in pH by way of CO_2 production.

Warren (1990) distinguished the following mineral assemblages among the sedimentary carbonates from the intermittent lakes in the Coorong area of Southern Australia: 1) dolomite & Mg-calcite; 2) aragonite & Mg-calcite; 3) dolomite & magnesite; 4) dolomite & aragonite & magnesium hydroxide carbonate; 5) aragonite & magnesium hydroxide carbonate & magnesite; and 6) aragonite & gypsum. As Warren (1990, p.852) pointed out: "Dolomite \pm Mg-calcite is by far the most common dolomite-bearing assemblage in cores from the coastal plain and is the exclusive dolomite assemblage in 85 % of the Coorong lakes that contain dolomite. This assemblage is found in all lakes containing dolomite." Much like Rosen et al. (1988, 1989) had done, Warren (1990) was able to distinguish two different sorts of dolomite (with differences in isotopes, mineralogy, accessory minerals, and petrography). Type A dolomite is slightly richer in MgCO₃ than pure dolomite and invariably found together with magnesite (plus magnesium hydroxide carbonate). Type B dolomite approaches more the ideal stoichiometric composition of pure dolomite, or it shows a slight excess of CaCO₃ in its composition, and is invariably found together with Mgcalcite. Even in electron microscopy these two types of dolomite could easily be distinguished. There is little difficulty in explaining the occurrence of two distinctly different sorts of (lowtemperature) dolomite. As can be seen in the extended phase diagram for the anhydrous system CaCO₃ - MgCO₃ (Fig.11), the narrow stability field of dolomite can be reached from two different sides. From the CaCO₃ side (i.e., when Mg-calcite is the metastable phase), but also from the MgCO₃ side (i.e., when magnesium hydroxide carbonate is the metastable phase). The observations made by Warren (1990) in the field, confirm the claim by Ostwald (1893), that more than one metastable phase may act as "the precursor" to the stable phase. And what's more, Warren (1990) has revealed, that possibly each of the metastable phases preceding the stable phase, will leave its traces behind. In this manner the way in which the irreversible geochemical reaction has taken place, can be reconstructed.

Breaking Ostwald's Rule, that is precipitating the stable phase instead of the metastable phase, necessitates an active role for fluctuations, in particular fluctuations in pH. As has been shown in my experiments on the low-temperature nucleation of magnesite, only through fluctuations formation of measurable quantities of this stable phase can ever be obtained under conditions of room temperature and atmospheric pressure. Such fluctuations in most cases have their origin outside the isolated spot in nature, where magnesite or dolomite nucleate. In this sense the basic requirement for applying equilibrium thermodynamics is not at all fulfilled.

From the existing descriptions of various natural parageneses of Recent magnesite indications concerning the significance of such fluctuations can be deduced:

1) The formation of modern magnesite in the Coorong area (South Australia) takes place only in the *ephemeral* (= fluctuating) lakes, but not in those lakes, that lack such fluctuations; as for example Alderman & Von der Borch (1961), Skinner (1963), Von der Borch (1965) and Langmuir (1965) have shown. Similarly the deposition of magnesite and various salts (such as glauberite, bloedite, carnallite, kainite, and picromerite) in the Kara Bogaz Gol (at the mouth of the Caspian Sea) takes place under fluctuating conditions, as indicated by the descriptions of Vakhrameeva

(1956), Polyakov(1959), Sedelnikov et al. (1968), and Andriyasova et al. (1973).

2) Quite obvious are the fluctuations typical of the tidal flats bordering the Persian Gulf, where modern magnesite has been found by Kinsman (1967, 1969) and Bush (1973).

3) In the variety of lakes studied by Müller et al. (1972), modern magnesite was found only in the *dynamic* lakes, i.e. those lakes that undergo pronounced seasonal fluctuations in water volume (and consequently in water chemistry).

4) The modern magnesite of British Colombia (Canada) occurs according to Renaut (1990) and Renaut & Long (1989) only in the ephemeral playas and not in the perennial lakes, or on neighbouring hill slopes.

DOLOMITE FORMATION

In classical chemistry the stability concept is related to the resistance of a compound towards decomposition, while being heated to higher and higher temperatures (e.g., Berthelot, 1879⁴⁴). However in many instances the definition of stability requires an addition. For example ferrous hydroxide is unstable, when in contact with oxygen; and sodium is unstable in the presence of moisture. Therefore describing some compound as being unstable, necessitates an addition with regard to what other compound or under what conditions. In this sense the statement of Kramer (1959, p.466), that "... dolomite is stable in sea water of normal composition with respect to calcite" is clear. In addition Kramer (1959, p.466) stated "Calcite ... is metastable and should alter to dolomite...". And even the possibility of the metastable magnesium calcite to be changed in dolomite should be considered: "... in sea water of average Mg:Ca ratio, stoichiometrically ordered dolomite is more stable than low-magnesium calcite" (Berner, 1966 B, p.188). As a result Kinsman (1967, p.1337) noted, that "Stability relationships of magnesium and calcium carbonate minerals at low temperatures are not well known and experimental and natural occurrence data are often complicated by the presence of metastable phases." As one of the few scientists not relying entirely on classical equilibrium considerations, Krauskopf (1967) warned, that perhaps more than just supersaturation might be involved in the low-temperature formation of dolomite. According to Rodgers et al. (1982) the hypersaline brines thought to be responsible for dolomite formation had been described by Adams & Rhodes (1960, p.1917) as "chemically unbalanced". "As to whether this implies a dependence on nonequilibrium phenomena with a supposed slow rate of reaction from a metastable to a stable state is unclear..." (Rodgers et al., 1982, p.657). And Kastner (1984, p.411) added, that dolomite "... seems to violate the laws of thermodynamics".

The longstanding enigma of the thermodynamic status of dolomite can now be solved. As shown in my laboratory experiments, the low-temperature nucleation of magnesite and dolomite requires large-scale fluctuations in pH (as controlled by the pCO_2). The differences in reaction rates between nucleation of the metastable and the stable phase, are accentuated by the periodically recurring phases of dissolution. Only in this manner the reaction rate for the precipitation of the metastable state, which is by definition larger than that of the stable state, can be overcome. The mechanism requires periodical alternations between a stage of dissolution of the metastable phase(s) and a stage of precipitation of the stable phase.

The fact that there may be more than just one metastable state seems to hold true for the system $CaCO_3 - MgCO_3 - CO_2 - H_2O$. In the high-temperature (and high pressure) experiments by Nordeng & Sibley (1994) magnesium calcite invariably formed first, and only after that dolomite



Fig.49 – Appearance and disappearance of metastable carbonate phases upon duplication of Liebermann's (1967) Exp.No.57 (my experiment M 227). The initial precipitate consists of aragonite with a minute amount of calcite and possibly some nuclei of dolomite (M 227 A).



Fig.49 B – After 3 cycles of dissolution by CO_2 bubbling through and titration with dilute NH₄OH aragonite still dominates, but the amount of dolomite has increased and magnesite nuclei are detected in X-ray diffraction (M 227 B).



Fig.49 C – After 5 cycles of dissolution by CO_2 bubbling through and titration with dilute NH_4OH some aragonite remains, but now magnesite predominates over dolomite and even over calcite (M 227 C).



Fig.49 D – After 8 cycles of dissolution by CO_2 bubbling through and titration with dilute NH₄OH a clear amount of magnesite has developed, while a small amount of dolomite remains (M 227 D).

started to form. In the explanation of Nordeng & Sibley (1994) this would confirm Ostwald's Step Rule, because magnesium calcite crystals were noted to grow faster than the dolomite crystals. But my experiments have shown, that calcite, aragonite or magnesium calcite are the metastable phases, from which dolomite may form through fluctuations. In duplicating Liebermann's (1967) Exp.No.57 invariably 0.2 g calcium carbonate in the form of calcite were used. X-Ray diffraction applied to the precipitate, which formed after the very first phase of dissolution, showed it to consist of aragonite. In the course of the experiment, that is to say after more and more phases of dissolution, magnesium calcite would appear. And only then the amount of dolomite (or magnesite, aragonite and magnesium calcite can be considered to be metastable with respect to dolomite under the fluctuating conditions necessary to *break Ostwald's Rule* (Deelman, 1999, 2001).

There can be no doubt at all, that irreversible reactions are involved in the low-temperature formation of magnesite or dolomite. The very observation that from a mixed Mg/Ca bicarbonate solution no dolomite precipitates, when withdrawing the carbon dioxide again (that is at room temperature & atmospheric pressure), has been made by numerous authors. Such a mixed Mg/Ca bicarbonate solution can be prepared by dissolving dolomite powder in carbonated water. Apparently the dissolution of dolomite is fundamentally different from its precipitation. Realizing the implications of this fact took more time. Nevertheless there have been several authors, who have noted the *irreversible* nature of the dissolution / precipitation reactions of magnesite and dolomite. For example Halla (1960) noted how a system consisting of a mixture of calcite, magnesite, and dolomite in water will not reach a state of equilibrium.⁴⁵ And in 1962 Halla and his co-authors stated, that irreversibility occurred in the dissolution / precipitation of dolomite. Stout & Robie (1963) concluded from the observed disagreement between the free energies calculated from solubility measurements for dolomite made by various authors, that "... true thermodynamic equilibrium may not be established" (Stout & Robie, 1963, p.2252).

Fluctuations in pH, as caused by periodically recurring changes in the amount of dissolved CO₂, have been demonstrated to be fundamental. And ultimately all of the objections raised against the suggestion of Von Morlot (1847 A, B) on the reaction between calcium carbonate and a solution of magnesium chloride or magnesium sulfate, have been confirmed. As a result the theoretical foundations of most "models of dolomitization" have been shown to be nonexistent. But not all, because there were in fact theories involving a dynamical model. For example the role of fluctuations had been hinted in the experiments by Pfaff (1894), but is particularly clear in the paper by Sherman et al. (1947, p.43): "Periodic rainy and dry seasons are essential to the dolomitization process." In his description of modern precipitates of Mg-calcite and dolomite occurring in supratidal deposits along the South Louisiana coast, Kocurko (1986) noted the periodic changes in the geochemistry of this particular environment: "Seasonal fluctuations produce changes in groundwater chemistry" (Kocurko, 1986, p.19). Aragonite, high-magnesium calcite and dolomite sensu stricto were found there cementing quartz sand in association with algal mats. "Seasonal variation causes fluctuations in the groundwater chemistry which, in turn, controls dissolution and precipitation of the carbonate cements. The result is periodic dissolution and removal of aragonite, and probably to some extent, the more unstable phases of high magnesium calcite ...": Kocurko (1986, p.20). But no word by Kocurko (1986) on the active role of fluctuations in the nucleation of dolomite.

