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MAGNESITE, DOLOMITE AND CARBONATE GROUPS

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ABSTRACT

Experiments by Xu et al. (2013) have shown, how the kinetic barrier delaying the formation of anhydrous magnesium carbonate in the laboratory consists of disorder among the carbonate groups, and does not involve the often assumed dehydration of magnesium cations. Meanwhile four different low-temperature syntheses of magnesite have become known, which illustrate the possibility to obtain magnesite in reproducible experiments at temperatures of 313 to 316 K. All four syntheses were based on, or were variations of, experiment number 57 by Liebermann (1967). The present note offers a theory based on the observations of Lander (1949), who stressed the importance of cation size in bringing about disorder among the carbonate anion groups. Lander's mechanism is being extended here to include mixed crystals with two different cations such as for example the anhydrous Ca/Mg carbonates. It is concluded, that the size differences between calcium and magnesium cations, through their different effects on the position of carbonate groups, must be responsible for the kinetic barrier encountered in static low-temperature tests on dolomite and magnesite formation. Throughout building the present theory, the leading principle was the fundamental observation, that the formation of dolomite, the calcium magnesites and magnesite involves irreversible reactions, which can take place only under nonequilibrium conditions. The necessary ordering of the carbonate groups requires open systems under the influence of fluctuations in p , T , x . Driving force of all irreversible low-temperature reactions in the system calcite - dolomite - magnesite is the universal tendency of attaining the lowest possible potential energy for the lattices being formed.

INTRODUCTION

Ever since the discovery of anhydrous magnesium carbonate as a mineral by the Irish mineralogist George Mitchel and its description by Lampadius (1800) and Lampadius & Mitchel (1802), uncertainty has existed as to its possible mode of formation. High-temperature syntheses of anhydrous MgCO_3 have become known, but considerable doubt remained as to its possible low-temperature formation. Magnesite is known to occur in the sedimentary environment, where it must have formed under conditions of low-temperature and atmospheric pressure.

By now four different, reproducible laboratory syntheses of magnesite have become known (Deelman, 1999; Alves dos Anjos et al., 2011; Hobbs & Xu, 2020; Vandeginste, 2021). All four laboratory syntheses have in common, that magnesite formed at a temperature of around 313 K (at atmospheric pressure). However, an adequate description of the mechanism involved still awaits publication. Much the same is true for the inorganic low-temperature formation of dolomite. The present account makes a first attempt at a full-scale explanation for the low-temperature phase relations among calcite, dolomite and magnesite.

TAKING THE BARRIER: No dehydration barrier - Carbonate group disorder - Rotation and tilting - A most daring hypothesis - Molal volume

No dehydration barrier - Based on their laboratory experiments with formamide, an organic solvent resembling water, Xu et al. (2013) were able to precipitate anhydrous, if amorphous, magnesium carbonate. On the basis of this success Xu et al. (2013) observed, that apparently not the often invoked dehydration barrier of the magnesium cations, but instead disorder among the carbonate groups must be responsible for the (kinetic) barrier encountered in the low-temperature formation of magnesite. As a logical next step Xu et al. (2013) postulated, that the generally accepted theory of cation hydration forming the main obstacle toward the possible nucleation of magnesite (and dolomite), needs to be reconsidered. The present note aims at doing just that, and postulates that the interaction between carbonate groups and the calcium and magnesium cations forms the key element in the low-temperature phase relations between calcite, dolomite and magnesite.

Carbonate group disorder - The laboratory experiments by Xu et al. (2013) have shown, what the barrier in the low-temperature nucleation of magnesite really consists of. In their experiments Xu et al. (2013) created anhydrous amorphous magnesium carbonate in pure formamide (an organic solvent with a high dielectric constant and closely resembling water with respect to density, dipole moment and surface tension). **"These findings exposed a previously unrecognized intrinsic barrier for Mg^{2+} and CO_3^{2-} to develop long-range order at ambient conditions"**: Xu et al. (2013, p.17750). It is only logical to conclude, that this very mechanism will operate not only in the case of the nucleation of magnesite, but also in the cases of dolomite, the magnesium calcites and of the calcium magnesites. Accepting this observation will open up the possibility to fully comprehend the low-temperature phase relations of calcite, dolomite and magnesite. In other words, the mechanism discovered by Xu et al. (2013) may well turn out to be of truly **universal significance**.

The four different (and successful) syntheses of magnesite in aqueous solutions at temperatures between 313 and 316 K have shown, that it is possible to overcome the energy barrier caused by the disorder among the carbonate groups. Accepting the fact, that the kinetic barrier really is caused by disorder among the carbonate groups, calls for an

explanation not only to account for the rotation and tilting of the carbonate groups, but also for the actual mechanism capable of preventing and cancelling out this form of disorder.

Rotation and tilting - Based on his high-temperature tests with barium-, strontium- and calcium carbonate Lander (1949) concluded, that the structural changes in the alkaline earth carbonates are determined "... by an increase in the number of configurations of rotational oscillation available to the carbonate ion" (Lander, 1949, p.897). Such a transition would take place with a marked increase in disorder among the carbonate groups. However, in the case of calcium carbonate these transitions do not lead to disordered anion configurations. Because there one ordered configuration changes into the next ordered one, or even a third: three polymorphs of calcium carbonate are known. Lander's (1949) tests have shown, how an increase in temperature leads to a stepwise decrease in density for barium- and strontium carbonate.

A most daring hypothesis - It has been claimed by Lander (1949), that the explanation for the disorder among the carbonate groups is to be found in effects caused by the cations involved. Which in the case of all of the mixed crystals between calcite and magnesite, would be Ca^{2+} and Mg^{2+} . (No solid solutions occur in this system at low-temperature & atmospheric pressure; only mixed crystals with a layer lattice, possibly only partial such as in the case of the magnesium calcites. See for all underlying details: Deelman, 2013.) Cations would exert such large (ionic) attraction on nearby carbonate groups, that rotation and tilting would become inevitable.

