# CHAPTER THREE

## **NEODOLOMITE RE-EXAMINED**

#### THE PRECURSOR

The lack of reproducible low-temperature syntheses of dolomite may well find its origin in the incorrect supposition, that dolomite forms as dolomite. It may well be totally wrong to assume, that dolomite actually nucleates under low-temperature conditions. This is in a few words the philosophy behind the introduction, and the use, of the concept of "neodolomite".<sup>1</sup> The idea that dolomite forms only in the course of considerable epochs of time from some anhydrous Mg/Ca carbonate different from dolomite itself, is often encountered in the literature. The widely spread custom to explain dolomite formation in terms of a precursor phase, which would gradually change into dolomite, is based on two dogma's. The first dogma concerns the crystallographic nature of the precursor as being different from that of dolomite. It will be demonstrated in this chapter, that both dogma's (like so many other dogma's) are open to serious doubt.

In 1956 Graf & Goldsmith published an account of their high-temperature experiments with magnesium calcites. The tests had shown that a temperature of at least 673 K is required for the successful synthesis of dolomite. Below that temperature no dolomite would form. Even so at a temperature of only 473 K an anhydrous mixed Mg/Ca carbonate had been formed. Because that carbonate originated from the same material, which at higher temperatures would have led to dolomite, Graf & Goldsmith (1956) concluded, that a metastable form of dolomite would have been formed. A slow process of conversion would change the initial phase (the "precursor") into well-ordered dolomite by way of cation ordering during solid state diffusion or recrystallization.

The suggestion that the newly defined mineral "neodolomite" would be imperfectly ordered in comparison with dolomite *sensu stricto*, and would attain in the course of time the highly ordered structure of dolomite, has thereafter often been used in geological theories. The assumed gradual change of this precursor phase seemed to add an extra dimension to the longstanding belief in theories on the so-called "dolomitization" of pre-existing limestone.

The definition of neo- or protodolomite as a phase resembling dolomite, but lacking the well-ordered arrangement of dolomite, was based on the absence of X-ray peaks in the diffractograms. Only 6 out of a series of 37 attempts to synthesize dolomite from magnesium calcite in high-temperature tests (at 573 K) showed after rapid cooling the presence of a "... small amount of a poorly ordered, crystallized dolomite-like mineral. Only the strongest reflection, (112), is visible in the X-ray diagrams": Graf & Goldsmith (1956, p.176). Although the reader was warned by Graf & Goldsmith, that identification of any mineral on the basis of only one of its X-ray reflections must be subject to error, the very definition of neo- or protodolomite was based on such evidence (or rather the lack of evidence). Natural dolomite possesses, in addition to the diffraction pattern of the rhombic carbonates, two superstructure reflections<sup>2</sup> at 25.382 nm and 20.645 nm. The superstructure lines typical of dolomite *sensu stricto* were interpreted by Graf & Goldsmith as evidence of the existence of a "... rather high degree of short range Ca-Mg order, a structural arrangement which would be relatively more



Fig.9 – Creation of "order reflections" from crystallographic planes with identical atomic population [such as (111) = A] in contrast to the X-ray reflections by crystallographic planes with two different kinds of atoms [such as (200) = B] (after Bragg, 1914 A).

stable ... than would complete disorder": Graf & Goldsmith (1956, p.181). The postulated neoor protodolomite phase did not possess such superstructure reflections, and therefore its degree of order would be less than that of dolomite *sensu stricto*.

Although the newly introduced neo- or protodolomite phase by definition did not possess the extra superstructure lines, Gaines (1977) suggested to re-define protodolomite in such a way, that it would include the dolomite with superstructure lines. The confusion created by Gaines was commented by Gidman (1978) and Deelman (1978).<sup>3</sup> The latter author pointed out, that there was no need to re-define the protodolomite introduced by Graf & Goldsmith (1956). Instead a critical re-evaluation of the actual crystallographic nature of protodolomite itself seemed to be required.

## SUPERSTRUCTURE REFLECTIONS

Because superstructure (or order-) reflections appear to play a crucial role in the discussions on the nature of protodolomite, some attention must be devoted to this phenomenon.<sup>4</sup> Superstructure reflections were first observed by Bragg in 1914. In thinsectioned NaCl cut parallel to (111) Bragg (1914 A) not only found the peaks of the (111) dspacing and its multiples, but also a number of additional peaks. The additional lines were located at regular intervals. The (100) diffractogram of NaCl did not show such additional X-ray peaks. Bragg explained the extra lines as follows: the (100) planes of NaCl contain both Na and Cl atoms in one and the same crystallographic plane, whereas the (111) planes contain either Na atoms or Cl atoms in alternating monolayers (Fig.9). The presence midway between these (111) planes of chlorine atoms between sodium populated planes considerable weakens, but does not fully destroy, the first order reflection. On the other hand the reflection of the second order is reinforced to give a high intensity. The intensities of the second and third order peaks are, in Bragg's explanation, largely determined by the position of the lighter atoms in the lattice. The position of the lighter atoms in planes parallel to the planes of the heavier atoms (i.e., complete sorting out of the two components) greatly affects the resulting X-ray diffraction pattern. The arrangement of the heavy atoms according to their own specific lattice structure determines the position of the first order peaks. The intensities of the first order peaks, as well as the possible occurrence and intensity of second order peaks, are a function of the position of the lighter atoms in the crystal structure. Separation of the lighter atoms in monolayers halfway between the planes of the heavy atoms (Fig.9 B) creates a reduction in the intensity of the first order peak and a simultaneous increase in the intensity of the second order reflection.

Only when the two different atoms are completely sorted out into mono-atomic layers (= monolayers), such superstructure lines will be formed. If the path length difference between the rays of a monochromatic X-ray beam diffracted by two subsequent differently populated monolayers is not identical, and if the scattering factors of these two kinds of atoms are not identical, an extra diffraction line will result. In solid solutions, where the individual crystallographic planes are not monolayers but are populated at random by two different kinds of atoms, any extra outgoing beam that might have been formed will be cancelled out, because it will be out of phase with every random ray it meets.

In metallurgy the presence or absence of superstructure reflections in the X-ray diffractograms of alloys is used as criterion for the presence or absence of order in the way the atoms are arranged on their lattice sites (Nix & Shockley, 1938). The first descriptions of these superstructure lines in X-ray analyses of alloys were published by Bain (1923) for  $Cu_3Au$  and by Phragmén (1925) for Fe<sub>3</sub>Si.

## DEGREE OF ORDER

The structure of protodolomite has been described as a dolomite-like lattice with "... a rather high degree of short-range Ca-Mg order, a structural arrangement which would be relatively more stable ... than would complete disorder" (Graf & Goldsmith, 1956, p.181). Therefore it will be necessary to cast a closer look at the "degree of order" concept.