The mechanism proposed here is fundamentally different from that described by Sibley (1990) in his paper "*Unstable to stable transformations during dolomitization*", and not only because Sibley (1990) made his observations on high-temperature tests (491 K). The

transformations taking place in his hydrothermal experiments from calcite via magnesium calcite into Ca-rich, poorly ordered dolomite and ultimately into ordered, stoichiometric dolomite, were explained on the basis of the theory of Avrami (1939). But that theory presupposes the presence of nucleï of the second (stable) phase inside the first ("... the new phase is nucleated by tiny "germ nuclei", or "ultra-nuclei", which already exist in the old phase, and whose effective number can be altered by temperature and duration of superheating": Avrami, 1939, p.1104). It is important to note here, that Sibley (1990) did not describe one particular compound as *the precursor*, but clearly delineated a series of unstable precursors. Concerning the transition of these precursors (magnesium calcite and CaCO₃-rich, poorly ordered dolomite) into stoichiometric dolomite, Sibley (1990) pointed out three factors. In the first place factors capable of causing inherently slow nucleation and/or growth of dolomite would be required (such as high concentration of dissolved magnesium; the higher surface free energy of the nuclei of dolomite compared to that of nuclei of highmagnesium calcite). Even so "... there is not a simple relationship between the stoichiometry of the dolomite and the Mg^{2+}/Ca^{2+} ratio of the dolomitizing solution" (Sibley, 1990, p.747). In the second place stoichiometry would be related to the overall reaction progress. And in the third place the change from the precursor into stoichiometric dolomite might be a step-wise process. Indications for such a step-wise process had been found by Sibley (1990) in observations during scanning electron microscopy.

The nucleation of dolomite under conditions of room temperature & atmospheric pressure requires fluctuations of pH of certain amplitude and frequency. The boundary values have yet to be established in laboratory experiments. But the underlying theory does not at all exclude the possible formation of mixed crystals in those situations, where the fluctuations in pH are insufficient to create the (most) stable phase, i.e., dolomite. Dissolution in intervals of initially deposited aragonite or low-magnesium calcite, may well lead to high-magnesium calcite. The second type of magnesium calcite may well be enriched in $MgCO_3$ compared to the magnesium calcite, which was initially present. In an environment with varying amplitudes or frequencies of the changes in pH mixed crystals between calcite and magnesite can be formed, with compositions varying over a wide range. But as soon as the fluctuations in pH cease, no more changes in mineralogy towards the more stable phase will take place. Removal of the carbonate sediment from the dynamic setting is responsible for "freezing in" the mineralogical evolution. Only in this way the wide range of stoichiometric compositions of the mineral dolomite and the very closely related magnesium calcites can be understood. The two different types of dolomite distinguished by Halenke (1872) on the basis of chemical analyses, the "complete" (fertige) and the "incomplete" (unfertige) dolomites, do possess an inherent dynamical significance. For only the "complete" dolomite with its composition of 1 mol CaCO₃ plus 1 mol MgCO₃ represents the truly stable phase in a thermodynamic sense. This form of dolomite has "taken all the barriers" and is at rest and will remain so. All mixed crystals between calcite and magnesite with an excess of calcium carbonate over magnesium carbonate are truly speaking not dolomites, but magnesium calcites (as Deelman, 1979 A stressed). And as shown in the laboratory experiments, such magnesium calcites will change further under the influence of fluctuations in pH until dolomite sensu stricto has been formed (or even until magnesite forms). In other words the wide variety of stoichiometric compositions of "dolomite" reflects an equally wide variety in amplitudes and frequencies of pH fluctuations in a dynamic environment. The mineralogy of the anhydrous Mg/Ca carbonates in the sedimentary environment is capable of recording the dynamics of the system as such.

From my experiments I am able to conclude, that the low-temperature nucleation of dolomite (apart from the necessary fluctuations in pH) sets the following requirements with respect

to geochemistry. 1) There should be no $CaSO_4$ in solution; 2) Calcium sulfate may have been removed by bacterial sulfate reduction or deposited elsewhere by prolonged desiccation; and 3) The solution should not contain MgCl₂ as the only magnesium salt in solution: some MgSO₄ should be present as well.

In my experiment D-222 urea was used in addition to the salts of the artificial brine used by Liebermann (1967) in his Exp. No. 57. The choice of this compound had been inspired by Mansfield's (1980) observations on the formation of pure dolomite as uroliths in a Dalmatian dog. One way to explain the active role of urea in the low-temperature nucleation of dolomite, would be based on its effects on de-sorption of chlorine ions and the adsorption of carbonate ions. For chlorine ions (of the magnesium chloride in the artificial sea water) have been shown by Douglas & Walker (1950) to adsorb onto calcite surfaces even stronger than hydroxyl or bicarbonate anion groups. No additions of urea were required in the low-temperature synthesis of magnesite. This fact can be understood, when realizing that calcium is in fact a stronger cation than magnesium (see the section *Laboratory evidence* of Chapter 1). Therefore the bond between chlorine anions and calcium is stronger than that between magnesium cations and chlorine, and the replacement of adsorbed chlorine atoms by carbonate groups may require the catalytic actions of the urea molecule. No such mechanism needs to be involved in the case of the nucleation of magnesite, because there only the somewhat weaker magnesium ions are involved.

There are intriguing aspects to the formation of dolomite and magnesite on Pacific atolls, more in particular concerning the possible presence of a lagoon. The occurrence of such a lagoon has been discussed at length in Darwin's book on the formation of coral reefs (Darwin, 1842). Summarized into a few sentences by Daly (1916, pp.664-665): "According to Charles Darwin's much-discussed theory, a barrier reef represents the upgrowth of a coral reef which orginally fringed a sinking (generally volcanic) island; and an atoll reef represents a further upgrowth, completed in typical form after the central island has sunk below sea-level. Between the upgrowing reef and the subsiding, central island is a concavity or "moat". Through the accumulation of detritus and shells and skeletons of organisms inside the reef, the moat is slowly filled. Above the detrital covering of the moat surface is the water of the "lagoon". The subsidence is supposed to have progressed until the deepest part of each moat has sunk scores, hundreds, or possibly thousands, of meters." And concerning biological production in the lagoon Daly (1916, p.666) noted: "The rain of planktonic and nektonic shells and skeletons to the bottom will, of itself, be nearly uniform in the lagoon ...". But Daly (1916) did not discuss, whether the water in the lagoon was sea water, brackish or sweet. The distinction may well play a crucial role in the low-temperature formation of dolomite and magnesite. For if a direct contact with the surrounding ocean is lacking, the moat or the lagoon will be filled with rain water. Because contact with the large buffering reservoir of the open sea is lacking, stratification takes place of a layer of rain water on top of sea water in the moat or the lagoon. Stratification has been measured by Bourrouilh-Le Jan et al. (1985) in the lagoon (lagon fermé) of Clipperton. The top layer (of about 14 m) of rain water has a salinity of only 4 ‰, whereas the underlying sea water a salinity of 33 to 34 ‰. Quite pronounced is the difference in pH between the top layer and the sea water below it: the top layer is distinctly alkaline (pH = 8.7 to 9.3), but the underlying sea water is slightly acidic (pH = 6.6). The large amounts of dissolved carbon dioxide create acidic conditions, but high amounts of dissolved hydrogen sulfide do much the same. In the view of Murray (1880) the atoll itself might well have been formed through the dissolution calcium carbonate by water rich in CO₂. The significance of a closed basin of sweet or brackish water in the middle of an atoll has been stressed by Reuling (1934): only in such enclosed basins reducing conditions could ever be build up (as for example Elschner, 1913 had pointed out).

"There are numerous other emerged atolls in the Indian and Pacific Oceans, some extensively dolomitized, a number of which were tested by Skeats (1903) and by Elschner (1913), but the most significant data were gathered by Marshall(1930), who systematically sampled the emerged lagoon and rim ("makatea") of Atiu Island, in the Cook Islands. He says: "The tests also showed a definite and gradual decrease in dolomitization from the inner towards the outer side of the Makatea." This is most interesting, because if - as Skeats and Reuling suggested - the dolomitization is a phenomenon of the restricted core of the atoll, this is exactly what one should expect. The interior of the island should be highly dolomitized, and the degree of dolomitization should decrease from the inner edge of the rim toward the outside, where open marine conditions would counteract the reducing environment of the interior": Fairbridge (1957, p.149). Those atolls that have closed lagoon are therefore likely to be prone to dolomite (and even magnesite !) formation. And atolls lacking such a lagoon (or moat) are unlikely to have accumulated much dolomite. "Most of the present-day atolls, however, have deep-cut passes, owing to Pleistocene lowered sea levels, so are not very favorable environments. Only those atolls that are thus closed would provide the right environment": Fairbridge (1957, p.145). Perhaps here the ultimate explanation can be found for the fact, that certain atolls do contain modern dolomite and other atolls do not. For there can be little or no doubt, that the whole hydrological system of an atoll undergoes distinct fluctuations ("The wells in coral islands rise and fall with the tide ...": Murray, 1880, p.513).

On the basis of his extensive work on the subsurface geology of Eniwetok Atoll, Schlanger (1963, p.1011) listed 10 questions on the formation of dolomite on Pacific atolls. Especially the obvious lack of any correlation between dolomite formation and the original texture, porosity and fossil content of the pre-existing carbonate deposits, needed explanation. To test the mechanism of dolomite formation described by me, an attempt will be made to provide the answers to the 10 questions of Schlanger (1963).

"1. The vertical distribution of dolomite in all drilled atolls. Undue emphasis on the pattern of dolomitization below Funafuti has led to the acceptance, by many geologists, of Reuling's pressure hypothesis which is obviously inapplicable to Kita-daitô-jima and Eniwetok." Answer: Reuling (1934) had re-examined the samples from the Funafuti drilling, and reached the conclusion, that it must the rate of precipitation of calcite (*Ablagerungsgeschwindigkeit*), which controlled the possible formation of dolomite. In Reuling's own words: "Man kann davon ausgehen, daß die Dolomitisierung eine Frage der *Ablagerungs-Geschwindigkeit* sei, indem das Wasser auf Kalk dolomitisierend einwirke, überall und solange es ihn erreichen könne": Reuling (1934, p.11). For example Schmalz (1956) has postulated a direct relation between dolomite formation and pressure. And only because dolomite occurred in the core from Funafuti at depths below 194 m, this suggestion was made into a hypothesis to be applied later on a universal scale. Evidence to the contrary from a large number of drillings from other Pacific atolls has meanwhile caused some doubts concerning the truly universal character of the hypothesis. As a consequence Schlanger (1963, p.1008) remarked on the pressure hypothesis of Skeats (1903): "Although pressure may be a factor in some occurrences of dolomitization, it is certainly not a limiting one."

"2. The presence of dolomite as a distinct mineral phase in limestones that contain as little as 2 to 3 percent $MgCO_3$. Leaching of originally magnesium-rich rocks could not account for these traces of dolomite. Further, the lack of dolomite in magnesium-rich limestones, such as those in the upper 50 feet of the Funafuti section, indicate that a high initial magnesium content does not necessarily foster dolomitization. The magnesium in these oft discussed limestones below Funafuti is due to an abundance of algal calcite." Answer: This is of course very convincing evidence against any relapse into the "leaching theory" of Forchhammer (1849), Bischof (1855), and Högbom (1894). Not the Mg/Ca ratio of sea water, nor the magnesium content of limestones, are the decisive factors in the low-temperature nucleation of dolomite.