Although Lander's mechanism was originally restricted to barium-, strontium- and calcium carbonate, it may well be applied to all of the mixed crystals between calcite and magnesite (i.e., the magnesium calcites, dolomite, and the calcium magnesites). However, when doing so, the effects of the considerable difference in size between calcium and magnesium come into play. The magnesium ion (= 8.6 nm) is around 30 % smaller than the calcium ion (= 11.4 nm) (ionic radii from Shannon, 1976). It was pointed out by Goldschmidt (1926), that in ionic crystals a solid solution can be formed only, when one of the two different cations is less than 15 % smaller than the other (expressed as a percentage of the smallest cation). Layer lattices (even superlattices) will form, when cations of a mixed crystal differ by more than 15 % . In other words, not only dolomite possesses a layer lattice, but all of the mixed crystals with compositions in between that of calcite and that of magnesite will be seen to form (possibly incomplete) layer lattices instead of solid solutions.

The observation made by Goldschmidt (1926) can be carried beyond the question of the existence of a solid solution or layer lattice. It will also provide the theoretical basis for the presence or absence of disorder among the carbonate groups of the anhydrous Ca/Mg carbonates. The large size of the calcium cations leads to large openings in the lattice available for incorporation of the rather small magnesium cations. Considerations on symmetry make it likely, that the small magnesium cations will cause little or no disturbance of the calcite lattice. Hence, there are no problems during the low-temperature formation of magnesium calcites. In contrast a lattice made up from the small magnesium cations, will quickly become disturbed by the incorporation of only a few of the large calcium cations. In that case a considerable energy barrier (in fact caused by steric hindrance) will arise, not only when trying to form dolomite, but notably in the case of the calcium magnesites and that of magnesite itself.

Molal volume - Because the dissolution/precipitation reaction of magnesite in water containing carbon dioxide, is not a reversible reaction (much like that of dolomite), classical thermodynamics can not be applied to the system calcite - dolomite - magnesite. This observation at once provides an adequate explanation for the exceptionally wide range of the solubility products published for dolomite and magnesite, including all of the vain attempts to

use this solubility product and/or saturation index to explain the possible low-temperature nucleation of dolomite and/or magnesite (see for example Land, 1998).

After ruling out all of the many parameters typical of equilibrium thermodynamics, only few parameters remain of possible interest. The first to be considered here, will be molal volume. After plotting the decrease of the molal volume in the system calcite - dolomite - magnesite against the composition in terms of mol percent calcite and mol percent magnesite, Althoff (1977) noted a clear linear dependency between molal volume and the incorporated percentage MgCO_3 (Fig.1). This is of course not really a surprising observation, when considering the aforementioned large size difference between calcium and magnesium cations. Nonetheless it reveals, how little influence all of the carbonate groups have on the change of molal volume with a change in composition of the mixed crystals. In other words, it underlines the conclusion of Lander (1949), that the (disorder/order) arrangement of the carbonate groups is largely controlled by the cations involved.

A SEQUENCE OF DIFFERENT MINERALS: Observations made - Multistep reactions - The Redlich sequence - No solid state diffusion

Observations made - Concerning the appearance and disappearance of different minerals when duplicating Liebermann's Exp.No.57, a rather surprising observation can be made: "... precipitates were obtained, that should represent subsequent stages in an overall reaction" (Deelman, 1999, p.294).

For example in one of my experiments (conducted at 333 K) aragonite, calcite and a trace of Mg-calcite were detected after the very first cycle. It should be noted, that the starting material was calcite only. After 3 cycles aragonite, a little dolomite plus a trace of magnesite were found. After 5 cycles mainly aragonite, a little dolomite and clearly magnesite were noted. And after 8 cycles only pure magnesite was found. In another experiment (at 313 K) I have noted the presence of calcite, aragonite, and a small amount of Mg-calcite (with its main peak at 29.0 nm) after the first cycle. After 3 cycles aragonite together with a Mg-calcite (main peak at 28.8 nm) were found. After 5 cycles a small amount of aragonite, calcite and a Mg-calcite (several high diffraction peaks between 29.4 and 27.8 nm, with the predominant one at 28.8 nm) After 8 cycles aragonite, magnesium calcite and a little magnesite originated. After 14 cycles only pure magnesite was found.

These observations on the variability occurring among the precipitates formed after duplicating Exp.No.57 by Liebermann (1967), have been confirmed by Alves dos Anjos et al. (2011, p.214), who performed several duplication tests at 313 K, and have noted the variation among the end-products: "In experiments 2 and 4, the precipitate formed consisted of magnesite, dypingite and aragonite. In exp.3 magnesite and aragonite were formed."

An important aspect of the mechanism involved in the step-wise formation of the anhydrous Ca/Mg carbonates is the degree, to which each and every time the existing phase will be dissolved. Is it really necessary to remove all of the initial phase before being able to start a new one with an increased percentage of incorporated magnesium carbonate? Observations made by Hobbs & Xu (2020) seem to point toward a different process taking place. In their TEM-EDS analyses of the composition of along the radius of (massive) calcium magnesite spheres, a stepwise increase in MgCO_3 from centre to edge was measured. As can be seen in Fig.5 D in Hobbs & Xu (2020), the measured percentages change rather abruptly from 64 to 71 to 81 % magnesium carbonate. In other words, there seems to be no "monotonic shifting" of the percentage MgCO_3 , but a step-wise one in accordance with the very nature of the macroscopic reaction itself. Even in the X-ray diffractograms made at the end of each experiment (for example Fig.7 in Hobbs & Xu, 2020) such step-wise changes can