Originally the concept of the degree of order has been introduced by Gorsky (1928), to describe the phenomenon of superlattice formation in copper-gold alloys. Because its first use was not free from ambiguity, the concept has meanwhile been re-defined. "Short range-", "short distance-" or "local" order is, in the definition of Bragg & Williams (1934), a measure of how well on the average each atom in a mixed crystal is surrounded by unlike neighbors. "Long range-" or "long distance" order delineates to what extent lattice sites appropriate to type A atoms are actually filled by A atoms, and to what extent B atoms occupy their own specific sites. In the definition of the degree of order by Gorsky (1928) this degree of order could vary from 1/2 (random distribution of A and B) to 1 (superlattice with A and B in a regular 1 : 1 alternation) (see also: Guggenheim, 1952). The numerical values of "short range order" and "long range order" as defined by Bragg & Williams (1934) may vary between 0 (disorder) and 1 (order). The exact values depend on the configurational model used. In this respect it must be noted, that at least two different models are known: that of Bragg & Williams (1934) and that of Bethe (1935). (Cowley, 1960 remarked, that because properties such as diffraction intensity and electrical resistance were functions of  $S^2$  rather than S, the definition of the long-range order parameter had to include an autocorrelation or Patterson function instead of the arbitrary concept of "right" and "wrong" sites for certain atoms.) It is the long-range order, that can be detected in X-ray diffraction: the presence or absence of superstructure lines is indicative of the existence or non-existence of a superlattice structure.<sup>5</sup> In a solid solution, where no long-range order exists, the numerical value of short-range order will give the number of places, in which two like atoms are closest neighbors and it will be a function of the initial composition (Hume-Rothery, 1950).

Short-range order will not create any diffraction lines in X-ray analysis (Hume-Rothery & Raynor, 1962). Instead short-range order will produce diffuse bands or even diffuse maxima in between the diffraction lines (Gerold, 1961). Guinier (1964) made a distinction between the diffraction of X-rays in mixed crystals with substitutional disorder (where the atoms are of comparable size) and mixed crystals with planar disorder (i.e., superlattices with stacking faults). In the latter case the intensities of the superlattice lines will be reduced proportional to the square of the degree of long-range order. The long-range order parameter S can thus be measured by comparing the intensities of a normal line in the X-ray diffractogram with that of a superlattice line (Guinier, 1964). Examples involving the measurement with X-ray diffraction of the long-range degree of order in Cu<sub>3</sub>Au and in  $\beta$ -brass were published by Wilchinsky (1944) and Chipman & Warren (1951) respectively. Calculations on the degree of order applied specifically to the mineral dolomite have become known too. Khoury et al. (1982) compared the intensities of the (221) and (210) reflections of dolomite from magnesium clay deposits in the Amargosa Desert, Nevada (USA), and found a degree of order, that varied from 26 to 46 %.

In their 1956 paper Graf & Goldsmith did not explain their indications for assuming the existence of "... a rather high degree of short-range Ca-Mg order", but such evidence was in fact published by Graf et al. (1957). In that publication Graf and co-authors reported asymmetric c-axis reflections in natural and synthetic dolomites. Such an asymmetry in c-axis reflection compared to a-axis reflections, indicates an irregular stacking sequence of calcite and magnesite monolayers in the direction of the c-axis. The absence of long-range order in certain dolomites can be explained by stacking faults between subsequent calcite and magnesite monolayers.

After subjecting six samples containing dolomite as well as magnesium calcites from a core taken in Tomas Savannah (Ambergris Cay, Belize) to Rietveld analysis, Gregg et al. (1992) found a systematic increase of the calcium site occupancy with increasing depth. Especially in the upper 15 cm of this core the observed trend was clear; with a further increase in depth fractional site occupancy approached unity (perfect order) in an asymptotic manner. From these observations the conclusion was drawn, that calcium-rich dolomite initially deposited would be subject to recrystallization under the influence of a reduction of surface free energy (Ostwald ripening). "However, increasing stoichiometry (Mg/Ca ratio) of the dolomite with age was not observed, indicating that cation ordering and stoichiometry are not necessarily related": Gregg et al. (1992, p.157). Doubts must be expressed here with regards to the possible significance of Rietveld analysis towards establishing "site occupancies of the cations in dolomite". Rietveld (1969) developed a method for structure refinement for the neutron powder spectrometer, based on recalculation of profile intensities. The method has been shown to extract the maximum available information from any powder diffractogram, including conventional powder X-ray diffractometry (Young et al., 1977). As a consequence the Rietveld method can be used to analyse finely crystalline and/or poorly ordered compounds such as clay minerals. But the Rietveld method is essentially a refinement technique: a structural model is still required at the outset of each analysis (Post & Bish, 1989). Therefore this method of signal analysis will provide more precise unit cell parameters, but the essential structural questions remain.

## FORMATION OF SUPERLATTICES

At high temperatures, near the melting point of metals, a large number of alloys will show a random distribution of the components. When quickly cooling down these mixtures ("quenching"), the random arrangement will be frozen in: a solid solution. Certain mixtures will not form such a solid solution, but these will instead be seen to form a superlattice, when cooling their melts. Once formed superlattices are quite stable, and these superlattices often possess remarkable properties (see for example Hilliard, 1979; Schuller, 1980).

The possibility to form superlattices depends on the size difference between the radii of the atoms involved. To give only one example: superlattices are found in the system Cu-Au, but not in the system Ag-Au (Hume-Rothery, 1950). The latter two metals are virtually identical in size (Au = 40.77 nm and Ag = 40.70 nm), and therefore mixtures of these two metals will not form a superlattice, but a solid solution. The size difference between Cu and Au (Cu = 36.07 nm and Au = 40.77 nm) is such, that only superlattices can exist at low temperatures, and no solid solutions will be formed (Hume-Rothery, 1950). With regard to ionic crystals much the same holds true, even though in certain instances (as in the case of dolomite) superlattices involve two different cations together with a common anion.

From a large number of observations on the mineralogy of mixed crystals Goldschmidt (1926) had been able to formulate a boundary value for the difference in ionic radii: a maximum difference of 15 % marks the distinction between solid solutions and layer lattices.<sup>6</sup> Only when one of the two different cations is less than 15 % smaller than the other (expressed as a percentage of the smallest cation), a solid solution can be formed. When cations of a mixed crystal differ by more than 15 % , layer lattices (superlattices) will form. Dolomite confirms to the Goldschmidt Rule: the magnesium cation (= 6.5 nm) is about 50 % smaller than the calcium cation (= 9.9 nm) (data on radii from Pauling, 1960). Other anhydrous double carbonates, such as ankerite CaCO<sub>3</sub>.FeCO<sub>3</sub> , kutnohorite CaCO<sub>3</sub>.MnCO<sub>3</sub> , minrecordite CaCO<sub>3</sub>.ZnCO<sub>3</sub> and bütschliite, CaCO<sub>3</sub>.K<sub>2</sub>CO<sub>3</sub> obey the same rule and form layer lattices (see on the structure of ankerite for example Beran & Zemann, 1977; on the structure of kutnohorite see Farkas et al.,

1988; on the structure of minrecordite see Garavelli et al.,1982; and on the structure of bütschliite see for example Knobloch et al., 1980). The ionic radius of calcium (= 9.9 nm) and that of the bivalent iron (Fe<sup>2+</sup> = 7.6 nm) in ankerite differ by 30 %. The calcium cation and that of manganese (Mn = 4.6 nm) in kutnohorite differ by as much as 115 %. The calcium cation and the zinc ion (Zn = 7.4 nm) of minrecordite differ by 34 %. The potassium cation (K<sup>+</sup> = 13.3 nm) and the calcium cation of bütschliite differ by 34 % (data from Pauling, 1960).

Metal alloys follow the same rule: Hume-Rothery et al. (1934) showed, that the 15 % boundary also controls the possible formation of superlattices among metals. Laves (1959) summarized all of the known metallic superlattices, and showed, that in all cases a difference of more than 15 % existed between the sizes of the metals involved. The examples studied included AuCu<sub>3</sub>, CaSn<sub>3</sub>, CePb<sub>3</sub>, PrIn<sub>3</sub>, ZnPt<sub>3</sub>, MgCd<sub>2</sub>, LiHg<sub>3</sub>, LaHg<sub>3</sub>, ThAl<sub>3</sub>, InNi<sub>3</sub>, LiBi, TiAl, CoPt, PdFe, IrMn, CuAu, HgZr, BeCu, MgLa, ScRh, VFe, TaRu, OsTi, AgMg, and CaNi.