"3. The differing susceptibility of any single fossil group to dolomitization. In hole E-1 coralline algae are preferrentially dolomitized, although at Funafuti and Kita-daitô-jima these same fossils resist dolomitization." Answer: There is a rather simple reason, why especially coralline algae are prone to "dolomitization". For such coralline algae live in the intra-tidal zone and add their own distinct fluctuations (of pCO_2 in day/night frequency) to the tidal periodicity. And fluctuations in pCO_2 of sufficient amplitude (and adequate frequency) are responsible for the dissolution intervals, required for the low-temperature nucleation of dolomite. When subjected to such fluctuations in pCO_2 , pre-existing calcium carbonate, whether just an aragonite-needle deposit or a specific fossil consisting of aragonite or a fossil made up from Mg-calcite, will be dissolved and dolomite will be deposited.

"4. The apparent lack of primary porosity on dolomitization. Evidently, both dense finegrained and porous coarse-grained limestones are equally liable to dolomitization." Answer: When considering a reef-like depositional model in a carbonate environment, there are two distinct zones subjected to the tidal fluctuations in sea level. The reef itself experiences the tidal changes, and the shoreline with its intra-tidal areas is also subject to the ebb/flow alternations. In this intratidal and the neighboring supra-tidal environment usually dense, fine-grained carbonates ("mudstones" in the classification of Dunham, 1962) will be deposited. The reef structure is in general made up from a porous coarse-grained framework called "grainstone" by Dunham (1962). Because of the tidal fluctuations in the back reef basin, no dolomite is to be found in the packwackestones (Dunham's classification) deposited there.

"5. The lack of coexistent dolomite and aragonite, which suggests that atoll limestones may have to be leached and recrystallized to secondary calcite before they can be dolomitized. This view is in opposition to that held by some workers who believe that aragonitic limestones are more easily dolomitized than calcitic ones." Answer: Not as much as the existence of isomorphism between calcite and magnesite, but stability relations (i.e., thermodynamics in combination with reaction kinetics) really are responsible for the preferred dissolution of aragonite. In my experiments in which the reaction was interrupted after 1, 3, 5, or 8 cycles, the disappearance of aragonite was quite obvious. Although initially fine grained calcite had been added, it invariably reprecipitated into aragonite after only one phase of dissolution by the excess dissolved CO_2 . The reason was of course the presence of a relatively large amount of magnesium cations (as magnesium chloride and magnesium sulfate) in the artificial brine.

"6. The lack of correlation between length of immersion in sea water and intensity of dolomitization suggests that mere soaking in magnesium-rich water does not by itself cause dolomitization." Answer: This is exactly the point made by Liebe (1855), Hoppe-Seyler (1875), Leitmeier (1915), Linck (1937) and Rivière (1939 A); because in their experiments calcium carbonate soaked in sea water, in magnesium chloride or in magnesium sulfate solutions, would not change into dolomite. Little wonder because these were essentially static experiments, illustrating in a convincing manner, that there is no such thing as the supposed "dolomitization" reaction postulated by Von Morlot (1847 A). It has been shown in my experiments, that periodic alternations in pH are required for the low-temperature nucleation of dolomite.

"7. The wide variety of secondary textures seen in limestone from these atolls suggests that emplacement of dolomite takes place in several ways with differing paragenetic sequences." Answer: At present I am not at all convinced, that there is more than one fundamental mechanism according to which dolomite (and magnesite) can be formed under conditions of low temperature & atmospheric pressure. It remains a challenge for future investigators to reveal yet another, fundamentally different way to precipitate dolomite (as well as magnesite or huntite) under conditions of room temperature and atmospheric pressure.

"8. The fact that the dolomite from these atolls is structurally calcium rich." Answer: Taking this observation as factual evidence, and at present I am in no position to express my doubts, the excess of calcium may be indicative of "insufficient digestion" of the metastable phase or phases. Only when the fluctuations in pCO_2 are of sufficient amplitude, a stoichiometric dolomite can be formed. Perhaps the conditions on the various Pacific Atolls are not always ideal with respect to the amplitude or the frequency of the required fluctuations.

"9. The fact that most of the limestone from both atoll and high islands in the Pacific is not dolomitized. Therefore one must look at dolomitization as an "abnormal" rather than a "normal" diagenetic effect." Answer: Apart from the fact, that neither "dolomitization" nor "diagenesis" do really exist, this observation is quite to the point. The low-temperature nucleation of dolomite takes place exclusively under the alternating conditions of especially periodic changes in pH (as caused by changes in the amount of carbon dioxide dissolved in aqueous solution). In the absence of such pronounced fluctuations in pCO₂, any pre-existing calcium carbonate sediment is not likely ever to be changed into dolomite.

"10. That the three-dimensional distribution of dolomite in the subsurface of any atoll is unknown. Future drilling may show that dolomite forms a sheath around the outside of the limestone column; perhaps it is present only in a central plug or is scattered randomly throughout. A knowledge of whatever pattern exists is vital to any general hypothesis of atoll dolomitization." Answer: Creating more and more problems must be a good way to ensure additional project funding. But joking aside, there really is no reason at all to believe, that the three-dimensional distribution of dolomite in each and every Pacific atoll would have been required to solve the "dolomite problem". Only if the main interest would be the local subsurface geology of the Pacific atolls, the above claim could be maintained. If looking for the mechanism for dolomite formation under conditions of room temperature and atmospheric pressure, laboratory experiments will do nicely.

ORGANIC OR INORGANIC ?

Numerous geologists have noted the association between the mineral dolomite and organisms. In fact it was De Dolomieu himself, who stated, in his paper describing the large masses of the new carbonate in the mountains of Northern Italy, that he had observed "...some impressions of shells" in these rocks.⁴⁶ Similarly Tennant (1799) reported on the presence in dolomite strata of fossils, that consisted of dolomite instead of calcium carbonate ("In this quarry, the stone is frequently crystallized in a rhomboidal form; and petrified shells, not calcareous, but similar in composition to the stone itself, are sometimes, but very rarely, found in it": Tennant, 1799, p.311). The question remains, in how far organisms are instrumental in the low-temperature nucleation of dolomite.

While analyzing the composition of Pleistocene clays from Southern Sweden, Högbom (1894) made the observation, that calcite dissolves more quickly than dolomite from a mixture containing both. This observation was then brought into relation with the $MgCO_3$ -content of

calcareous organisms such as *Porites, Millepora, Oculina, Lithothamnium*, and various gastropoda. Especially the calcareous algae of the *Lithothamnium* genus were effective in concentrating magnesium carbonate: Högbom measured percentages MgCO₃ from 2 to 13 mol %. And after (partly) dissolving such a *Lithothamnium* sample in dilute acetic acid the percentage MgCO₃ had increased to about 20 mol %. On these two different observations Högbom (1894) based the following hypothesis: calcareous algae such as *Lithothamnium* would play an active role in the formation of dolomite, because the algae form an outer crust on reefs and atolls. Through leaching, the calcareous algae would rapidly become enriched in magnesium carbonate, leading ultimately to the formation of dolomite.

Concerning the change of the initially deposited calcium carbonate of the coral reefs into dolomite various theories have been proposed. The fact hat the initial precipitate had been calcium carbonate, whether calcite or aragonite, could not be doubted at all. But the nature of the possible conversion remained a problem. According to Scheerer (1866) it was especially the large-scale porosity of the coralline structures, that had to be responsible for dolomite formation by way of exposing the pre-existing limestone to the "dolomitizing agencies". Land (1967), Richter (1974 A,B), Davies et al. (1975), Lohmann & Meyers (1977) and Richter & Füchtbauer (1978) discussed the formation of dolomite in terms of magnesium cations being re-located during the recrystallization of biogenic magnesium calcites, thereby following the example of Schlanger (1957).

Others have pointed out the possible significance of algae in the low-temperature formation of dolomite. For example Gebelein & Hoffman (1971, 1973) tried to explain the alternations between dolomite and limestone on a millimeter scale. Observations on Recent algal mats formed the main part of their paper. The layers of stromatolites consisting mainly of algal filaments, had been formed as surficial mats during periods of non-deposition. Such algal layers originated in ponds of seawater, occurring in most instances in the intratidal zone. The underside of the algal mats is populated by extremely high amounts of bacteria. As a result the rate of decomposition of algal mucilage is quite high underneath the algal mat. This layer of partially decomposed algal material is the site of carbonate precipitation. Large amounts of minute carbonate crystals (measuring about 1 to 4 micrometer) were found underneath the algal mats. The carbonate there consists of magnesium calcite with 14 to 19 mol % MgCO₃. In their laboratory experiments with blue-green algae (*Schizotrix calcicola*) Gebelein & Hoffman (1973) noted, that the living algae are capable of concentrating magnesium to values 3 to 4 times higher than the concentration of the surrounding solution.

Not only in the case of algal mats bacterial activity would be an intrinsic part of the process of the low-temperature formation of dolomite, but also in the case of the reef building organisms such as corals. As Dana (1872) had observed, coralline carbonate will often be dissolved through bacterial decomposition after the death of the organism itself. Dissolution (or partial dissolution) of CaCO₃ is caused primarily by the carbon dioxide set free by the bacteria. For as Gebelein & Hoffman (1971, 1973) pointed out, only the topmost layer of the algal mat consists of living algae. Considerable amounts of carbon dioxide and ammonia will result from the bacterial activity. In other words it is not difficult at all to explain the low-temperature nucleation of dolomite (and/or magnesite or huntite for that matter) in association with coral reefs or algal mats on the basis of my duplications of the experiments of Liebermann (1967). It is the alternation between phases of dissolution of the metastable carbonates (by carbon dioxide in solution) with phases of precipitation (caused by the introduction of ammonia into the solution), that leads to measurable amounts of dolomite, huntite or magnesite. Presumably not as much the presence of corals, algae and/or bacteria is causing the formation of dolomite, but rather the combination of several biochemical reactions leading to large-scale alternations between intervals of CO₂ production and the production of ammonia.

In experiments lacking the required fluctuations in pH not a trace of dolomite has ever formed. For example in the more than 200 different experiments conducted by Gebelein & Hoffman (1973), no dolomite at all precipitated in their algal cultures. The laboratory tests carried out consisted essentially of adding small amounts of filtered algal sheath material to quantities of sea water with different salinities and Mg/Ca ratio's. In all of the experiments small amounts of ammonium carbonate were added. All solutions had been sterilized before adding the algal material. The only precipitates formed, were Mg calcites with 17 to 20 mol % MgCO₃. Of course no dolomite was found, because the experiments by Gebelein & Hoffman (1973) did not involve any sort of fluctuation.