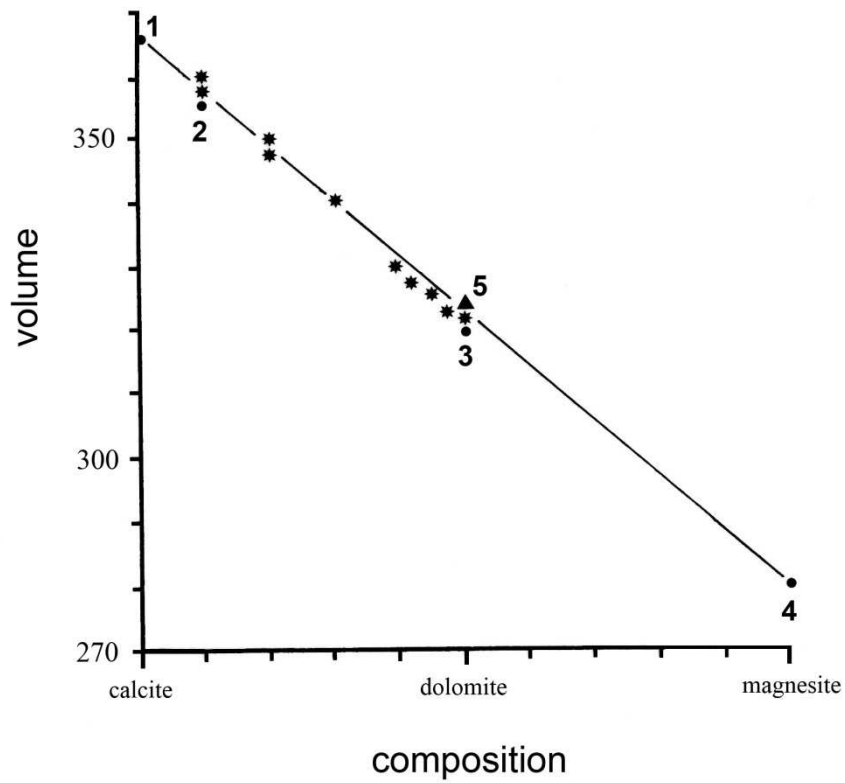


Fig.1 - Decrease of the molal volume in the system calcite - dolomite - magnesite. Abscissa: molal volume in cubic Ångstrom. 1 - Calcite calculated from Chessin et al. (1965); 2 - various magnesium calcites; 3 - dolomite; 4 - magnesite calculated from Oh et al. (1973); 5 - mixture of 50 mol% calcite plus 50 mol% magnesite (after Althoff, 1977).

be discerned.

Multi-step reactions - Concerning the variability found in the mineralogy of the phases formed during the subsequent steps typical of Liebermann's Exp.No.57, the following observation has been made: "It is surprising to note, how such variability in the final results of nucleation experiments has also been found by Tammann (1903), Othmer (1915) and Kornfeld (1916). The statistics typical of the atomistic approach not only explain the observations made, but also predict how an increase in the number of nucleation experiments would decrease the spread among the results" (Deelman, 1999, p.298).

The question might be raised, why the various experiments have shown an increase in the percentage MgCO_3 incorporated after each cycle of dissolution and precipitation. The only reasonable explanation being, that Exp.No.57 of Liebermann (1967) is in fact an irreversible reaction taking place in an open system. What pertains during the whole of the experiment, are non-equilibrium conditions in an open system. After each dissolution cycle all solid phases have disappeared, and the phase at the end of the interval of precipitation will be formed under conditions of the newly decreased potential energy. As explained above (in the section on **Molal volume**) each (stepwise) incorporation of more magnesium into the mixed crystal being formed, effectively lowers the molal volume of the nuclei. As a consequence a lower state of potential energy (of the lattice being formed) is being attained after each cycle of this particular multi-step reaction (**Fig.2**).

The Redlich sequence: Redlich (1907, 1909, 1917) described, how during his field work on Austrian magnesites, he had often observed the sequence calcite - dolomite - magnesite. The observation as such has been confirmed by Leitmeier (1916, 1953). Could it be, that this particular sequence finds its ultimate origin in a fundamental aspect of the process of selection by rates denoted as "breaking Ostwald's Rule"?

No solid state diffusion - Of fundamental importance to the low-temperature phase relations among the anhydrous Ca/Mg carbonates is the lack of any measurable degree of solid state diffusion at temperatures of around 298 K.

In the experiments by Graf & Goldsmith (1956) temperatures of 763 K and more were used. At such high temperatures cation ordering will take place at a measurable rate driven by the increase in kinetic energy of the ions ("... at elevated temperatures ionic mobility is great enough for cation ordering to take place": Graf & Goldsmith, 1956, p.174). At low temperatures (around 298 K) the two different cations of dolomite do not possess sufficient kinetic energy for solid state diffusion and "spontaneous" processes of cation ordering. Measurements with radioactive isotopes confirm this observation.

The measurements by Brätter et al. (1972), Mucci et al. (1985), Fisler & Cygan (1999) and Kent et al. (2001) turned out to support the earlier observations of Lahav & Bolt (1964), who had measured the self-diffusion coefficients of Ca^{45} added in the form of calcium chloride to suspensions of calcite or dolomite (at room temperature). The calcite and dolomite were ground to a grain size smaller than 5 micron. For calcium cations in solution in contact with calcite powder a self-diffusion coefficient of $8 \times 10^{-16} \text{ m}^2/\text{sec}$ was found. For calcium cations in solution in contact with ground dolomite, a value of about $10^{-16} \text{ m}^2/\text{sec}$ was measured. Such extremely low values for diffusion coefficients effectively preclude any active role for the process of solid state diffusion in the low-temperature formation of dolomite. Thus Graf & Goldsmith (1956, p.185) had to conclude, that : "The virtual absence of dry diffusion in carbonates at earth-surface temperatures is shown by the persistence of metastable magnesian calcites in fossils as old as Eocene (Chave, 1954) that were embedded in relatively impervious shales." Much like Brätter et al. (1972) before them, the diffusion experiments led Fisler & Cygan (1999) to the conclusion, that dolomite formation at low temperatures (around 303 K) cannot take place by way of the diffusion of cations. Instead dolomite formation would involve "solution and precipitation" (Fisler & Cygan, 1999,