The ordered arrangement of a superlattice will be destroyed again, when temperatures near the melting point are reached ("As the temperature is raised, thermal agitation causes some atoms to interchange their positions so that they occupy "wrong" sites on the lattice, and order is progressively destroyed": Hume-Rothery & Raynor, 1962, p.149). High temperatures lead to a disordered atomic arrangement, and cooling of suitable alloys to low temperatures will initiate the spontaneous nucleation of superlattices. In most textbooks on metallurgy the transition is therefore discussed in terms of thermodynamic stability of the ordered arrangements, exceeding that of the disorder typical of a solid solution. The process is often discussed in terms of an "order-disorder transition" (e.g., Bragg & Williams, 1934; Nix & Shockley, 1938; Bethe & Kirkwood, 1939).

Similar to metal alloys that must be heated to high temperatures to form superlattices upon cooling, hydrothermal syntheses of dolomite require very high temperatures. ("The significant point is that at elevated temperatures ionic mobility is great enough for cation ordering to take place and thus develop the stable, ordered dolomite": Graf & Goldsmith, 1956, p.174.) Heating the ingredients to very high temperatures will introduce too much ionic mobility, and consequently ordered structures such as the superlattice will be destroyed. In other words there is a certain minimum temperature that must be surpassed, below which the atomic mobility is insufficient to create an ordered arrangement. These observations make it clear, that the nucleation of a superlattice requires an extra amount of energy compared with the energy needed to form a solid solution. The barrier of the critical temperature in systems capable of forming superlattices, can be overcome by the introduction of an extra "ordering energy" (Nix & Shockley, 1938). According to Hume-Rothery & Powell (1935) it is the presence of two atoms (ions) with different radii, which accounts for the required additional energy. Such a mixture of two different types of spheres is subject to deformational strain: the larger atoms will distort the lattice of the smaller ones. The strain can be relieved as far as possible, only when an ordered arrangement is attained. Short range repulsive forces result between like atoms in the disordered mixture, and these forces will eventually lead to the creation of the superlattice. Hume-Rothery & Powell (1935) showed, that a direct relation exists between the created strain and the extent of the difference in size of the two radii. If this difference is small, the deformational strain will only be small and no need exists to transform the random array of the solid solution into an ordered one. If however the difference is large a definite tendency toward superlattice formation will exist. If the difference is too large, the tendency toward phase separation is very large, and the two different components will refrain from mixing (i.e., exsolution takes place). In that case the two components are virtually insoluble in each other.

Recently the study of superlattices has received new impetus, and especially the possible application in microelectronics seems to be the driving force behind this renewed interest. Strictly speaking not atomic superlattices, but synthetic modulated structures (defined by Cowley et al., 1979 as periodically perturbed materials with a repetition greater than the basic unit cell) form the main subject of such studies.

Large-scale periodic lattices can be made by way of a technique known as molecular beam epitaxy. Semiconductor materials or metals are being sprayed, simultaneously though separately, in the form of two gas beams and the substratum on which the superlattice is to be formed, circles at high speed through these two gas beams (Esaki & Tsu, 1970; Cho, 1971). Two other techniques for the synthesis of modulated lattices have become known. The chemical vapour deposition technique developed by Blakeslee & Aliotta (1970), involves the periodically pulsing of PH<sub>3</sub> into a vapour growth apparatus filled with a AsH<sub>3</sub> - PH<sub>3</sub> - Ga - HCl mixture. The third technique, the liquid-phase epitaxy technique of Woodall (1972), forms an extension of the method advanced by DuMond & Youtz (1935, 1940). The latter two authors produced multi-layer arrangements of gold and copper by way of intermittent spurts of Au-vapour onto a glass plate being coated by Cu-vapour in vacuum. Woodall's (1972) method consists of rotating a GaAs substrate back and forth between two Ga/Al melts with different Al concentration.

One of the very first techniques used for the synthesis of what has become known as modulated structures, involved precipitation from a solution at room temperature. Deubner (1930) used electrolytic deposition of silver and gold from two different solutions by way of dipping a platinum substrate alternatingly into each of the solutions.

## **EXSOLUTION**

The marked difference in the atomic radii of calcium and magnesium accounts for the lack of miscibility not only between the carbonates, but also between the oxides (Bäckström, 1924; Haul & Wilsdorf, 1952). Melting the two oxides at a temperature of 1873 K does not lead to the formation of any mixed crystal with a composition in between that of the two end members (Ruff et al., 1933). In experiments conducted at temperatures above 2573 K, Rankin & Merwin (1916) could not detect the formation of mixed crystals or solid solutions between CaO and MgO. On the basis of their experiments Natta & Passerini (1929) concluded, that the difference in ionic radii between calcium and magnesium is such, that no solid solution or mixed crystal can be formed at all. At temperatures above 1873 K a small possibility seemed to exist for the formation of mixed crystals between CaO and MgO according to Konopicky & Trojer (1947). But even then the miscibility is very limited: no measurable amounts of CaO can be found in MgO, and only 2 to 3 % MgO can be incorporated into CaO at this high temperature (Trojer & Konopicky, 1949).

Early observations on the occurrence of exsolution phenomena in the system  $CaCO_3$  - MgCO<sub>3</sub> were published by Kulp et al. (1951). In their differential thermal analyses Kulp and coauthors noted, that among the Ca-Fe-Mn mixed carbonates complete ionic substitution could take place among the Ca-Mn and Fe-Mg pairs, but even at high temperatures limited substitution between calcium and magnesium could be found. Baron (1960) suggested, that a solid solution of magnesite in calcite might exist, but because of the size difference between Mg<sup>2+</sup> and Ca<sup>2+</sup> cations, such a solid solution would be unstable.

Not only in high-temperature laboratory experiments exsolution of dolomite from calcite occurs (Harker & Tuttle, 1955 A; Goldsmith, 1960; Goldsmith & Heard, 1961), but also in the field, in metamorphic carbonates and in carbonatites (Coomáraswámy, 1902; Joplin, 1935; Goldsmith, 1956, 1960; Van der Veen, 1965; Cortelezzi, 1966; Puustinen, 1974). Goldsmith (1956) described how metamorphic marbles, which consisted mainly of calcite, contained small amounts of dolomite, distributed in a distinct pattern within the host rock. The finely disseminated dolomite crystals showed the very same crystallographic orientation as the

surrounding calcite (as witnessed in single crystal X-ray diffraction).<sup>7</sup> That this type of dolomite formed as an exsolution product of magnesium-containing calcites has been confirmed by Goldsmith in a laboratory test, wherein an echinoid fragment (which contained initially some 10 % MgCO<sub>3</sub> in its lattice) was heated to 773 K. Dolomite crystallites exsolved in a crystallographic orientation, that was identical with that of the host crystal (Goldsmith, 1956, 1960).

Exsolution is not limited to the separation of dolomite from magnesium calcites heated to high temperatures. A comparable phenomenon of phase separation takes place with magnesite. Through the use of X-ray diffraction, wet chemical analysis, petrographic microscopy, electron microscopy, microprobe, and spectrographic analyses, Joffé (1976) was able to show, that MgCO<sub>3</sub> will be separated from initially homogeneous solid solutions upon cooling down from temperatures near melting point.