Although Oppenheimer & Master (1965) used algal mats and carbonate sand infected by local marine bacteria, and measured distinct fluctuations in pH , Eh and alkalinity, only a trace of dolomite formed in their experiments. At present the conclusion concerning the experiments of Oppenheimer & Master (1963, 1965) should be, that perhaps the required amplitude of pH fluctuations was not enough (the minimum pH reached was that of pure sea water: pH = 7.6). Comparable experiments by Kocurko (1986) with algal mat material were in fact much more successful. It may well be concluded here, that in the experiment of Kocurko pure dolomite actually formed due to algal activity.

A close relation between plant growth, in particular of Ruppia maritima Linn., and the occurrence of dolomite of Recent age in an intermittent lake in south-east Australia has been postulated by Alderman & Skinner (1957). During the dry summer months Kingston Lake would desiccate completely, but after the first rains of winter, water accumulates to a depth of 30 to 60 cm, and plant (and animal) life begins to reappear. During November and December the weather becomes warmer and plants proliferate. A fine white sediment consisting of calcite and dolomite, forms during these months of the year. The precipitation of these carbonates would, in the interpretation of Alderman & Skinner (1957), be the result of a rise in pH. The presence of abundant plant growth in the shallow water of Kingston Lake would exert a considerable influence on the pH of the solution. In this relation Alderman & Skinner (1957) mentioned the observations of Baas-Becking (1934), that the photosynthesis of plants, through its effects on the partial pressure of CO₂ in solution, could change a night time pH of below 8 to a value of 9.3 during the day. Because Ruppia maritima was the most abundant water plant present in Kingston Lake (although sedges and algae were found as well), its effects on the changes in pH would predominate. Dolomite precipitation took place, when plant growth was most plentiful. "That there is a close relation between plant growth, rise in pH, and precipitation of dolomite in Kingston Lake seems certain ... More or less continuous records of pH changes and correlation with precipitation and such factors as sunlight, temperature and salinity appear to be necessary": Alderman & Skinner (1957, p.566). Skinner (1963) concluded, on the basis of dolomite occurrences in the lakes of southeastern Australia, that a direct relation exists between dolomite and plant growth.⁴⁷ Observations by Baltzer et al. (1982) indicate, that perhaps living trees have something to do with dolomite formation. For Baltzer et al. (1982) found more dolomite there, where mangrove trees grow on the sediments of the Mehran River (Iran) than there, where no trees grew. The possible role of plants and trees in the low-temperature nucleation of dolomite might well explain the occurrence of dolomite in coal (in the form of "coal balls").

There is as yet no certainty as to the exact role of bacterial sulfate reduction in the low-temperature nucleation of dolomite (despite wide spread publicity). As Hecht (1933) stressed, the



 $Fig.50 - Fluctuations in H_2S$ concentration measured 1 meter above a tidal flat near the island of Sylt, Germany (modified after Jaeschke et al., 1980).



Fig.51 – The seasonal change in temperature (...) causes an almost synchronous change in the total amount of ammonia (---) produced by microbes in the sediment. But the net amounts od ammonia (-.-) sampled in the top layer (maximum 14 cm core depth) fluctuate more due to mixing effects and bioturbation. Right hand Y-axis: units for ammonia production in μ mol/cm² per day. Modified after Blackburn (1983).

decomposition of the remains of the marine macro-fauna initiates the production of both ammonia and hydrogen sulfide. An alternation between the amounts of ammonia (a strong base) and hydrogen sulfide (a weak acid) may well produce the required pH fluctuations. But perhaps the periodical release of hydrogen sulfide might be capable of achieving the same. For after its formation in underlying reducing layers, the upward movement of H₂S into the overlying sediment with oxidizing conditions, will lead to its oxidation into the strong sulfuric acid. At the interface between the reducing and the oxidizing zones there may well develop a small interface with acidic conditions capable of dissolving almost any calcium carbonate present. Even small changes in the position of this interface create fluctuations in pH. At the same time it should be realized, that most probably the changes in day and night temperatures are responsible for clear fluctuations in the amounts of H₂S emanating from tidal flats (such as for example near the German island of Sylt: see Fig.50). In sediments a distinct seasonal fluctuation in the amounts of ammonia production by microorganisms caused by temperature changes has been detected by Blackburn (1983) (see Fig.51).

Most sediments in the marine environment are buffered by sea water: in general the pH of such sediments will be seen to vary at maximum between 6.9 and 8.3 (Ben-Yaakov, 1973). Measurements in the sediments of Saanich Inlet (British Columbia, Canada) by Nissenbaum et al. (1972) revealed pH values between 7.6 and 8.0. And what precipitated there, was calcium carbonate and not dolomite. At the same time Birnbaum & Wireman (1984) have suggested the occurrence of considerable fluctuations in pH due to the activities of sulfate-reducing bacteria: "The sediment may alternately experience a pH increase due to the release of ammonia during decomposition ... followed by a pH decrease as the excess ammonia diffuses away and organic acids are produced by microbial fermentation; an aerobic environment will be followed by one which is anaerobic" (Birnbaum & Wireman, 1984, p.143). According to Baas-Becking et al. (1960) there might be a relation with the geological setting: for example in estuaries there may be an annual isolation of more saline deep water after an influx of river water in the spring of each year. After a summer boom in plankton growth, the subsequent settling of large amounts of organic remains may well stimulate the activity of sulfate reducing bacteria. "A desert lake in Victoria, Australia, shows the formation of a stratified salt crust; black layers, showing sulfate reduction alternating with clear salt, formed in the dry period. An important periodic change in the characteristics must have taken place": Baas-Becking et al. (1960, p.265).

A reconstruction of the actual process of dolomite nucleation as uroliths cannot be given at present, simply because too much essential information on this particular occurrence is lacking. For example the mineralogical nature of the dog's first incidence of uroliths had not been established. In addition various (bio-) chemical analyses of the dog's blood and urine in the second instant of stone formation are not available. But from what is known, a theory can be constructed, giving at least a possible explanation for the phenomenon. The symptoms and analyses mentioned by Mansfield (1980) leave open the possibility of a somewhat modified interpretation. Could it be, that the high white blood cell count, along with the blood, the epithelial cells and the mucus in the urine of the dog? Such an inflammation might have been caused by the renal calculi themselves, especially those that were already too large to pass through the urinary tract without becoming lodged. Mechanical damage to the contacting tissues may well explain a possible infection. Urinary calculi usually form there where the concentration of the urine is highest, i.e., in the renal papillae of the kidney (Drach, 1978). But "As soon as these crystals form, they can flow within 3 to 5 minutes into the renal pelvis, down to the ureter, and into the bladder where they remain for a period of

approximately 3 to 6 hours": Drach (1978, p.796). Whether urinary calculi will become mechanically lodged in the ureter (= the duct, that leads from the kidney to the bladder), or in the bladder itself, is determined by their size. But once in the bladder serious problems will result: the calculi, that were able to pass through the ureter, will start to block the urinary outlet (= urethra). The urinary calculi that are too large to pass through the urethra, remain in the bladder and continue to grow every time the urine becomes supersaturated with the substance, that makes up the uroliths (Drach, 1978). In both instances the Dalmatian dog described by Mansfield (1980) had developed calculi, that were so large, that the urethra had been blocked. That such large calculi are capable of mechanical damage to the contacting tissues, seems only logical.

Not only the fact that the uroliths of the Dalmatian dog consisted of a carbonate is remarkable, but especially the high amounts of incorporated magnesium are unusual. Calcium together with phosphate anion groups is used in relatively large amounts in mammals for bone formation. Mammals also require magnesium, but in markedly smaller amounts than calcium. Magnesium is mainly required for the bone tissue; in smaller amounts it is used in the cardiac muscle, in skeletal muscles, in nervous tissues and in a number of enzymes (Hays & Swanson, 1977; Urlach, 1985). The excretion of magnesium takes place exclusively by way of the kidneys (Aikawa, 1980). Usually little or no magnesium will be excreted, since 96.5 % of the magnesium passing through the kidneys will be resorbed (Durlach, 1985). Only in rare instances the magnesium level will reach values higher than 1.25 mol/m³: in virtually those instances kidney failure is involved (Siegenthaler, 1979). Depending on the mineralogical nature of the uroliths recovered in manipulation or in surgery, the method of subsequent chemotherapy has to be selected. If for example calcium oxalate calculi had been found, the usual approach would be to administer thiazide drugs, phosphate or magnesium oxide. Calcium phosphate calculi are counteracted with the administration of thiazide, and urinary calculi consisting of uric acid are being treated in most cases with allopurinol (Drach, 1978). Benzothiadiazine ("thiazide") drugs are frequently used, because of their effectiveness in promoting renal secretion of water. The diuretic properties of the thiazides are based on the inhibition of carbonic anhydrase, i.e., the inhibition of the re-absorption of bicarbonate anions by the kidney (Beyer, 1958; Goldberg, 1973).

Perhaps an explanation for the unusually high concentrations of magnesium in the kidneys of the Dalmatian dog is to be found in one of the following observations. In the first place there is the experimentally established fact, that calcium phosphate renal stones are induced by magnesium depletion (Whang & Welt, 1963). The same mechanism of magnesium depletion leads to calcium oxalate renal tubular crystals in laboratory rats (Gershoff & Andrus, 1962; Rushton et al., 1981). In the second place it must be realized, that not only in inorganic crystallization tests with urine the prophylactic actions of magnesium oxide or -hydroxide has been noted (Hallson et al., 1982). Because Dalmatian dogs are well-known for the high levels of ureum in their urine, and subsequently often suffer from ureate uroliths (Osborne et al., 1972), the possibility cannot be excluded at beforehand, that the veterinary in the case described by Mansfield (1980) simply ordered ingestion of magnesium hydroxide carbonate in the first instance. From clinical practice much the same effect of orally administered magnesium has become known (Gershoff & Prien, 1967; Silver & Brendler, 1971). The theory of Breaking Ostwald's Rule effectively accounts for the formation of dolomite as kidney stones in a Dalmatian dog. For as Murray & Hastings (1925) have pointed out, although most of the carbon dioxide will be removed from the blood via the lungs, part of the dissolved CO₂ will be removed through the kidneys in order to maintain the acid-base equilibrium. Because the base used for this purpose in mammals is ammonia, and because excretion from the kidneys takes place under decidedly fluctuating conditions (e.g., Pitts, 1973), all of the



Fluctuations in SO_2 and NH_3 concentrations in the air of Venice (modified after Amorosa & Fassina, 1983).

requirements seem to be fulfilled. What remains however is the question concerning the source of relatively large amounts of magnesia. Only the possible intervention of a veterinarian, who might have prescribed the use of relatively large amounts of magnesium to cure the supposed ureate kidney stones, would ultimately explain Mansfield's (1980) observations.