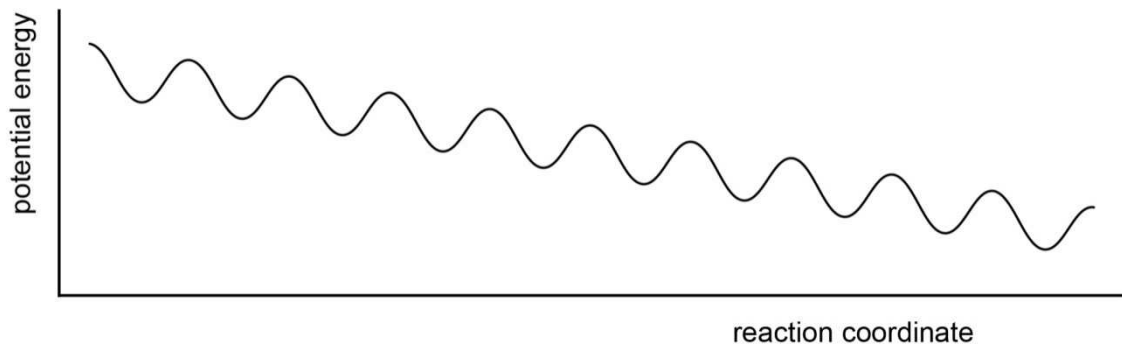


Fig.2 - The step-wise decrease of potential energy in a multi-step reaction. Along the route a variety of different precipitates will form, most of which will disappear again during the successive dissolution intervals. Ultimately only the most dense phase, in this case magnesite, will survive the sequence of the numerous alternations between precipitation and dissolution.

p.1398).

More observations which contradict the suggested role of solid state diffusion, have become known from isotope studies. On the basis of measurements of the exchange between isotope-labelled carbon dioxide and calcite at a temperature of 576 K Haul et al. (1953) concluded, that no diffusion into the crystal can take place. Only an extremely thin outer layer of the crystal, in fact only one monolayer of calcite, would be involved in exchange processes. Using the same technique of isotopic exchange, Haul & Stein (1955) measured a diffusion coefficient of CO₂ into calcite of 5×10^{-17} cm²/sec at a temperature of 973 K. Anderson (1969), using isotopes as tracers, demonstrated that diffusion of oxygen or carbon does not take place in carbonates at room temperature.

COMPETITION BY RATES: Carathéodory's Principle - The atomistic approach - Overcoming the barrier - Breaking Ostwald's Rule - The driving force

Carathéodory's Principle - It is almost impossible to explain Carathéodory's (1909) re-definition of the second axiom of equilibrium thermodynamics without making use of complex mathematical operations (Pfaffian differentials), but not entirely so. There is for example the explanation published by Born (1949): "The central point of Carathéodory's method is this. The principles from which Kelvin and Clausius derived the second principle are formulated in such a way as to cover the greatest possible range of processes incapable of execution: in no way whatever can heat be completely transformed into work or raised to a higher level of temperature. Carathéodory remarked that it is perfectly sufficient to know the existence of *some* impossible processes to derive the second principle. I need hardly say that this is a logical advantage. Moreover, the impossible processes are already obtained by scrutinizing Joule's experiment a little more carefully. They consisted in bringing a system in an adiabatic enclosure from one equilibrium state to another by doing external work: it is an elementary experience, almost obvious, that you cannot get your work back by reversing the process. And that holds however near the two states are. One can therefore say that there exist adiabatically inaccessible states in any vicinity of a given state. That is Carathéodory's principle" (Born, 1949, p.39). It has been observed by Turner (1960), that Carathéodory's (1909) re-definition of thermodynamics was no longer based on the hypothetical Carnot cycle, because the new approach avoided the concept of heat as a measurable quantity.

The rather abstract theorem by Carathéodory (1909) forms the theoretical basis for all of the subsequently developed theory of nonequilibrium thermodynamics, because it has made clear, that apart from the rather exceptional (and man-made) conditions of a closed system at indefinite equilibrium there are many more situations of nonequilibrium.

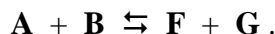
The second principle of nonequilibrium thermodynamics is known as Onsager's Reciprocal Relations. The Onsager Reciprocal Relations provide the theoretical basis for the fact, that in the case of nonequilibrium two or more reactions will be able to take place simultaneously (Denbigh, 1971). When for example three different reactions take place in an open system, each of the three reactions individually will be reversible (Onsager, 1931 A, B; Miller, 1960). At the same time three different reaction rates will be involved, which need not be identical.

The atomistic approach - Carnot (1824) had been building the foundations of thermodynamics on the macroscopic gas laws by Gay-Lussac (1802). Following the example of Von Mayer (1842) and Holtzmann (1845), Clausius (1850) had explained the heat movement to be the result of the movement of the smallest parts of a substance ("*einer Bewegung der kleinsten Theile der Körper*": Clausius, 1850, p.370). The distinction made by Clausius between two different branches of thermodynamics, "general" thermodynamics and

"special" thermodynamics, received support from Boltzmann (1896). The first branch concerns the two theorems known as the first and the second axiom of thermodynamics; the second branch (known today as statistical mechanics) rested on the view, that essentially heat consists of the manifold movements of atoms and molecules. The general approach would be more rewarding from the point of view of macroscopic measurements, but as Boltzmann argued, in a number of instances recourse must be taken to a more detailed description based on the behaviour of the individual particles. Boltzmann (1896) rejected an abstract approach constructed in the complete absence of any corpuscular theory, and he wondered what in the end the significance would be of different forms of energy.