Details of exsolution effects taking place in mixtures of calcite and magnesite heated to temperatures between 773 and 1173 K were described by Harker & Tuttle (1955 A,B). In order to prevent the dissociation of the carbonates, carbon dioxide pressures ranging from 1.3 to 3.1 kbar had to be applied. Unmixing took place to such an extent, that for example at a temperature of 773 K only about 5.4 mol % MgCO<sub>3</sub> at maximum can be incorporated in the calcite lattice. A mixture of calcite plus magnesite would change into a mixture of dolomite plus calcite, after heating it during 1 hour at 773 K. Close inspection of this calcite showed, that its X-ray diffraction peaks were shifted towards the pattern of dolomite. Chemical analyses revealed it to contain magnesium carbonate. A true solid solution between calcite and magnesite could also be detected by Harker & Tuttle, but only at very high temperatures: around 1073 K. Such solid solutions were found, when the samples from the high-temperature tests were cooled very rapidly, or when the reaction time had been very short. For example the solid solutions formed only in those tests, whereby the reaction time had been more than half an hour. Even the mixtures showing solid solution formation would eventually succumb to exsolution, because as Harker & Tuttle (1955 B, p.276) put it "... the percentage of magnesium was too high for it all to be accomodated in the calcite".

#### PHASE RELATIONS

What is known today on the phase relations in the system  $CaCO_3 - MgCO_3$  concerns mainly anhydrous mixtures of calcite and magnesite, heated to high temperatures (between 473 and 1473 K) under high carbon dioxide pressures to prevent their dissociation into the respective oxides. Such high-temperature experiments performed on dry mixtures of the Mg/Ca carbonates are not entirely realistic. Even though Rosenberg & Holland (1964) performed their high-temperature tests with water present, the use of solutions containing 2 mol calcium chloride plus 2 mol magnesium chloride per dm<sup>3</sup> water seems somewhat hypothetical with respect to natural conditions. Nevertheless a short review of the known data on phase relations will be given here, if only to illustrate the highly individual status of the mineral dolomite within the system CaCO<sub>3</sub> - MgCO<sub>3</sub>.

From a magnesium bicarbonate solution kept at room temperature, magnesium carbonate trihydrate (nesquehonite) will precipitate instead of magnesite (Pfeiffer, 1902; Von Knorre, 1903; Wells, 1915; Kline, 1929). It is therefore of some interest to know, under what conditions nesquehonite will be converted into magnesite. This question was answered by Schloemer (1952): the transition takes place at a temperature of 533 K (under atmospheric pressure). Under a pressure of 3.2 kbar the conversion temperature would be as low as 323 K. At the same time Schloemer (1952) was able to establish, that the thermal decomposition of



Fig.10 – Phase relations of the system  $CaCO_3 - MgCO_3$  at temperatures from 773 to 1173 K (after Harker & Tuttle, 1955 B).

magnesite, reacting with water to give brucite plus carbon dioxide, starts under atmospheric conditions at 623 K. At 3 kbar pressure the reaction between magnesite and water would take place at about 523 K.

The behavior of dolomite being heated open to the atmosphere, adds further evidence to the individualistic status of dolomite. Experiments by Hedvall (1925) have shown, that the thermal decomposition of dolomite starts at about 853 K and is complete at around 1183 K. Earlier both Garnett (1923) and Mitchell (1923 A) had found, that dolomite did not dissociate in several stages, and therefore it could not be considered to be a mere mixture of two separate carbonates. Bäckström (1924) expressed his doubts regarding these observations, and showed that Mitchell's (1923 A) data on the thermal dissociation of dolomite needed revision. In Bäckström's view dolomite would dissociate in two distinct stages, and not in one. Investigations by Faust (1944), Schwob (1947), Kulp et al. (1951), Haul & Heystek (1952), and Graf (1952), support the two-step dissociation reaction. This two-step decomposition also takes place, when dolomite is heated in contact with water.<sup>8</sup> Schloemer (1952) found, that under those conditions decomposition started at 663 K (at 500 bar pressure). At higher pressures (3 kbar) the start of decomposition was at 573 K. Schloemer described the decomposition of dolomite in contact with water at high temperature as:

$$CaCO_3.MgCO_3 + H_2O \rightarrow CaCO_3 + Mg(OH)_2 + CO_2$$
 (eq.4)

Early observations on the subsolidus relations in the system CaCO<sub>3</sub> - MgCO<sub>3</sub> were published by Harker & Tuttle (1955 B). After heating dry mixtures of calcite and dolomite powder to temperatures between 773 and 1173 K, Harker & Tuttle (1955 B) made the same observations as Goldsmith & Graf had made in 1953: part of the calcite present had incorporated magnesium, and the calcite had been changed into magnesium calcite. Additional experiments by Harker & Tuttle (1955 B) confirmed the formation of such magnesium calcites. Upon heating mixtures of calcite and magnesite, not only magnesium calcite would be formed: in every instance dolomite originated as well. Depending on the amount of calcite used, magnesium calcite would be formed. To give an example: mixing excess calcite powder with magnesite and heating the mixture under CO<sub>2</sub> pressure of at least 2.7 kbar to a temperature of 1173 K for about 1 hour, created a magnesium calcite containing 28 mol % MgCO<sub>3</sub> plus a dolomite with 47 mol % MgCO<sub>3</sub>. A mixture of excess magnesite with little calcite led, after being heated under the same conditions, to a mixture of magnesite (with only 2 mol % calcite incorporated in it) and dolomite (with 49.5 mol % MgCO<sub>3</sub>) (Fig.10). At lower temperatures the amount of MgCO<sub>3</sub> incorporated would decrease: at 773 K only 6 mol % MgCO<sub>3</sub> was present in the magnesium calcite mixed crystal. A comparable tendency to incorporate less of the second component at lower temperatures was found for the magnesium-rich mixtures. The actual degree of calcite incorporation into magnesite was at all temperatures significantly lower than in the case of magnesite incorporation into calcite. A maximum of only 2 mol % CaCO<sub>3</sub> could be measured in samples rich in MgCO<sub>3</sub> heated to 1173 K (Fig.10).<sup>9</sup>

Not only the reaction time and the initial composition of the carbonate mixtures determine what phase will develop in the high-temperature tests. The carbon dioxide pressure is a third factor of importance. It is surprising to find, that in a large number of the investigations discussed in this section, the exact value of the  $pCO_2$  for the points of measurement has been left out of consideration. The lines that border the various fields in the CaCO<sub>3</sub> - MgCO<sub>3</sub> phase diagram may very well have to be changed in their respective positions as the result of large differences in CO<sub>2</sub> pressure. This observation must be the more disturbing, because at very high CO<sub>2</sub> pressures completely different phases will be formed. At such high carbon dioxide pressures magnesium calcites plus periclase (MgO) may form instead of the more usual



Fig.11 – Phase diagram of the anhydrous system calcite – dolomite – magnesite. Phases involved are: A – calcite with MgCO<sub>3</sub> incorporated, B – magnesium calcites, C – dolomite, D – calcium magnesites, and E – magnesite with incorporated CaCO<sub>3</sub> (modified after Goldsmith & Heard, 1961).

association of magnesium-free CaCO<sub>3</sub> plus MgO (Graf & Goldsmith, 1955). At ultra-high pressures of CO<sub>2</sub> (between 5 and 30 kbar) and at temperatures between 1300 and 1700 K, a divariant field containing periclase, a calcium-rich dolomite and vapour will intersect with the top of the stability field of the magnesium calcites (Irving & Wyllie, 1975; Goldsmith, 1980). At extremely high pressures (of some  $2 \times 10^6$  to  $5 \times 10^6$  bar) and temperatures (between 1500 and 2000 K) dolomite breaks down into a calcite + magnesite mixture without carbonatation, as experiments by Biellmann et al. (1993) have shown.