Fluctuations, or rather the alternations between conditions of precipitation and conditions of dissolution, offer at present the sole possible explanation for one of the most curious occurrences of modern dolomite. As mentioned in Chapter 4 modern dolomite has been detected by Del Monte & Sabbioni (1980) on the weathered marble surfaces of various buildings in the city of Bologna, Northern Italy. Originally only magnesium calcite with 2 % MgCO₃ had been present in the marble used. According to Del Monte & Sabbioni (1980) air pollution in the form of acid rain may have been involved. This explanation seems quite likely, the more when considering that pollution often involves gases such as SO₂. Rain containing dissolved sulfur oxide is distinctly acidic. But for example large amounts from nearby industries will also dissolve in rainwater, and subsequently lead to rain with an alkaline pH. In the air of Venice (Northern Italy) such an alternation between intervals of high SO₂ concentrations alternating with intervals of high NH₃ concentrations have been measured by Amoroso & Fassina (1983) (see Fig.52). Because the alternations between sulfur dioxide peaks and ammonia peaks is on a scale of several months, the resulting rains will show periodical alternations between acidic and alkaline conditions. The acidic rain leads to dissolution of the marble's surface, and conversely an alkaline rain initiates to (re-)precipitation of any of the dissolved carbonate. In other words the conditions for the low-temperature formation of dolomite according to the mechanism described above, are given.

REPLACEMENT?

The most important conclusion to be drawn from the present low-temperature syntheses of dolomite is of course, that the dissolution of metastable carbonates such as aragonite or magnesium calcite is an intrinsic part of the process of dolomite formation. And in the case of the low-temperature nucleation of magnesite dissolution of metastable phases such as for example magnesium hydroxide carbonate is fundamental. The principle of Breaking Ostwald's Rule (Deelman, 2001) is based on the difference in physical-chemical characteristics of two or more kinds of nucleï, each possessing its own rate of precipitation and conversely each possessing its own rate of dissolution. Because of this difference in the rates of dissolution, recurring stages of dissolution will in the end lead to a selection of the least soluble (i.e., the most stable) phase. The whole principle of this selection on the basis of dissolution rates relies on the existence of two different kinds of nucleï. Therefore the possible application of electron microscopy to the process of the low-temperature nucleation of dolomite and magnesite can only reveal the very existence of two different nucleï from the start of the reaction. At the same time electron microscopy will show, that any molecular replacement of for example part of the lattice of aragonite by dolomite can be excluded. Simultaneous dissolution of the metastable precursor and precipitation of the stable phase, as suggested for example by Reeder (1982), most likely can be excluded too, for it really is the alternation between two sets of contrasting conditions, that leads to sustained growth of the stable phase in the form of separate nucleï.

When understanding the actual mechanism of dolomite formation, the question of "replacement or no replacement" is reduced to a mere semantic dispute. Not knowing the principle

of the selection between the two different nucleï (on an atomic level that is), will almost certainly lead to the conclusion reached by so many other authors concerning replacement. The impression of replacement depends apparently on the scale of the observation made. On two different levels the traces of a process of dissolution seem to be unmistakable. In the field the dolomite rock may be seen to contain fossils, known to have consisted originally of calcium carbonate, and now consisting of dolomite. This observation can remain unchallenged, but why not look at some more dolomite in the field? In so many instances dolomite is present in finely laminated deposits with numerous indications known from the intratidal and/or supratidal environment. These indications are so very compelling, that there have been authors, who thought it necessary to start doubting such basic principles as Playfair's (1822) *Actualism*.

The second level of observation is that of a thin-section. Evidence on the leaching of individual bioclasts preceding burial compaction, can be detected in thin-sections. The removal of for example part of the aragonite shell of a gastropode, and its replacement by dolomite crystals can be documented in detail. Leaching of pellets followed by the apparent replacement of calcite by dolomite, can be demonstrated in thin-section by applying staining methods. Subsequently it is seen how some of the calcium carbonate has disappeared, and in the voids a smaller amount of dolomite has been precipitated. The mistake usually made, lies in the interpretation of grain contacts as seen in thin section in terms of a sequence in time. Sure enough removal has taken place: it is evident, that a piece of the initial grains or of a fossil has been removed. And there is no denying the precipitation of dolomite in the voids left behind by this process of removal. But what evidence tells us, that the process of dissolution did really precede the deposition of dolomite? Could it be, that perhaps the two were more or less synchronous? At present the latter explanation seems the most likely, not in the least because of evidence from laboratory experiments. Perhaps additional experiments, involving a realistic change of part of a Recent bioclast carbonate sediment into dolomite or magnesite, will be needed to convince the most sceptic of scientists.

In thin-section the picture suggesting "replacement" may seem to be quite convincing. To quote from only one of a multitude of similar accounts: "The tests of *Operculina, Polystrema*, and *Rotalia* are soon converted into dolomite while that of the other genera remain as unaltered calcite. In the very large number of each of these genera examined no exception to the rule was seen. Exactly the opposite condition was found in regard to the calcite mud with which the small chambers have been filled. These genera in which the skeleton has been changed to dolomite have their chambers filled with unchanged calcite mud. On the other hand those genera which retain the unchanged calcite skeleton have chambers filled with dolomite which is obviously derived from original calcite mud" (Marshall, 1930, p.62). What such descriptions provide is of course pictorial evidence against any assumed "dolomitization model": for what large-scale hydrological flow model would explain the intricate contradictions found in the description given?

Dolomite does not in a strict sense *replace* any magnesium calcite, aragonite or vaterite. The very term "replacement" finds its origin in the supposed "dolomitization reaction" of Haidinger and Von Morlot (1847 A, B). As shown in chapter one, there is no evidence at all, that this supposed reaction has ever created dolomite under conditions of room temperature & atmospheric pressure; evidence to the contrary is abundant. Instead the low-temperature nucleation of dolomite requires alternations between a dissolution stage and a precipitation stage. Through these fluctuations the inevitable formation of the metastable phase can be overcome, leading after a certain minimum amount of fluctuations of sufficient amplitude to recognizable crystals of dolomite. The amplitude of these fluctuations is defined by the amount of protons set free to dissolve the metastable carbonate formed initially. Not only the metastable phase formed will be dissolved, but depending

on the amount of H⁺ even the surrounding carbonate sediment (calcite, aragonite) as well.

Especially if the surrounding carbonate sediment contains recognizable components such as fossils, this dissolution stage will clearly leave its traces. The presence of modern dolomite in siliciclastic (tidal) flats shows, that perhaps not very large amounts of calcium carbonate are required for dolomite nucleation. In other words the dissolution of any contacting carbonate sediment is often an inevitable by-effect of dolomite formation; but by-effect it is.

Hecht (1933) performed experiments on the dissolution of shells of various lamellibranchiata, and found how the amount of dissolved $CaCO_3$ is determined mainly by the surface area exposed. However *in situ* experiments, in which such shells were buried for months in the siliciclastic muds of German tidal flats, showed how small the amounts of dissolved $CaCO_3$ in fact were. But quite high rates of dissolution were noted, there where the calcium carbonate shells rested on peat deposits. After preparing a number of thin-sections of (partially) dissolved shells, Hecht (1933) observed gypsum crystallites deposited on the inside of the leached shells. Because Hecht (1933) knew, that dissolution of calcium carbonate had preceded the precipitation of gypsum, Hecht (1933) refrained from suggesting any "replacement" of CaCO₃ by gypsum.

While studying the process of cementation of Holocene sediments of the Persian Gulf, Taylor & Illing (1969) measured pH values as low as 6.2 in pore water. The acidic pH had to be responsible for observed dissolution of especially aragonite, and was caused by bacterial sulfate reduction. ("The cream surface sediments turn greyish at a depth of a few cm, marking the change from oxidizing to reducing conditions. The grey sands smell of hydrogen sulphide and the associated oxidation of the entombed organic matter to carbon dioxide and possibly other products causes acidic conditions": Taylor & Illing, 1969, p.89). Much the same observations were made by Butler (1969) on the sabkha sediments of the Trucial Coast (where modern dolomite was found). At depths of 50 to 150 cm pH values clearly below 7 were measured in these Holocene carbonate sediments. "The overall acidity of the brines in the sediments has probably been caused by decomposition of organic matter releasing carbon dioxide and hydrogen sulphide ...": Butler (1969, p.167). The low pH values measured by Taylor & Illing (1969) confirmed the observations by Curtis et al. (1963), who had measured pH = 6.0 to 6.2 in the sabkha sediments of Abu Dhabi; similarly Patterson & Kinsman (1982) measured pH values between 6.32 and 7.26 in those sabkha sediments. Perthuisot (1971) measured pH = 6.0 to 6.5 in the sediments of sabkha El Melah (Tunisia); whereas Pierre et al. (1984) found pH values between 6.1 and 7.1 upon measuring sediments from the Ojo de Liebre lagoon (Mexico) (at all of these sites modern dolomite has been found).

The pH of seawater collected away from land and not directly influenced by an abundant marine flora is often around 7.6 to 8.0 (Baas-Becking et al., 1960). But this constant pH value is most likely the result of the absence of large changes in the amount of dissolved CO_2 , and not so much due to the natural buffering capacity of sea water. For as Baas-Becking et al. (1960, p.259) put it: "... the pH control seems to be the delicate balance between dissolved carbon dioxide and calcium carbonate, which is usually almost at saturation in sea water." Additional support for the importance of the CO_2 balance came from the laboratory experiments, in which 0.2 g $CaCO_3$ was added to 300 ml of natural seawater. After CO_2 at approximately 1 bar had been bubbled through during one night, pH values of 6.10 to 6.15 were reached. At the same time the active participation of bacteria in influencing the pH of the solution, from which magnesite or dolomite will be precipitated, should be considered. Bacteria bring about a variety of biochemical reactions influencing the hydrogen-ion concentration (such as production of carbon dioxide, production of organic acids, oxidation of hydrogen sulfide, reduction of sulfur to hydrogen sulfide, formation of

nitrite, production of ammonia from compounds such as amino acids, urea, proteins: ZoBell, 1946). Oppenheimer & Kornicker (1958) have shown in laboratory experiments, how sulfate reduction in a sample of marine sediment will lower the pH from originally 7.6 to 6.3 in the anaerobic zone, whereas the pH of the overlying aerobic zone remained constant at 7.7. Saturating a sample of the same sediment with H_2S led to a drop in pH from 8.5 to 6.8; and saturating it with CO_2 lowered the pH from 8.5 to 6.1. Not as much the production of organic acids by bacteria, but especially the formation of H_2S and CO_2 within the sediment during the microbial decomposition of organic matter influences the pH according to Oppenheimer & Kornicker (1958).

Often measurements of the pH of pore water samples are given, based on a few samples taken during the (rather restricted) time of field studies. As a consequence any variations in pH during the year will go largely unnoticed. But "Permanent conditions are hardly ever realized in the natural environment. ... In the photosynthetic zone there is a diurnal increase and a nocturnal decrease in the characteristics. There is an annual cycle in a great many environments ...": Baas-Becking et al. (1960, p.264).