Boltzmann's picture of a gas involves particles, which attain a wave-like motion in the course of a multitude of collisions with other atoms and molecules. Such waves prohibit the clear recognition of the linear displacement as such at most temperatures. The distinctly fluctuating movement of individual particles is closely related to the oscillations, which occur when the path length in between successive collisions has been reduced to virtually zero (i.e., in the solid state). Even though Boltzmann based his considerations on mechanical considerations rather than on actual observation (it must be remembered, that in 1896 X-ray diffraction and electron microscopy were still unknown), he was convinced of the importance of the corpuscular nature of matter. The space taken up by matter, whether in a gas, in a fluid, or in a solid, is not filled in a continuous manner. Matter consists of infinitesimal, yet still discrete, entities. A continuum would have to involve an amount of elements, which would be mathematically endless. However, a small part of such a continuum cannot be considered to contain an endless amount of these entities. Therefore on small parts of a continuum, such as a small amount of liquid or an individual crystal nucleus, no mathematical calculations involving functions of progression, and especially no calculations based on the use of differentials, can be performed. The mathematical requirement of "approaching infinity" cannot be met in all of those cases. Therefore such calculations do not represent any form of reality.

Taking the barrier (Fig.3) - On the subject of overcoming a kinetic barrier Kramers (1940) has suggested, how mere chance would enable only few atoms (or molecules) taking part in the incessant heat movement, to pass over a potential energy barrier. Subsequent considerations based on the measurement of macroscopic properties such as pressure, temperature and concentration, combined with an assumption of equilibrium, are no longer sufficient to obtain an adequate explanation. Underlying mechanisms have to be approached in terms of reactions on an atomic level. Such an approach will be used here. Applying Onsager's reciprocal relations allows for the assumption, that the reaction between the reactants **A** and **B** may well give rise to reaction products other than **C** and **D**. If, for example **C** and **D** are metastable compared with the stable **F** and **G** phases, this second reaction can be written as:



Progress of this second reaction can be quantified through the use of the equations

$$v_3 = k_3 \cdot [\mathbf{A}] \cdot [\mathbf{B}] \quad \text{and} \quad v_4 = k_4 \cdot [\mathbf{F}] \cdot [\mathbf{G}] .$$

Because the reaction between reactants **A** and **B** leads in one case to the metastable **C** and **D** phases, and a different reaction may well lead to the stable phases **F** and **G**, thus v_1 does not equal v_3 . By definition the reaction rate for the metastable phases **C** and **D** ($= v_1$) will be greater than the rate of the reaction giving rise to the stable phases **F** and **G** ($= v_3$).

Ultimately it were two papers by Stranski & Totomanow (1932, 1933), which for the first time provided an adequate explanation for the phenomenology summarized into

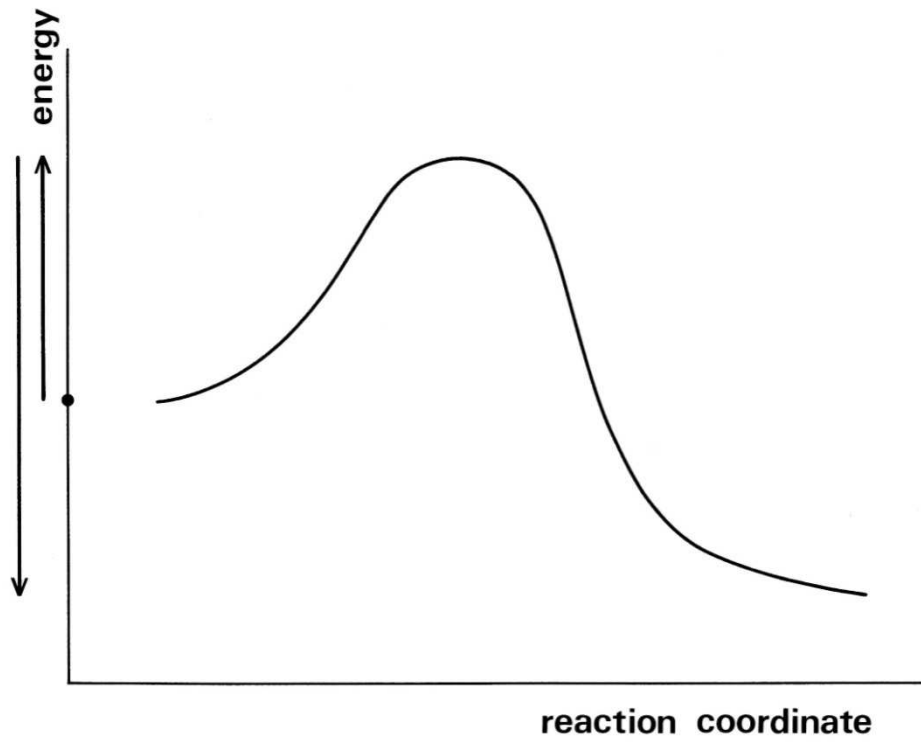


Fig.3 – Under static conditions, in a closed system, this curve represents a barrier. Under dynamic conditions, characteristic of an open system, this curve represents a fluctuation.
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Ostwald's Rule. When considering the possible formation of two polymorphic modifications from a supersaturated solution, one of the equations by Volmer & Weber (1926) could be used to delineate the probability for each of the two different polymorphs. It turned out, that the non-stable (i.e., metastable) modification would form more easily than the stable one. At lower temperatures of the supersaturated solution the stable polymorph would form more easily ("*leichter*") than the metastable one.

The occurrence of two distinctly different reaction rates for a metastable and a stable phase will lead, in the event of a system subject to periodical alternations between dissolution and precipitation, to the step-wise removal of more and more of the metastable phase (with its higher dissolution rate) and so favour the formation of more and more of the stable phase (coined "Breaking Ostwald's Rule": Deelman, 2001).