The stability field for dolomite was found to be very narrow indeed, even though the amazing observation has been made by Harker & Tuttle (1955 B), that depending on the initial mixture, two different dolomites can be formed at the same temperature. In those cases where a more calcite-rich mixture of ingredients was used, a more calcium-rich dolomite would result, and in those cases where magnesite predominated in the initial mixture, a more magnesium-rich dolomite would be formed. For example when the reaction was carried out at 1173 K, one mixture of carbonates would produce a dolomite with 46.6 mol % MgCO<sub>3</sub>, but a dolomite with 49.5 mol % MgCO<sub>3</sub> resulted from another, more magnesium-rich mixture (Fig.11).

Harker & Tuttle (1955 B) have confirmed the fact, that dolomite may well contain more  $CaCO_3$  than the stoichiometric 50 mol %; a phenomenon noted earlier for example by Foote & Bradley (1914). But Harker & Tuttle tended to explain excess calcium carbonate in dolomite as an artefact: "... we have not yet produced any unequivocally pure synthetic dolomite, dolomite free from any relicts of unreacted carbonates" (Harker & Tuttle, 1955 B, p.278).

Some thought will have to be devoted to the question, why so little has become known about the mixed crystals with a compostion in between that of dolomite and that of magnesite.<sup>10</sup>

A continuous series of mixed crystals between calcite and dolomite is known (the magnesium calcites), but little or nothing has become known about the calcium magnesites. One of the few accounts mentioning a dolomite with excess MgCO<sub>3</sub> is the paper by Glover & Sippel (1967). In their experiment 158 a mixed anhydrous Mg/Ca carbonate with 62.9 mol % MgCO<sub>3</sub> (determined by titration) was formed (at a temperature of 308 K).<sup>11</sup>

Possibly the size difference between magnesium and calcium cations plays an important role. Monolayers of calcite and magnesite are so similar, that these can be stacked on top of each other. Perhaps the "*Mischungslücke*" (= miscibility gap) between dolomite and magnesite (Fig.11) finds its origin in the fact, that the magnesium cation layer of the lattice is too small in its *c*-axis dimensions to accommodate calcium cations, but that the reverse is very well possible.<sup>12</sup> One calcium cation will disturb an entire monolayer of magnesite, but one magnesium cation may not be able to disturb the arrangement of a calcite monolayer (because it is smaller than the calcium "opening", it will remain in the middle of the field of forces<sup>13</sup>).

#### DISORDERED DOLOMITE ?

Harker & Tuttle (1955) concluded that complete miscibility between MgCO<sub>3</sub>-rich calcite solid solutions and dolomite might exist at temperatures above 1173 K. In their experiments Harker & Tuttle had not been able to reach such high temperatures, but they felt, that the phenomenon of complete miscibility would be "... complicated by the order-disorder transition which would take place somewhere between the calcite solid solutions and dolomites" (Harker & Tuttle, 1955 B, pp.278-279). Six years later Goldsmith & Heard (1961) were able to demonstrate, that complete miscibility exists in fact at a temperature of about 1348 K. The problem of the order-disorder transition, foreseen by Harker & Tuttle, was indeed encountered by Goldsmith & Heard. At temperatures of 1348 K and higher no unmixing effects were discernible anymore, and the magnesium calcites and the dolomite phase became identical. "It is

not correct, however, to regard this region of miscibility simply as a series of solid solutions between calcite and dolomite, for the dolomite structure (space-group R  $\overline{3}$ ) is ordered with respect to Ca and Mg, whereas the intermediate solid solutions have a disordered Ca - Mg array with the calcite space group R  $\overline{3}c$ . A phase change between the two structures is thus required...": Goldsmith & Heard (1961, p.51).

Because dolomite is obviously not identical with magnesium calcite, at least when interpreting magnesium calcite as a solid solution between calcite and dolomite, the possibility will have to be considered, that a disordered form of dolomite exists. Disorder in the form of stacking faults, reflected in excess amounts of calcite over magnesite, has been mentioned. A second kind of disorder can be found in dolomite formed at very high temperatures: "... cation disorder in stochiometric dolomite becomes observable at appr. 1,273 K " (Goldsmith & Heard, 1961, p.45).

A detailed study on the progressive crystallization and the concomitant increase in ordering of dolomite has been published by Schneider (1976). In that investigation hydrothermal experiments, conducted at temperatures between 363 and 683 K and at a constant pressure of 500 bar, were described. Especially the influence of the duration of each test on the formed product was studied. Twenty-four different tests were conducted with a starting material, which had been prepared by adding sodium bicarbonate to an equimolal solution of calcium- and magnesium chloride. When such mixtures were heated to a temperature of for example 363 K during 14 days, aragonite and magnesite formed, along with small amounts of what was described as "... dolomites with a high defect density" (Schneider, 1976, p.579). This dolomite-like material showed in X-ray diffraction only one peak, situated there where in the case of dolomite *sensu stricto* the main peak would have been (at 28.8 nm). In the interpretation of Schneider this dolomite-like phase would possess a random succession of more or less ordered cation domains (producing a long-range mosaic-type disorder) along with tilting and dislocation of the individual CO<sub>3</sub>-groups. The latter observation was based on infrared spectroscopic analyses.

After heating the ingredients to 418 K for periods from 2 to 7 days, the products formed were dolomite, aragonite, and magnesite. In that case the dolomite again showed only one peak in X-ray diffraction (part of the main peak) with a weak to very weak intensity. In a few cases two different maxima were detected, when measuring this peak's intensity in detail. The degree of line broadening (encountered by Schneider, 1976 in virtually all of his samples) varied from one sample to another, as did the exact position of the main diffraction peak. Schneider explained this variation among individual samples by pointing out variations in chemical composition and degree of perfection of individual crystallites.

After heating the ingredients to a temperature of 418 K for periods of 7 to 14 days, a clear increase in the degree of order could be noted in the dolomite crystals: more lines were found in the X-ray diffraction pattern. Line broadening was still a prominent feature in these samples. Even when analyzing the dolomites, which had been formed after heating the ingredients to 418 K during 14 to 28 days, line broadening was found. The samples heated to 418 K for at least 14 days (Schneider's Stage II dolomites), showed all of the lines of the diffraction pattern of dolomite *sensu stricto*. In a number of instances splitting of some of the diffraction peaks was noted. When the ingredients were heated to 418 K for periods between 42 and 119 days, line splitting would be even more pronounced. This splitting of the diffraction lines indicated, in the explanation of Schneider (1976), that two different dolomite phases would be present. At the same time little or no line broadening took place, and the X-ray diffraction pattern resembled in all details that of an ideal dolomite. The phenomenon of line splitting was not found in dolomites, which had been formed after heating the samples to temperatures between 463 and 683 K for a period of at least 21 days.

In the discussion of the results of his high-temperature experiments Schneider stressed the fact, that only when temperatures of 463 K or more had been maintained for at least 21 days, true dolomite would have been formed. This observation agrees relatively well with the statement of Usdowski (1967), that "protodolomite" can be found only during the first 30 days of high-temperature tests conducted at 393 K, or during the first 12 days if the reaction took place at 453 K. After that initial period the "protodolomite" would be converted into dolomite *sensu stricto*. In the view of Usdowski the formation of "protodolomite" had to be the result of a reaction not given enough time to reach its equilibrium.<sup>14</sup> Thus the experiments of Schneider (1976) confirm the role played by the reaction time in high-temperature syntheses of dolomite.