In seawater fluctuations in pH result mainly from periodical changes in the amount of dissolved CO₂. Notably the life cycle of algae such as diatoms influences the pCO₂ of seawater. As for example Wattenberg (1936) noted, the bloom of diatoms each year reduces the amount of dissolved CO₂; whereas the death of large amounts of diatoms half a year later greatly increases the pCO₂. Especially in semi-enclosed basins such as the Black Sea this life-cycle of diatoms introduces a distinct annual rhythm of a number of physical-chemical factors. Emery (1946) suggested, that the sea water of rock pools may hold so much carbon dioxide in solution, that dissolution of calcium carbonate takes place. Measurements of the total amounts of dissolved CO₂ showed a daily rhythm from about 90 mg/dm³ at sunrise to some 40 mg/dm³ just before sunset. Biological activities of plants as well as animals combine to render distinctly fluctuating amounts of dissolved carbon dioxide. During sunlight hours plants will withdraw CO₂ from the seawater. At the same time solubility of calcium carbonate is reduced by a higher temperature of the water than at night. At night plants produce CO₂, much like the animals inhabiting tidal pools. The lower night temperature is another factor in enhancing the dissolution of CO₂ in seawater. Large variations in pH of the seawater will be restricted to shallow rocks pools with a rather small amount of sea water.

In intertidal rock pools, especially in pools containing decaying sea weeds, the pH may be lowered significantly as Newell (1970) indicated. But in most sea water pools the pH seldom reaches values below that of sea water, despite the pronounced day/night fluctuations in algal activity. Even so "... The maximum variation in the oxygen concentration and pH depends primarily upon the balance between algae and animals" (Newell, 1970, p.67). And "Rock pools high in the intertidal zone would therefore be expected to show more marked variations in oxygen concentration and pH than those lower on the shore ..." (Newell, 1970, p.68).

Fluctuations in pH of considerable amplitude in a marine sediment have been revealed in the *in situ* measurements performed by Gnaiger et al.(1978). "The pH of the surface sediment reaches maximum values, up to 9.6, at daytime low tide. Shortly after sunset the pH decreases below that of seawater, and still lower readings are obtained during the night, when reducing conditions prevail up to the surface and the odor of hydrogen sulphide diffuses over the beach. Maximum daily fluctuations of up to 1.5 pH units are limited to the topmost 0.5 cm of sediment": Gnaiger et al. (1978, p.853). Not as much changes in temperature were noted to influence the pH, but especially dark/light changes, affecting the photosynthesis of algae in the uppermost layer of the sediment. In the view of Gnaiger et al. (1978) these fluctuations in intra-tidal pH values can only be detected by way of *in situ* measurements; a delay of several hours between sampling and pH

measurement (in the laboratory) will eradicate the differences in pH again. Kühl (1964) found fluctuations in pH occurring in the North Sea tidal flats near Cuxhaven (Germany). The measured pH values ranged from around 7 to more than 9, and were correlated to virtually synchronous fluctuations in temperature of the sea water and its oxygen content. The oxygen content was largely controlled by the daily fluctuations in photosynthesis of diatoms and the seasonal growth of these algae. When darkening part of the sediment in an *in situ* experiment, no fluctuations in pH or oxygen content could be measured by Kühl (1964).

Schmalz & Swanson (1969) measured diurnal fluctuations in pH, in the amounts of dissolved CO_2 and in carbonate saturation of sea water on various tropical and sub-tropical locations. Especially in restricted water bodies such as pools and the lagoon at Eniwetok the fluctuations in pH were pronounced. From their laboratory experiments Schmalz & Swanson (1969) were able to conclude, that the measured fluctuations in pH had to be the result of the photosynthetic activity of green plants during alternating phases of light and dark. "It is noteworthy that the amplitude of the diurnal changes observed is related to the volume of water in the aquaria": Schmalz & Swanson (1969, p.257).

Kuenen (1950) was convinced, that especially rain and groundwater would be able to dissolve the calcium carbonate of reef limestone. ("The chemical erosion of reef limestone is frequently prepared for and supported by the solvent action of the groundwater. It is a well-known fact that rainwater containing carbonic and humic acid strongly attacks limestone ...": Kuenen, 1950, p.437). In a study of Kapingamaringa Atoll McKee (1958, p.255) explained: "Showers on the islands normally are short but violent, and permeable surfaces allow most of the water to enter readily with a flushing that probably accounts for the general lack of saline residues. Migrating waters combine with carbon dioxide given off by plants to form carbonic acid which is active in the dissolution of limestone. Much evidence of such solution is seen in the bedrock". Baas-Becking et al. (1960) measured how considerable fluctuations occur in rain water during thunder storms (probably related to the formation of nitric acid): rapid changes by as much as 2 pH units within 10 minutes were observed. The pH values of normal rain water (769 samples) listed by Baas-Becking et al. (1960) ranged from pH = 3.00 to pH = 7.17.

In general rain water contains only a small amount of dissolved carbon dioxide (Schoeller, 1962 gave analyses of some 0.8 to 2.5 mg $CO_2 / dm^3 H_2O$). Much higher amounts of CO_2 occur in groundwater, notably in soils. As Schoeller (1962) stressed, respiration by plant roots and soil-inhabiting organisms, bacteria and fungi, and chemical processes such as bacterial ammonification and nitrification, contribute large amounts of dissolved CO_2 . In addition biological oxidation of sulfides (including H_2S) and the production of organic acids all contribute to the creation of acidic conditions in the soil. The continued production of dissolved carbon dioxide explains the dissolution of almost all calcium carbonate of a soil, especially of aerobic soils (Schoeller, 1962). Dana (1872) pointed out, how the increased amounts of dissolved CO_2 must be originating from the decomposition of organic compounds. But at present attention should be focused on the role of plants and especially the role of soils in increasing the amount of dissolved carbon dioxide in pore water. Elschner (1913) described, how on the Pacific atoll of Nauru large-scale dissolution of reef limestone takes place, leading to a karstic landscape with kaar fields and even giving rise to large caves with stalactites consisting of dolomite.

The weathering of limestone formations on land is greatly enhanced by an overlying soil profile as Adams & Swinnerton (1937) noted. *In situ* measurements of pH in soils ranged, according to a listing by Baas-Becking et al. (1960) from pH = 2.8 to pH = 10. A prominent aspect of the soil environment is the seasonal rhythm in the uptake of CO₂ (Boynton & Reuther, 1939).

High concentrations of dissolved CO_2 are not only responsible for a variety of occurrences of modern magnesite and dolomite in soils, but are instrumental in the deposition of these stable phases in the cave environment as well. For as Holland et al. (1964 B) pointed out, after the uptake of carbon dioxide from the soil, this groundwater seeps into underlying carbonate rocks and dissolves parts of these. The resulting bicarbonate solution seeps further downward until a cave is reached, whereupon due to a loss of dissolved CO_2 into the cave air and/or by way of evaporation of the solution, precipitation of carbonates will take place. However it is of considerable importance to realize, that the uptake of CO_2 in the soil is not at all a static process (because p CO_2 varies with the seasons of the year). Measurements performed by Holland et al. (1964) on the composition of cave waters, showed marked changes in magnesium and calcium concentrations during the year.

Not only microbial production produces considerable amounts of carbon dioxide in the soil, but the respiration by plant roots aids in the process. Reardon et al. (1979) recognized three different sources of CO_2 production in forest soils: 1) root respiration; 2) oxidation of organic material; and 3) microbial respiration. Drastic changes in pCO₂ profile (as measured in several Auger drillings) could be attributed to increased microbial activity in the soil, which was in turn caused by an increase in soil moisture. Reardon et al. (1979) concluded, much like Langmuir (1971), that the dissolution of carbonates in the unsaturated upper zone of this particular soil takes place in an open system.

The pH values measured in sediments and soils are not static properties. As for example Lundegårdh (1927), Reiners (1968), Witkamp (1969), Gerstenhauer (1972), Richter & Jacobs (1972), and Garret & Cox (1973) have pointed out, seasonal changes in pCO₂ are clearly measurable. The *in situ* field measurements by Anderson (1973) have shown, that although soil temperature and soil moisture levels are factors of significance, the distinctly annual large-scale fluctuation in pCO₂ is mainly the result of intrinsic microbiological activity. Carbon dioxide production in wood lands takes place predominantly in the humus layer and to a lesser extent in the leaf litter layers. In general the rate of decomposition of organic matter in heterotrophic soils, and as a result the rate of production of CO₂, is determined by the nitrogen content of the organic input.

In limestone areas the seasonal production of carbon dioxide in the soil leads to a distinctly rhythmic pattern of fluctuations in calcium ion concentration in rivers (as for example Sweeting, 1964 has noted). According to Pitty (1971) fluctuations in calcium carbonate precipitation and dissolution in river water have to be attributed to seasonal changes in temperature, which in turn control the biochemical production of CO_2 in the soil. Rightmere (1978) noted, how a seasonal increase in the amount of CO_2 in the soil will be removed by prolonged periods of rain ("Recharge from this rainfall could effectively flush the biogenically derived CO_2 from the soil": Rightmere, 1978, p.691). Therefore the seasonal changes in p CO_2 are necessarily reflected in seasonal changes in the amount of bicarbonate dissolved in the runoff from that particular soil area.

Perhaps the low-temperature phase relations in nature are somewhat complicated, but there are indications concerning the metastability of aragonite and magnesium calcite in particular with respect to dolomite. For example: "Mineralogical analyses indicate that nowhere in these atolls do aragonite and dolomite coexist, a situation that suggests that either the removal of aragonite by solution or its replacement by calcite is a prerequisite to dolomitization" (Schlanger, 1963, p.991). On the basis of his analyses of core samples from Eniwetok and Bikini Schlanger (1963) came to the conclusion, that this removal of aragonite had to be related to a rising of an atoll above sea level and the development of a fresh-water lens of some thickness. Not all of the effects of this lens of rain water on the carbonate sediments were known, but it was clear, that "... solution of the emergent section takes place probably at least down to the upper surface of the lens" (Schlanger,

1963, p.997). Thus were formed several "leached zones", in which the original aragonite often had been changed into the more stable calcite or into dolomite. The repeated phases of emergence were recorded in other ways too. For example in the fossils found. The presence of shells of land snails and pollen and spores indicative of "high forested islands" has been noted in cores from Bikini, Eniwetok and Funafuti.

The conversion of aragonite into calcite could take place by way of a re-arrangement in the solid state, but Schlanger (1963) thought it more likely, that re-crystallization had involved dissolution & re-precipitation. The removal of amounts of strontium often present in the aragonite, and not found in the resulting calcite, provides convincing evidence in this regard. Because aragonite that remained submerged in sea water had not been changed into calcite, Schlanger (1963) stressed the importance of the freshwater lens in modifying the mineralogy of carbonate sediments of atolls such as Eniwetok.

All of the preceding observations on the conversion of aragonite into calcite on atolls can be applied equally well to describe the conversion of pre-existing calcium carbonate (or even magnesium calcite) into dolomite and magnesite. For it is in reality not the time factor as such, that controls the conversion of the metastable "precursors" into dolomite, as much as the time factor does not control the conversion of aragonite into calcite. It is a series of changes in pH of sufficient amplitude and of sufficient duration, that controls the low-temperature nucleation of dolomite and magnesite. In addition it should be realized time and again, that the structural chemistry of aragonite excludes the incorporation of any magnesium. As shown in my laboratory experiments normal sea water will lead, even under conditions of fluctuations in pH, to the nucleation of aragonite, apparently preventing any further change into dolomite, huntite or magnesite.