The driving force - In the case of the low-temperature phase relations between calcite - dolomite - magnesite the universal principle of an increase in potential energy leads to a (step-wise) increase of the molal density of the precipitate. The theoretical background for all of the step-wise reactions involved, can be found in a branch of physics, which originated long before the development of equilibrium thermodynamics by Carnot (1824) and Clausius (1850). It must be realized of course, that the Principle of Least Action clearly predates the development of equilibrium thermodynamics, The Principle of Least Action (as advanced by Moreau de Maupertuis, 1744 and Helmholtz, 1887; see for example Brunet, 1938). Planck (1915), after demoting equilibrium thermodynamics, has claimed the Principle of Least Action to constitute the pinnacle of theoretical physics.

ORDERING INTO DOLOMITE: Nucleation and growth of dolomite - Clustering and nucleation - Spontaneous self-organization - Clustering, fluctuations and selection - A simple energy landscape

Nucleation and growth of dolomite - In my 1981 paper I have tried to explain the low-temperature nucleation of dolomite on the basis of the Sommerfeldt Theorem, which applies to all mixed crystals not consisting of solid solutions with their random distribution of the components (Sommerfeldt, 1901, 1902). For example the mixed crystals of KI-I₂ form crystallites with very thin individual layers of iodine. Their mode of formation would be caused by the combination of adsorption in combination with step-wise fluctuations during the growth process. Solid solutions will follow simple physical principles and thereby grow from a homogeneous solution in a homogeneous manner. But the mixed crystals made up from two isomorphous compounds with a layered lattice, will be seen to require periodical changes in the concentration of the solution, or fluctuations in temperature or pressure. The original text is as follows: "... *eine Zonarstruktur kann bei denselben nur durch Veränderungen, welche das Lösungsmittel in seiner procentischer Zusammensetzung erleidet, veranlaßt werden, oder durch beträchtliche Schwankungen der äußeren Variablen (Druck und Temperatur)*": Sommerfeldt (1902, pp.61-62). Summarized into English this theorem by Sommerfeldt would read: "Alternations in the chemical composition of a mixed crystal with a layer structure formed between two isomorphous compounds, can be attained only through fluctuations of the contacting solution in concentration, temperature or pressure."

However, direct application of Sommerfeldt's Theorem to the nucleation and growth of dolomite is complicated by crystallographic considerations. For as Hartman (1982) explained, dolomite crystals do not grow in the direction of (001), as would be implied by the Sommerfeldt Theorem, but instead dolomite crystals are known to grow by way of the rhomb faces {104}. Following Hartman & Perdok (1952) the latter appear as **S** (stepped) faces in **Fig.4**, even though Hartman (1982) denoted those very rhomb faces as **F** (flat) faces. In other

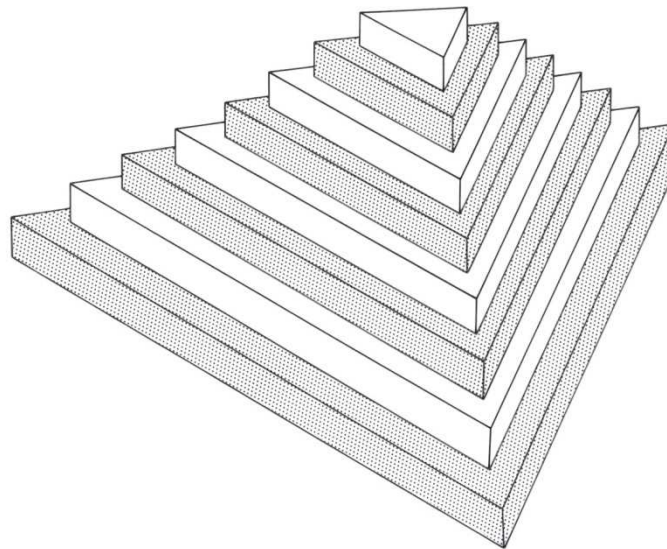


Fig.4 - The apex of a dolomite rhomb reveals the fundamental difficulty encountered, when trying to use step-by-step nucleation (the Volmer-Kossel-Stranski model) to explain the low-temperature formation of the mineral dolomite. Continuing the dolomite lattice through the addition of calcium carbonate molecules (white layer) and magnesium carbonate molecules (grey layer) is not difficult, because it involves adsorption onto a stepped surface, and is therefore energetically favoured. The real problem is to initiate *ab initio* the regular sequence of calcite- and magnesite monolayers alternating in the direction of the *c*-axis; such a sequence can only be realized during two-dimensional cluster formation.

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words, there is a major problem concerning the exact mode of growth of dolomite, as well as of the very start of growth during the stage known as nucleation.

Once a nucleus with the initiation of a dolomite lattice has formed, no major problems remain concerning its continued growth. The main question is this: how to obtain such a mixed layer arrangement of calcite layers alternating with magnesite monolayers? No doubt can possibly exist concerning the important role played by the possible role of fluctuations (in p , T , x) as suggested by Sommerfeldt (1902). In the following section the fundamental role of pre-nucleation clusters will be shown, and the all-important dynamic picture of ultra-high speed changes in temporary bonding and the formation of a multitude of possible molecular configurations will be emphasized. Only when invoking the mechanism of clustering prior to actual growth of dolomite nuclei, the enigmatic riddle sketched above can be solved.

Clustering and nucleation - Modern analytical techniques in combination with computer-based simulations have made it possible to observe, how prior to classical nucleation (that is step-by-step and layer-by-layer according to the model approach by Volmer, Stranski and Kossel), a very small number of particles (atoms, molecules) will become (at least temporarily) associated with each other. In a solution such clusters are initially amorphous, but reorganization takes place rapidly into **a variety of different multi-particle arrangements** known as clusters. Driving force for the initial formation of pre-nucleation clusters as well as for the subsequent re-arrangement into well-defined nuclei is the incessant heat movement (Brownian motion) of atoms and molecules.