The special significance of Schneider's investigation is to be found in the detailed interpretation of the possible structure of the disordered dolomite-like phases. After combining diffraction data (d-values, but also line broadening, relative intensities, and peak splitting) with IR-spectroscopy, Schneider was able to distinguish 5 different stages in the process of ordering.<sup>15</sup> Stage I would show considerable variability in chemistry and the degree of perfection of even individual crystallites. Both chemical variability and the lack of sufficient order were explained to be the result of the random succession of more or less ordered cation domains in combination with tilting and dislocation of part of the carbonate groups. The phase that formed after heating at 418 K for at least 7 days (stage II), was described by Schneider as being still strongly disordered. The diffraction pattern suggested in this case, that a higher degree of order within the lattice planes perpendicular to the *c*-axis existed. At the same time the diffraction pattern indicated a relatively good degree of ordering of calcium and magnesium cations into very small domains. The random succession of such ordered domains would be responsible for a long-range, mosaic-type of disorder, which would explain the lack of superstructure reflections. Stage III material possessed all of the diffraction lines typical of dolomite, including the superstructure lines. The structure must have consisted, following Schneider (1976), of large domains with an ordered cation distribution. The line splitting phenomenon encountered in these stage III samples showed that the crystallites were composed essentially of two components, each with a different chemical composition. The superstructure lines were pronounced: the two different cations must have been arranged in two separate monolayers. Ideal dolomites, possessing the well-known structural chemistry of dolomite sensu stricto, were formed in stage V, whereby temperatures of 473 K or more were reached.

The investigation of Schneider (1976) forms an extension of the observations of Goldsmith & Heard (1961), who had found that the dolomite-like phases formed at temperatures of around 773 K, would show "... very obvious diffuseness or smearing out of the reflections from planes near-normal to the *c*-axis" (Goldsmith & Heard, 1961, p.61). Similarly Schneider (1976) observed, how dolomite formed at temperatures between 363 and 463 K. possess a markedly disordered structure. Dolomite formed in Schneider's experiments at temperatures above 463 K, and only if that temperature had been maintained for at least 21 days, would possess the fully ordered structure of ideal dolomite. Schneider did not conduct experiments at higher temperatures (and pressures), but Goldsmith & Heard (1961) did. In their experiments temperatures of up to 1473 K were reached, and it was found, that at temperatures between 1273 and 1473 K cation disordering (substitution disorder among  $Ca^{2+}$  and  $Mg^{2+}$ ) took place. Reeder & Nakajima (1982) using high-resolution electron microscopy on thin foils of dolomite, that had been heated to temperatures of 1423 K and more, found a domain structure with smooth boundaries. Although this domain structure suggested the existence of anti-phase domains, translation appeared not to have caused the domains but instead a 180° rotation. Therefore the domain structure was that of twin domains. The transition in space groups from R 3 c (calcite) to R 3 (dolomite) could be explained by Reeder & Nakajima (1982) as the result of the formation of twin domains upon heating above the critical ordering temperature.

By now it is clear, that there are at least two different types of disorder affecting the dolomite lattice. At very high temperatures cation disordering may take place, and at low temperatures a different type of disorder, that may be described as layer disorder, domain disorder, or as the occurrence of stacking faults, appears. These two main types of disorder had been denoted by Goldsmith & Heard (1961) as "point and layer disorder". It will be of some importance to note, that Goldsmith & Heard added, that virtually all of the low-temperature dolomites found in the sedimentary environment showed the layer-type disorder.<sup>16</sup>

In hydrothermal experiments conducted at temperatures of 491 K Sibley (1990) found two different unstable precursor phases preceding ordered dolomite. When reacting calcite powder with calcium chloride/magnesium chloride solutions with a Mg/Ca ratio = 1.0 in sealed pressure bombs, a magnesium calcite with 37 mol % MgCO<sub>3</sub> (calculated from X-ray diffractogram) formed after 4 to 5 hours. After 7 hours the reaction product was found to be a very poorly ordered dolomite (with 42 mol % MgCO<sub>3</sub>). But after 14 hours reaction time in this particular experiment a pure dolomite with the required three superstructure reflections was found. From experiments on the nucleation of dolomite conducted at a temperature of 466 K, Nordeng & Sibley (1994) were able to draw conclusions concerning the kinetics of the reaction involved. Much like Schneider (1976) and Katz & Matthews (1977), Nordeng & Sibley (1994) found the nucleation of dolomite to be rather sluggish: an induction period always preceded the actual appearance of dolomite in their high-temperature experiments. In most experiments the first phase to be formed was magnesium calcite, followed by calcium-rich dolomite and only then the real (ordered, stoichiometric) dolomite would precipitate. By way of comparing continuous high-temperature experiments with experiments in which a number of cooling cycles was incorporated, Nordeng & Sibley (1994) were able to draw conclusions regarding the nucleation of critical clusters and the subsequent growth or dissolution of these clusters. In this way quantitative information could be obtained concerning the relative stability of the two different phases involved. "If these reactions follow Ostwald's Step Rule because of differences in activation energy, then the length of time required for critical nucleation of each phase should correspond to the order in which each phase appears as a reaction product" (Nordeng & Sibley, 1994, p.192). The experiments revealed how both magnesium calcite and dolomite nucleate quite early in the reactions (but magnesium calcites always before dolomite), and that only upon prolonged heating dolomite will grow at the expense of the magnesium calcite present. In other words magnesium calcite grows faster than dolomite, even though nucleï of dolomite are present. In order to explain this observation Nordeng & Sibley (1994) suggested a major role to be played by surface free energy during the process of nucleation. At the same time another confirmation for Ostwald's Step Rule had been found, because the metastable magnesium calcite appeared in the reactions before the stable dolomite phase.

Through the use of  $O^{18}$  isotopes in the solutions in contact with the solids Malone et al. (1996) were able to measure reaction rates in the conversion of Mg-calcite into dolomite. In their hydrothermal tests small amounts of magnesium calcite ("... a mixed Ca-Mg carbonate containing 41.7 mol % MgCO<sub>3</sub> with no observable ordering reflections": Malone et al., 1996, p.2190) reacted in closed PTFE-lined stainless steel bombs with solutions of NaCl, NaHCO<sub>3</sub>, CaCl<sub>2</sub>.2 H<sub>2</sub>O, MgCl<sub>2</sub>.6 H<sub>2</sub>O and SrCl<sub>2</sub>.6 H<sub>2</sub>O in varying amounts at temperatures of 323, 373, 423 or 473 K. At all temperatures the reaction rates for the conversion of magnesium calcite into dolomite were very rapid at the outset, but slowed down considerably in a few days time. As a rule the higher reaction rates were measured in the tests conducted at the higher temperatures. Recrystallization was accompanied by a marked increase in crystal size, but despite an initial rapid increase in the percentage MgCO<sub>3</sub> incorporated the stoichiometric composition of pure dolomite was not reached.

#### DISCUSSION

Instead of following in an uncritical manner the widespread use of the "neodolomite" (or "protodolomite") concept, this discussion will be used to re-examine the very arguments, which were used to launch the concept. Usually a new mineral will be described on the basis of new data, which are specific for that substance. In the case of the "protodolomite" phase no such new data were presented. The introduction of that new phase took place on the basis of the very absence of certain superstructure reflections typical of dolomite *sensu stricto*. A second argument to support the introduction, perhaps somewhat more convincing, was the "... distinct compositional break between these materials and the magnesian calcites". The often quoted sentence that used to define the "protodolomite" phase<sup>17</sup> furthermore contains a number of aspects that need critical re-evaluation.