There is in principle at least nothing against dissolving either calcite or aragonite and so forming dolomite. Possibly the initial carbonates leave their traces behind in the newly formed stable phase. And in fact Weber (1964) claims to have found in trace element analyses of 300 different specimen of dolomite, a statistically significant partition into one group of dolomites containing higher concentrations of Al, Ba, Fe, K, Li, Zn and Na, and another group with significantly higher levels of Sr. The latter sort of dolomite must have originated, in the view of Weber (1964), from metastable aragonite; whereas the first group must have been formed from calcite.

It has been claimed by various authors, that aragonite would dissolve better and faster than calcite (e.g., "It is found that the first material to change into dolomite is the skeleton of organisms which originally is formed of aragonite": Marshall, 1930, p.62). In most instances that claim was based on observations made with the microscope in thin-sections, where the change of aragonite into calcite could be observed. This conversion of aragonite into calcite can be understood on the basis of stability. For example Leitmeier (1910 A) has pointed out, that under conditions typical of the earth's surface, aragonite is metastable and calcite is the stable compound.⁴⁸ But the conversion of the metastable aragonite into the stable calcite would be taking place at a very slow rate. Leitmeier (1910 A) concluded, that the conversion of aragonite into calcite took place through a process of dissolution and re-precipitation and not through any solid state conversion.

Sibley (1982) claimed, that especially aragonite and high magnesium calcite would be changed quickly into dolomite, but low magnesium calcite would be markedly slower in its conversion into dolomite (the same observation had been made previously by Steidtmann, 1911; Fairbridge, 1957; Schofield & Nelson, 1978; Buchbinder, 1979; and Armstrong et al., 1980). Possibly the effects of grain size on the rate of dissolution are as large or even larger than mineralogy.⁴⁹ As a consequence fine grained carbonate mud will be seen to convert quicker into

dolomite than a coarser grained carbonate sand (as for example Murray & Lucia, 1967 have noted in field studies). Experiments by Bullen & Sibley (1982, 1984) conducted at 523 K and 39 bar, confirmed this role of grain size. Bullen & Sibley (1982, 1984) found, that grain size is more important than mineralogy, and that grain size controls the rate at which a fossil consisting initially of calcium carbonate, will be changed into dolomite.

When trying to adhere to the idea of a replacement process as being responsible for dolomite formation, certain contradictions in basic logic will inevitably be encountered. For example Friedman & Sanders (1967) observed, how at one and the same location some of the skeletal materials would be changed into dolomite, but the same fossils would not be affected at all in other locations. Calcareous red algae were noted to have been converted into dolomite at Eniwetok Atoll (Schlanger, 1957) and on the Plantagenet Bank near Bermuda (Gross, 1965). But the same species of red algae did not show any trace of dolomite formation on Mallorca (Friedman, 1964), on Funafuti, or on Kita-daito-jima (Schlanger, 1963). Why calcareous algae of the *Lithothamnion* sp. in particular are prone to dolomite formation, has been indicated to some extent by Tracey Jr. et al. (1948). The zonation of the Bikini Atoll is such, that these calcareous algae form the seaward margin of the reefs. The *Lithothamnion* "ridge low" is in general broadly arching, sloping gently towards the sea. "There are no islands to impede circulation of water, and on the windward side new supplies from the sea cross the reef during ebb tide": Tracey Jr. et al. (1948, p.871).

Of great importance towards the oil industry is the relation between dolomite and porosity. After measuring the porosity of Plio-Pleistocene dolomites at Bonaire, and comparing it to that of contacting limestones, Lucia & Major (1994) made the surprising observation, that the mean dolomite porosity (of 11 %) was notably lower than the mean porosity of the limestone (of 25 %). This fact would suggest, that dolomite formation is not always accompanied by an increase of pore volume. The decrease of pore volume must have been caused by the precipitation of "excess" dolomite (Lucia & Major, 1994). But the conclusions by Lucia & Major (1994) were explicitly based on the calculation of Élie de Beaumont (1836), and therefore on the assumption of the process of "dolomitization". But by now we know better. The low-temperature formation of dolomite formation may eventually create a sediment consisting entirely of dolomite. Whether or not any porosity remains in a lithified sediments, depends foremost on burial pressure and mechanical processes during lithification.

Murray (1930) rejected the theory of Élie de Beaumont (1836), because no factual evidence in the form of measurements on dolomite samples had been provided. The one sample discussed by Élie de Beaumont (1836) of dolomite with 12 % porosity might have been mere coincidence, and not at all representative. At the same time Murray (1930) thought it highly unlikely, that dissolution typical of the conversion into dolomite would lead to neat little pores. Why would the process not initiate shrinkage and cracks instead of cavities. And of course, as Landes (1946, p.314) put it, "... one still finds it difficult how porosity established in sediments would survive burial and lithification". But the arguments given here against the 12 or 13 % porosity required by the assumed "dolomitization" reaction, do not rule out the formation of porosity. The process of the lowtemperature of dolomite necessarily involves stages of dissolution, and it will depend on the amplitude and duration of the fluctuations in pH on how much of the pre-existing calcium carbonate will be dissolved. If more CaCO₃ is being dissolved than dolomite is being formed, an increase in porosity will result.

The rate of dissolution of the metastable phase during the nucleation of dolomite depends

not only on the pH (as controlled mainly by the amount of dissolved CO_2), but also on the temperature of the solution. In general reaction rates increase markedly with an increase in temperature, and individual rates of dissolution or nucleation of different polymorphs or different phases are unlikely to respond in the same manner. As a result the nucleation of dolomite, huntite and magnesite takes place at different temperature intervals, even under "low temperature" conditions (i.e., around 298 K & atmospheric pressure). These differences in the respective temperatures of nucleation have been noted in my experiments. At present the number of laboratory experiments conducted is not sufficient to allow for any definite "phase diagram" involving dolomite, huntite and magnesite.

LOOKING BACK (AND FORWARD)

"We have seen that, during the progress of geology, there have been great fluctuations of opinion respecting the nature of the causes to which all former changes of the earth's surface are referable."

Ch. Lyell(1832, p.85)

At the end of the 19th century a discussion took place in the mineralogical literature on the possible existence of isomorphism between calcite and magnesite. The discussion had been started by Retgers (1891, 1892) and Brauns (1892), and concluded by Sommerfeldt (1901, 1902). It must be kept in mind, that at that time mixed crystals were generally being considered to be random mixtures of their components: the solid solution (*feste Lösung*) concept of Lehmann (1889). Such solid solutions usually formed a continuous series, when plotting a physical property against chemical composition. Nevertheless Retgers (1891) pointed out the existence of certain double salts, that were not part of a continuous series of mixed crystals, and he mentioned dolomite as one of the examples. The absence of reliable structural analysis based as it was on the use of X-ray diffraction, made itself painfully clear. The first application of X-rays in inorganic chemistry has been described by Friedrich, Knipping & Von Laue in 1912. The first structural analyses of crystals by way of X-ray diffraction were published in 1914 by Bragg. Therefore it will be no surprise to find, that for example Van 't Hoff (1890) and Bakhuis Roozeboom (1891) used only the solid solution model with its random distribution of the different components. Nernst (1892) argued, that a calculation of the change in free energy upon the incorporation of one component into another substance to form a mixed crystal, could be based only on the parallel with the mixing of two different inert gases. As a result Nernst (1892) restricted his considerations to the homogeneous type of mixed crystals, and excluded at beforehand any other type of mixed crystals.⁵⁰

Sommerfeldt (1902) refused to believe, that all mixed crystals were but submicroscopic random distributions of the different components. The homogeneity of such mixed crystals had to be tested before deciding, whether these consisted of a solid solution or a superlattice. Based on his observations of the coloring of growing crystals of KI by I_2 , Sommerfeldt (1902) described crystal growth in general not as a continuous process, but a step-wise process. The colourful alternations of layers of I_2 in KI crystals proved, that adsorption would predominate during the nucleation of mixed crystals.⁵¹ Sommerfeldt (1902), who followed in this respect Bodländer (1899), did not think the formation of the KI- I_2 mixed crystals to be characteristic for the formation of most mixed crystals.

In the case of KI and I_2 the intermittent growth and the adsorption of iodine in distinct monolayers would, in Sommerfeldt's explanation, result from a periodical depletion of I_2 in solution. Diffusion would after a few moments supply again more of the dissolved iodine and thus change the concentration in the solution layer immediately contacting the KI crystal from undersaturation to values near supersaturation. But in the view of Sommerfeldt (1902) a distinction had to be made between mixed crystals with fully miscible components and those that contain compounds capable only of adsorption onto each other. Mixed crystals made up from two isomorphous components would be able to attain a layered structure (*Zonarstruktur*) only through periodical changes in concentration, temperature or pressure.⁵²

In 1975 I have postulated an active role for fluctuations in free energy in the nucleation of dolomite, based on what I had coined "the Sommerfeldt Theorem". But the difference I had thought to exist between the lattice of dolomite and that of magnesium calcites (the disorder between Mg^{2+} and Ca^{2+} of which was explained to be the result of spiral growth) has not been substantiated by electron microscopic studies. In addition my suggestion concerning the nucleation of dolomite contradicted the PBC-theory theory of crystal growth, as Hartman (1982) pointed out. As a consequence I have hesitated for quite a while to postulate any active role for fluctuations again. After long consideration I have had to conclude, that the described low-temperature syntheses of dolomite and magnesite, i.e. the slight variations on Exp. No.57 of Liebermann (1967), decide very much in favor of the atomistic approach (and *mutatis mutandi* of statistical mechanics). Only by way of conducting numerous laboratory experiments, and after casting away all of the possible alternative explanations, the theory of fluctuations remained. However there is a considerable difference in both amplitude and frequency between the fluctuations involved in the Volmer & Weber (1926) / Stranski & Kaischew (1935) model of barriers created by the start of a new monolayer and the large-scale, relatively slow changes in pH characteristic of Liebermann's (1967) experiments. Perhaps the high-frequency, small scale fluctuations typical of the heat movement of the molecules, atoms and ions in a solution are responsible for the formation of two different nuclei, i.e., nucleï of the metastable and the stable phase. The much slower fluctuations in pH co-operate to dissolve more and more of the metastable phase, and so favour the accumulation of the stable phase.

What I have described as *Breaking Ostwald's Rule* (Deelman, 1999, 2001) is a mechanism quite distinct from that known as "Ostwald Ripening" (that name was coined by Liesegang, 1911 and propagated by Kolthoff, 1936^{53}). *Breaking Ostwald's Rule* is the only process capable of changing the very sequence of precipitation required by Ostwald's Rule, into a final result consisting entirely of the stable phase (or the stable state mixed with some of the metastable phase). Fluctuations are required to nucleate and support the growth of the stable phase.