Classical nucleation involves the formation of aggregates visible with the unaided eye (or with the optical microscope). In contrast formation of clusters can be studied only with the electron microscope, with atomic force microscopy, or approached with computer-based simulations. In other words the distinction between nucleation and cluster formation is founded solely on the respective dimensions of the aggregates formed. Observations with advanced technologies in combination with computer-based simulations meanwhile have provided nothing less than spectacular new insights into the corpuscular aspects of the process of clustering. Clustering describes a process taking place before actual nucleation starts: "Prior to nucleation there is continuous formation and dissolution of ionic or molecular clusters...": Walton (1967, p.2). Once formed clusters are subject to incessant structural changes (Hoare & Pal, 1972; Marks, 1985). In the definition of Castleman (1990) clusters are weakly bound assemblies of molecules, atoms, or ions, whose size distribution and composition can be comparatively easily shifted by changes in temperature, pressure, or concentration.

The formation of clusters is initiated by (density) fluctuations: Von Smoluchowski (1916), Haber (1922), Vekilov (2004), Bots et al. (2012). Numerous configurations of polymerized molecules can be formed: Martin (1983), Tribello et al. (2009), Raiteri & Gale (2010), Demichelis et al. (2011). More than one polymorph of ionic compounds, or even different compounds, can be formed simultaneously: Banfield et al. (2009), Pontoni et al. (2003). The change of clusters into crystalline nuclei takes place by dissolution and re-precipitation: Aizenberg et al. (2003), Lee et al. (2007). Aggregation of clusters into *mesocrystals* takes place by way of "non-classical crystallization". This mechanism consists of the spontaneous self-organization of different adjacent clusters (Niederberger & Cölfen, 2006; Sethmann & Wörheide, 2008). Notably magnesium calcite shows a microstructure typical of mesocrystals (Berman et al., 1990, Vielzeuf et al., 2008).

Spontaneous self-organization - One may wonder in how far the mineral dolomite really holds an exceptional position with regard to its low-temperature phase relations in the system calcite - magnesite. As is known, it is relatively easy to create various magnesium calcites in low-temperature, static experiments, but dolomite *sensu stricto* appeared to be almost impossible to create under those conditions. At the same time magnesium calcites

with 50 mol % MgCO_3 are not at all unknown; even magnesium calcites (or rather: calcium magnesites) with more than 50 mol % MgCO_3 are not unknown. Even so invariably these Mg-calcites with 50 mol % MgCO_3 are easily distinguished from true dolomite by the absence of the superstructure lines in their diffraction patterns. Therefore the special position of dolomite must be related to the fundamental differences among the disordered lattices typical of the magnesium calcites and the highly ordered atomic arrangement of dolomite *sensu stricto*. There is however a striking parallel with certain observations from physical chemistry, that is observations on the phenomenon of self-organization.

According to Yoshimura & Hachisu (1985) research on the spontaneous formation of superlattices started out with the laboratory experiments by Sanders & Murray (1978, 1980). Initially Sanders and Murray had attempted (with success) to synthesize gem-opal in experiments with silica gel particles, but their observations turned out to have a much wider significance. Meanwhile research into the formation of ordered arrangements in binary mixtures of monodisperse particles of two different sizes, has created a wealth of information with practical applications, especially in nanotechnology.

The very fact that it is the ratio between the two differently sized polystyrene microspheres, that controls the more or less spontaneous formation of superlattices, becomes obvious from the observation by Yoshimura & Hachisu (1985), that the AlB_2 superlattice occurred not only in mixtures of 8000 - 2800 Å particles, but also in those of 5600 - 2100 Å, 5500 - 2500 Å and 4700 - 2000 Å. Ultimately Yoshimura & Hachisu (1985) attributed the formation of superlattices in their model experiments with binary size distributions to the general tendency to attain the highest density.

Stauffer (1976), Kremer (1977), and Scarlett et al. (2011) all have concluded on a kinetic mechanism controlling multicomponent self-assembly. In contrast Volmer & Weber (1926), Becker & Döring (1935), Evans (1979), and Shen & Oxtoby (1996) all were convinced, that self-assembly would follow the lowest free energy routes in a more or less complicated energy landscape, as had been suggested originally by Stranski & Totomanow (1933). However, it has been shown by Sanz et al. (2007 A, B) and Peters (2009), that the "lowest free energy"-approach typical of Stranski & Totomanow (1933) fails in the case of a binary mixture of colloids, because of a lack of sufficient diffusion (at room temperature, that is). In other words, self-assembly in binary mixtures lacking sufficient diffusion, requires the use of a nonequilibrium approach. ("The failure of a widely-made assumption for perhaps the simplest example of compositionally inhomogeneous self-assembly confirms the need for the development of dynamical theories in order to describe the self-assembly of multicomponent structures, and challenges the idea that equilibrium structure is the natural target for the self-assembly of components of many types": Whitlam et al., 2012).

Experiments with binary colloidal particles led Velikov et al. (2002) to a number of conclusions concerning the possible formation of superlattices. In the first place a well-ordered binary mixture of spheres of colloidal size (small silica spheres of ~ 100 nm and larger ones of ~ 200 nm) would show spontaneous ordering ("self-assembly") phenomena during the step-wise additions alternating between large-particle and small particle dispersions. After each coating of the vertically placed glass slide used as a sample holder, the newly added layer was allowed to dry. After that, the next coating with the second kind of silica dispersion would follow. In the second place Velikov et al. (2002) concluded, that in their laboratory experiments not one particular mechanism would operate, but two different ones. One being the templating action of underlying monolayers (as per Van Blaaderen et al., 1997); the other was the tendency to attain the closest packing possible for the two kinds of spheres (as noted by Elridge et al., 1993). The volume fractions of the silica dispersion used, turned out to be of essential significance in controlling the lattice formed, in combination with the size ratio of the two different kinds of silica nanospheres.