When taking a strict point of view, there is really no convincing argument in favor of any "neodolomite" or "protodolomite" phase. The lack of the superstructure reflections typical of dolomite *sensu stricto* cannot be used to justify the introduction of any new phase. However such a strict point of view is, particularly in this case, not very useful. Obviously the phase that lacks the superstructure lines is not dolomite<sup>18</sup>, but still it is an anhydrous Mg/Ca carbonate. How to describe this phase in another, more adequate, manner?

An important argument used by Graf & Goldsmith (1956) to introduce their theoretical "protodolomite" phase was, that a clear compositional break would exist between the newly introduced phase and the magnesium calcites. Perhaps such a break may have seemed to exist in 1956, but today no such break can be discovered in the phase diagram of the system  $CaCO_3$  - MgCO<sub>3</sub> (see Fig.11). In the high-temperature range as well as in the realm of room temperature, mixed crystals with a composition in between that of calcite and dolomite are known. Although Harker & Tuttle (1955 B) had reported the existence of magnesium calcites containing between 33 and 44 mol % MgCO<sub>3</sub> (formed upon very rapid cooling from a melt at a temperature of 1173 K), it was from the paper by Goldsmith & Heard (1961) that complete miscibility became known. At temperatures above 1373 K calcite and dolomite will mix readily and completely.

After Chave (1952) had described a large number of biogenic Mg-calcites, that contained up to about 30 mol % MgCO<sub>3</sub>, additional analyses of Mg-calcites containing percentages of MgCO<sub>3</sub> up to that of dolomite, have become known. More, and rather revealing, evidence in this respect came from the laboratory tests of Glover & Sippel (1967). By way of increasing the amount of magnesium chloride in their (low-temperature) experiments, Glover & Sippel were able to synthesize magnesium calcites with percentages of MgCO<sub>3</sub> "... in the range of dolomite composition". In one experiment at least Glover & Sippel found, that they had created a magnesium calcite with a composition of virtually 50 mol % CaCO<sub>3</sub> and 50 mol % MgCO<sub>3</sub> (that particular test had been carried out at a temperature of 293 K).

The suggestion of Graf & Goldsmith (1956), that the "protodolomite" phase would be unstable, and would "... transform to dolomite if equilibrium were established" (Graf & Goldsmith, 1956, p.184), has never found the support of any experimental evidence. Astonishingly evidence to the contrary is abundant. Measurements on the self-diffusion rates of calcium in calcite have shown that cation replacement is unlikely to account for any dolomite formation under conditions of low-temperature (Brätter et al., 1972). Isotope studies by Anderson (1969) showed that solid state diffusion of oxygen or carbon atoms does not take place at measurable rates in dolomite at room temperature. A third argument can be found in the observations by Goldsmith & Heard (1961): cation disordering in dolomite requires so much (thermal) energy, that it does not start unless temperatures of 1273 K have been reached. The very fact, that no secondary change into pure dolomite appears to take place in the sedimentary environment has been realized by the two authors responsible for the introduction of the "protodolomite" concept: "It has not yet been demonstrated however, that it is possible for calcium-rich dolomites existing in natural sedimentary environments to reorganize to ideal dolomite ..." (Graf & Goldsmith, 1963, p.1053). In a sobering note Goldsmith (1967) came to the conclusion, that no post-depositional atomic rearrangement of  $Mg^{2+}$  and  $Ca^{2+}$  cations can possibly take place ("... a serious diffusion problem in the solid state at these low temperatures": Goldsmith, 1967, p.915).

From the evidence presented here, the conclusion can be drawn, that "protodolomite" clearly is an anhydrous Mg/Ca carbonate, but that its structure is more related to that of magnesium calcite than that of dolomite *sensu stricto*. This very conclusion has been drawn by Goodell & Garman (1969), Deelman (1979 A) and Sibley (1990).<sup>19</sup> Support for such a reinterpretation of "protodolomite" in terms of a magnesium calcite with a high percentage of MgCO<sub>3</sub> comes from the experiments of Fritz & Smith (1970). By way of duplicating the tests of Siegel (1961), Fritz & Smith synthesized a dolomite-like compound from a solution containing calcium nitrate, magnesium sulfate, and sodium carbonate heated to 351 K. Although Fritz & Smith had expected "protodolomite" to have formed, they found that the precipitate closely resembled a magnesium calcite: "The c/a values obtained are slightly higher than the c/a ratios known from well-ordered dolomite and compare very well with values found for magnesium calcites of similar composition" (Fritz & Smith, 1970, p.1165).

There is more evidence contradicting the suggested existence of "protodolomite". Graf et al. (1967) investigated the structural chemistry of "protodolomite" with a series of calculations on various structural models, designed to explain the observed X-ray diffraction data. Such theoretical model calculations (based on equations of Hendricks & Teller, 1942) had to be used instead of the more direct approach based on Fourier analysis of single crystal photographs. The latter technique requires a large number of single crystal X-ray photographs, and such photographs of the "protodolomite" phase were not available (Graf & Goldsmith, 1956 carried out their tests with such small amounts of reactants, that no sizeable monocrystals of "protodolomite" were formed). After comparing the calculated X-ray diffraction patterns with the actual one, Graf et al. (1967) concluded, that the diffraction pattern had to belong to "... random packet successions or an assemblage of calcite and magnesite, rather than a dolomite with imperfect order" (Graf et al., 1967, p.16). The previously suggested disorder model for "protodolomite" was abandoned: "... a simple mixture of solid solutions appears inadequate to explain the diffraction features exhibited" (Graf et al., 1967, p.31). Not only the molecular structure of "protodolomite" resembles that of a magnesium calcite, but this resemblance is found as well in the morphology of the individual crystals. "Morphologically the cationdisordered protodolomite appears to be identical to high-magnesium calcite and cannot be differentiated by purely optical means, including stereoscan observations" (Müller & Wagner, 1978, p.68). Much the same observation has been made by Nordeng & Sibley (1994).<sup>20</sup>

In this publication the concept of "protodolomite" will be avoided as much as possible. The main reason for this decision is, that "There is so far no reliable evidence that calcian dolomites have indeed acted as precursors of (non-metamorphic) well-ordered dolomite" (Lippmann, 1973, p.188). [Compare the observation by Wenk et al., 1993, p.773: "It appears that ordered dolomites are generally not caused by ordering of a disordered protodolomite but are the result of direct growth ...".] There really is no longer any need for the "protodolomite" concept. It should be shelved in the archives along with other curiosities such as the "gurhofian" of Karsten (1807 B) and Klaproth(1810) [ Redlich, 1912 defined gurhofian as "the colloïdal equivalent of dolomite" ]; the "hydrodolomite" of Von Kobell (1864), Scacchi (1885), Chester (1896), Dana (1904) and Caillère (1943)<sup>21</sup> ; the "hydromagnocalcite" of Rammelsberg (1875); the "leesbergite" of Blum (1907); the "gajite of Tučan (1911) (for more information on these "*wasserhaltige dolomitähnliche Mineralien*" see Leitmeier, 1912); the CaCO<sub>3</sub>.2 MgCO<sub>3</sub> described by Eardley (1938); the "amorphous dolomite" postulated by Shcherbina (1950); the

"cugnite" of Castanier et al. (1988); the hydrous calcium magnesium carbonate of Kelleher & Redfern (2001, 2002), and the "quasi-dolomite" of Babčan & Sevc (2001). Of course by not using the postulated "protodolomite" concept, the very problem of the low-temperature nucleation of dolomite will in no way be brought closer to its possible conclusion.