Surprisingly the influence of fluctuations even in the case of Ostwald Ripening is quite pronounced: re-crystallization under conditions of fluctuating temperature takes place notably faster than under isothermal conditions (Meißner, 1920; Hohmann & Kahlweit, 1972). The explanation for this phenomenon can be found in Volmer's(1922) observations on the presence of a mobile layer surrounding each crystal; in this layer two-dimensional nucleation takes place. In fact no real equilibrium between solution and crystal can be assumed to exist; crystal growth takes place in this mobile, partly adsorbed layer.⁵⁴

At present the conclusion must be drawn, that the approach based on classical thermodynamics has not provided the solution to the problem of the low-temperature syntheses of dolomite, huntite and magnesite. The reason for this failure is simple: the reactions involved are not reversible, and therefore no chemical equilibrium sets in (Deelman, 1981). But perhaps describing

how, why and when a particular reaction will be taking place, is not at all the realm of thermodynamics. And although thermodynamics have been applied to chemistry thanks to the work of Horstmann, Von Helmholtz, Planck and Gibbs, only equilibria are studied in most instances. The warning by Van der Waals (1908), that thermodynamics is not capable of describing all of the factors involved in unknown processes, and that therefore considering only the beginning and the end situation of an unknown reaction is not particularly useful, still possesses more than historic significance only.⁵⁵ In particular the phase relations amongst the anhydrous Mg/Ca carbonates have shown, how for example Gibbs' Phase Rule cannot be applied.

After realizing the limitations of classical thermodynamics, attention should be focused on those realms of science, that promise to provide more information on the nature of such irreversible geochemical reactions. A useful approach was found in the theory of fluctuations, because there no longer the assumption of homogeneity both in time and in place is used (as Von Smoluchowski, 1904 put it⁵⁶). The approach typical of classical thermodynamics turned out not to provide an adequate explanation for the phenomenon of nucleation. For the formation of only a limited number of nucleä contradicts the supposition of a homogeneous distribution of all atoms or molecules, as required by classical thermodynamics. The very fact that nucleation involves energy barriers representing fluctuations in free energy, is not always realized. Even in an ideal gas such a homogeneous distribution of all particles cannot be found: for, as Von Smoluchowski (1912) has pointed out, all particles are involved in a constant movement. As a consequence the particles will never show the equal distances from each other necessary to ascertain a "homogeneous" distribution.

It is most astonishing to find, how the notion that all natural processes are irreversible has not at all spurred intense research into the nature of irreversible processes, but research into reversible equilibria instead. According to Bridgman (1941) the reason for the apparent hesitation among scientists to investigate irreversible processes is to be found in a more or less general conviction, that such processes would not be amenable to simplification in terms of a few equilibrium reactions. The belief seems to have spread, that irreversible processes are much too complex. The possible lack of adequate instrumentation for measuring such reactions may have been another factor. Nevertheless observations on irreversible chemical reactions meanwhile have been published. For example Nernst (1921) stated, that in an irreversible reaction the rate of change would be extremely slow, even though the system itself might be far from equilibrium. Nernst (1921) mentioned the behavior of numerous organic compounds as an example: most hydrocarbon compounds typical of organic chemistry would still be unknown, if these compounds would reach their stable state at a measurable rate. Chemical systems far from equilibrium can be influenced considerably by an increase in temperature, because of the temperature dependence of the reaction rate. A temperature increase in systems of for example gaseous hydrocarbons invariably leads to quick oxidation reactions, often taking the form of fires or explosions. Such reactions are evidently irreversible: only one reaction rate (the one leading to reaction products such as H_2O , CO_2 or C) is being increased. No equilibrium will be attained, because after cooling down, the reaction products are not likely to form the initial hydrocarbons again. (That is to say, not in a time span reasonably within the limits of a human observer.)

When studying non-equilibrium systems, it should be taken into account, that fluctuations possess both amplitude and frequency (Von Smoluchowski, 1916). In other words the very presence of for example fluctuations in pH is no guarantee, that the stable phases will be formed instead of the metastable phases. Perhaps the amplitude of these fluctuations in pH is too small to allow for the mechanism to come into action. The selection between the stable and metastable

carbonates takes place on the basis of their dissolution behaviour, and if the pH does not reach low enough values, the process of dissolution does not take place to a sufficient degree. A possible illustration of the amplitude of the required fluctuations in pH can be found in the observations made by Skinner (1963). The carbonate samples from the most southern salt lake in this area of Australia contain clear amounts of dolomite, but the amounts of dolomite decrease, when taking samples from the more northern lakes. The samples from Margrath Flat in the Coorong Lagoon itself (the most northern location) contain no dolomite. The relation with the amplitude of the fluctuations in pH becomes clear, when realizing that the southernmost salt lakes go through a pronounced annual cycle of wetting of drying. Geographically intermediate lakes go through periodical changes in the amount of water, but the Coorong Lagoon water at Margrath Flat does not exhibit any such pronounced annual variations (Skinner, 1963). Not only in Australia the relation between dolomite formation and the amplitudes of the necessary fluctuations is exemplified. For example the sabkha of Abu Dhabi provides much the same evidence, for as McKenzie (1981, p.190) noted on the nucleation of dolomite at that location: "The degree of order increases with distance from the shoreline...". In the intratidal environment the distance from the shoreline represents a certain frequency in tidal flooding. Gunatilika (1991, p.51) even concluded: "A comparison between the Kuwait and UAE sabkhas indicates that it is the frequency of floodrecharge and reflux of tidal waters, which controls flow rates that determines the volume of dolomite formed in a sabkha."

In the described syntheses of dolomite, huntite and magnesite the importance of fluctuations in pH has been shown. There is no need to conclude at present, that in nature the low-temperature nucleation of these minerals requires fluctuations in pH *per se*. The theory of Haber and Volmer states, that fluctuations in free energy (i.e., pressure, temperature or concentration) are needed for the nucleation of the stable phase to take place. What must be concluded is of course, that at present my experiments have shown fluctuations in pH to be most effective. At the same time the *static control experiments* have demonstrated the essential role of the fluctuations in pH.

Now that the mechanism responsible for the low-temperature nucleation of dolomite, huntite and magnesite is known from the laboratory, it is time to go outdoors and check in the field in how far this mechanism applies to the known modern occurrences of these carbonates. In many instances the existing descriptions of modern occurrences of dolomite, huntite and/or magnesite are sufficiently detailed to conclude, that these minerals form exclusively in a *dynamic* environment. Under fully comparable chemical conditions, but in an environment lacking the required fluctuations in free energy, the metastable equivalents (i.e., magnesium hydroxide carbonate, magnesium calcite, and/or aragonite) will be precipitated. In other words when understanding the mechanism of low-temperature formation, the occurrence of the stable minerals can even be predicted.

At present, after describing successful low-temperature syntheses of dolomite, huntite and magnesite, I am in a position to judge, how close other scientists have come in attempting the same. In the first place without any doubt, it will remain a mystery forever why Liebermann (1967) himself did not observe the formation of magnesite in his experiments. Was it because he strongly believed the mechanism to be dependent on the pH as such, and therefore used either sodium hydroxide or ammonia solutions in the titrations? Or was it because he did not perform a sufficient number of experiments at 333 K? Or was it because he could not believe, that any magnesite would form in an experiment in which definitely 0.2 g of CaCO₃ had been added, and therefore a mixed carbonate such as dolomite should develop? Or was it perhaps because Liebermann (1967) placed his theoretical considerations above observations made in the laboratory?

In the second place there is the experiment described by Kocurko (1986), in which I am convinced dolomite *sensu stricto* had developed. But Kocurko (1986) was obviously enough quite puzzled by his own observation, and has not yet made a claim as to the low-temperature nucleation of dolomite.⁵⁷ Even so his experiment is in fact quite capable of producing dolomite at room temperature. Because culturing the field sample of an algal mat must have been capable of causing the necessary fluctuations in pH , the possibility existed to *break Ostwald's Rule*. The use of a culture of algae resembles of course that by Oppenheimer & Master (1963, 1965), but is different in that Kocurko (1986) used *an open system*. For the periodic flooding with filtered sea water of the culture chamber was followed each time by draining. ("The filter paper with algal material was placed on the sediment surface and covered with a thin layer of additional sand. The entire chamber was then flooded with filtered seawater. After flooding, the seawater was allowed to drain through the sediment column": Kocurko, 1986, p.16). After the 5 years this experiment by Kocurko (1986) took, ordered dolomite was found in X-ray diffraction ("... which was not present in the original sediment sample": Kocurko, 1986, p.17).

To my surprise one and the same theory was found to be capable of explaining the lowtemperature formation of dolomite, huntite and magnesite. And in addition, because the theory involves a most useful principle for especially the irreversible geochemical reactions taking place at the earth's surface, a multitude of other areas of investigation has been opened up. For "the theory of fluctuations" not only explains the possible change of an amorphous hydroxide-containing precipitate into the corresponding oxide, it also explains the low-temperature nucleation of the clay minerals (for example kaolinite) as well as minerals such as quartz, hematite, pyrite, and apatite (to name only a few).

What really needs an explanation, is the semi-obscurity into which the "theory of fluctuations" has disappeared in the course of the years. Is it really the ancient controversy again between the view typical of general thermodynamics (Gibbs and Ostwald) and that of statistical mechanics (Boltzmann and Von Smoluchowski)? But at least in the case of nucleation and crystal growth the atomistic view has long since gained the day. Ostwald's concept of metastability is characteristic for the overall approach typical of "energetics". But in fact it is merely an empirical rule, with broad appeal because little or no exceptions became known. This kind of appeal might well explain the longevity of the term.

The theory given in this chapter and described by me as *Breaking Ostwald's Rule* (Deelman, 2001) may seem to be quite new and revolutionary to some. But that is not the case. The foundations were laid down by Tammann, Othmer, Kornfeld, Haber, Marian von Smoluchowski, and especially Volmer. The "theory of fluctuations" has found its way into metallurgy, not in the least because of the work of Roman Smoluchowski.⁵⁸ [e.g., "The fundamental reason for the appearance of nuclei in a homogeneous substance is the existence of fluctuations (i.e., local deviations from normal state)."] But Tammann's and Volmer's textbooks have never really influenced geochemistry. This omission needs to be made good.

Perhaps the work on the more dynamic picture of the nucleation process, including the possible role of fluctuations, has generated too little interest thus far, because there were no practical applications. Most of the atomistic studies on nucleation processes have supplied detailed descriptions, but lacked any surplus value in predicting the nature of certain irreversible (geochemical) reactions. The need for the atomistic approach typical of for example the work of Boltzmann and Tammann has now been confirmed. Most of all the described low-temperature syntheses of magnesite and dolomite have shown, that there really is no point in placing theoretical speculations and computer-based advanced calculus above laboratory experiments. For as

expressed in the words by Henri Poincaré (1912) cited at the outset of the *Introduction* to this publication, only experiments are capable of providing anything new.