In their computer-based model experiments on the self-assembly of the growth of a one-dimensional array of two different blocks, Whitlam et al. (2012) observed, how "well-defined structures" will self-assemble only under conditions of nonequilibrium. In a more detailed account on the self-assembly of two component lattices, Whitlam et al. (2014) once more found in their computer-based simulations, that only an approach in terms of nonequilibrium will enable the required phase transition between different arrangements.

Clustering, fluctuations and selection - As explained in the section on clustering and nucleation, ordering of calcium and magnesium cations in combination with carbonate groups can take place only during the process of clustering. Since all of the clustering phenomena take place at ultra-high speed during the heat movement, such clusters of dolomite will be formed at high speed. At the same time a large number of such dolomite clusters will disappear again. Once formed, subsequent growth of those platelets consisting of alternating monolayers of calcite and magnesite into nuclei of dolomite will become possible, given favourable conditions during the intervals of precipitation. Because a rather dense packing has been attained at this stage (at least denser than a magnesium calcite with equal parts of calcite and magnesite), more and more of such a magnesium calcite arrangement will be dissolved during the periodical dissolution intervals. This process of enrichment in dolomite through a process of selection is of course none other than that described as "breaking Ostwald's Rule".

A simple energy landscape (Fig.5) - The universal driving force of the geochemical reaction leading to the low-temperature formation of dolomite, the calcium magnesites and magnesite itself, is the tendency to obtain a lower content in potential energy. In the case of clustering and nucleation of solids such as the anhydrous Ca/Mg carbonates, no important role has been recognized as yet for the kinetic energy. Except perhaps that the transition temperature between the mechanism based on alternations between dissolution and precipitation is likely to change fundamentally in the case of high-temperature/high-pressure reactions. Which observation leads to the idea, that the relatively high kinetic energy needed to produce dolomite or magnesite in laboratory syntheses, can also be supplied in small increments during the numerous fluctuations needed to complete the low-temperature formation of said minerals.

CONCLUSIONS

With the introduction of fluctuating conditions into experiments on the mineralogy of anhydrous Ca/Mg carbonates, Otto Liebermann has successfully opened up an entirely new field of study in geochemistry. As a direct result of his pioneering research a number of reproducible low-temperature syntheses of dolomite, calcium magnesites and magnesite has become known. Such *inorganic* laboratory experiments have the distinct advantage of involving just a few, well-defined chemicals. This allows for an adequate analysis of the processes involved. Only in this manner a truly scientific approach can ever be attained.

At first look it may be somewhat amazing to observe, how after each interval of dissolution and re-precipitation the precipitate formed, will contain more and more $MgCO_3$. However, when considering that the described method of laboratory synthesis involves an *open system*, and that at no moment in time any form of equilibrium will be reached, the necessary explanation can easily be found.

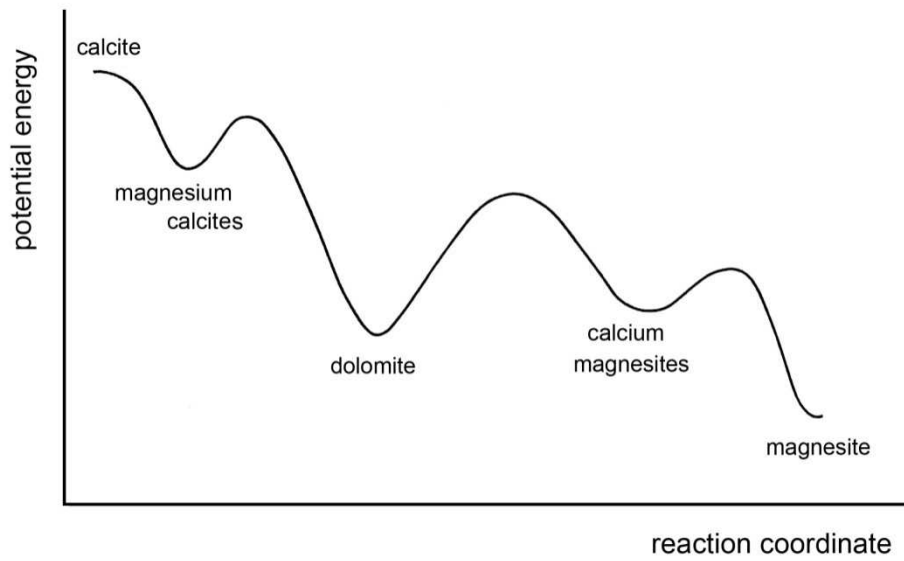


Fig.5 - Energy landscape of the low-temperature phase relations between calcite, magnesium calcites, dolomite, calcium magnesites and magnesite.
(copyright J. C. Deelman)

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In the second place I would like to make a truly fundamental comment. There are too many editors of science journals, who refuse to consider any computer file containing references to papers older than 10 years BP. Their argument being, that those older papers "... do not represent the present state of knowledge". This attitude leads to the neglect of all of those most valuable contributions made for example by Wilhelm Röntgen, Walther Nernst, Wilhelm Ostwald, Louis de Coppet, Johannes van 't Hoff, Fritz Haber, Marian von Smoluchowski, Max Volmer and so many others. This regrettable practice does seriously hamper the advancement of science in general. Or, to paraphrase a well-known certitude: "A science which neglects its past, has no future."

Here and now I want to express my sincere gratitude to the editors of the truly independent *HAL.archives-ouvertes* for publishing the present paper on the low-temperature phase relations of calcite, dolomite and magnesite.

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