The high-temperature relations in the system  $CaCO_3 - MgCO_3$  described in the literature allow for significant conclusions to be drawn, even for the low-temperature phase relations. The most significant conclusion is beyond any doubt, the recognition of the importance of exsolution phenomena. A phase diagram that resembles to a certain extent Fig.11, can be found in Ulich's "*Chemische Thermodynamik*" (1930) (as his Fig.9, p.114). The diagram then represents two components, that will crystallize independently, but that are also capable of forming an "ordered mixed crystal" (*geordnete Mischphase*). In the liquid state the two components are fully miscible. At lower temperatures only two initial components and an ordered phase with an approximate 1 : 1 composition can co-exist. Such a system would possess 4 curve pairs, delineating the solid/liquid transition, 2 curve pairs representing the boundaries between two co-existing solid phases, and two eutectic points. This type of exsolution seems to occur in the anhydrous system CaCO<sub>3</sub> - MgCO<sub>3</sub>.

In the phase diagram of Ulich's textbook there is room for only one "geordnete Mischphase", for only one mixed crystal with a layer lattice. In the phase diagram of the anhydrous calcium-magnesium carbonates too only one layer lattice (i.e., dolomite) is featured. But here an addition must be made. Another layer lattice is to be found: the mineral huntite, CaCO<sub>3</sub>.3 MgCO<sub>3</sub> (Graf & Bradley, 1962). Instead of one monolayer of magnesite alternating with one monolayer of calcite as in dolomite, one monolayer of calcite alternates here with three monolayers of magnesite. According to Zempolich (1985) mixed crystals with compositions of MgCO<sub>3</sub> : CaCO<sub>3</sub> of 1:2 , 2:3 , 3:4 , 4:5 , and 5:6 have been noted in high-temperature experiments. Rosenberg (1987) precipitated Mg calcites from Mg/Ca formate solutions in high temperature (418 to 493 K) & high pressure experiments. Through peak measurement of X-ray diffractograms the compositions were estimated: two metastable Mg/Ca carbonates with well defined compositions (75 mol % CaCO<sub>3</sub> + 25 mol % MgCO<sub>3</sub> and 67 mol % CaCO<sub>3</sub> + 33 mol % MgCO<sub>3</sub>) were observed. In this respect it will be useful to apply the concept of *stoichiometric* addition compounds used by Prigogine & Defay (1954). In those systems in which the mixed crystals provide evidence of limited miscibility, several zones of in-miscibility may exist. Two different kinds of mixed crystals are found to exist, each with a well-defined composition in terms of mole fractions. Thus for the system CaCO<sub>3</sub> - MgCO<sub>3</sub> only the 1 : 1 dolomite composition and the 1:3 huntite composition are stable; all of the mixed crystals with a composition not corresponding to one of these mole fractions, necessarily consist of two phases. It is difficult however to determine in how far huntite plays a significant role in the system CaCO<sub>3</sub> - MgCO<sub>3</sub>. Huntite "... has not been observed to form in experimental work in CaMg carbonate systems from 773 to 1523 K ": Graf & Bradley (1962, p.242).

Neither dolomite nor huntite contradicts in any way the strict requirement of Goldschmidt's Rule. Not even the magnesium calcites, the mixed crystals of mainly calcitic composition but with an appreciable amount of incorporated magnesite, contradict that rule. The re-interpretation of the Mg-calcites as being highly ordered polycrystalline aggregates (Garrido & Blanco, 1947; Nissen, 1963; Towe, 1967) instead of a solid solution (as Chave, 1952 claimed), explains the observed phase relations. The Mg-calcite mixed crystals can be regarded as layer sequences of calcite and magnesite in the form of domains, with more calcite layers than magnesite layers (in most cases that is). As Chai et al. (1995, p.942) have stated: "It is possible that intralayer ordering or clustering is a more common feature in rhombohedral carbonates than previously thought." The magnesium calcites that have formed under low-temperature conditions have to be situated in the exsolution field of the phase diagram of Fig.11. This diagram illustrates the observation, that no true solid solution can be formed under

low-temperature conditions. The magnesium calcites consist of layer sequences in a more or less irregular sequence; magnesium calcites do not consist of alternating complete monolayers as in dolomite. In the direction of the a-b plane (i.e., the direction perpendicular to the alternation sequence itself) the monolayers are broken up into separate regions or domains (Fig.8). It will be clear, that even in the case of the magnesium calcites the strict arrangement of the calcite lattice is being maintained. No random distribution of the two different cations can be found here. The only disturbance in the symmetry is to be found in the breaking up of individual layers into small, isolated islands of the two different carbonates. Most probably it is an incomplete coverage of underlying calcite layers by magnesite, which forms the reason for both domain structure and irregular stacking sequence. Raman spectroscopy used by Bischoff et al. (1985) on synthetic and biogenic calcites containing up to 25 mol % MgCO<sub>3</sub>, revealed the existence of positional disorder among the carbonate groups. Random replacement of calcium cations by magnesium could explain the phenomenon, as suggested by Bischoff et al. (1985). But there is no reason to believe, that the mosaic structure for the magnesium calcites would not initiate positional disorder among the carbonate groups too. For in the mosaic structure a multitude of "out of step" contacts between CaCO<sub>3</sub> and MgCO<sub>3</sub> units exists.

The re-interpretation of the magnesium calcites in terms of a highly oriented polycrystalline aggregate can be applied only to one of the two different kinds of magnesium calcite. The solid solution of MgCO<sub>3</sub> in calcite, Chave's model so to say, actually exists and it can be distinguished from the aggregate-type Mg-calcite, which forms under low-temperature conditions. In this respect it is necessary to realize, that the lines of the CaCO<sub>3</sub> - MgCO<sub>3</sub> phase diagram (Fig.11) are boundaries between different phases. These lines do not represent a boundary between the solid phase (or phases) and the liquid phase. Goldsmith (1980) indicated, that the liquidus in this system, when the system is pressurized to such a degree as to prevent the dissociation into oxides, will be located several hundred degrees above the temperature, at which mixing between calcite and dolomite occurs. In other words the liquidus must be situated well above the temperature of 1348, possibly at 1500 to 1600 K.

The existence of two different kinds of Mg-calcite was first reported in the work of Harker & Tuttle (1955 B). The true solid solutions were found to have a rather limited capacity for incorporating magnesium carbonate. At a temperature of 773 K the solid solution could contain at maximum 6 mol % MgCO<sub>3</sub> ; at a temperature of 1173 K this percentage had increased to as much as 47 mol %. The boundary that separates the stability field of the solid solution-type Mg-calcite from the exsolution field in the phase diagram of Harker & Tuttle (Fig.10), was found to be not entirely insurmountable. Finding the second kind of Mg-calcite was announced as follows: "... in some of the runs at this temperature (of 1173 K) metastable carbonates have been prepared having compositions lying in the two phase region.." (Harker & Tuttle, 1955 B, p.278). The distinction made between two different types of magnesium calcite, a distinction made on crystallographic criteria, does not coincide with the often used distinction into low- and high-magnesium calcites. According to Bøggild (1930) the low-magnesium calcites would contain only 2 to 3 mol % MgCO<sub>3</sub> and the high-magnesium calcites would contain about 12 to 17 mol % MgCO<sub>3</sub>. Similar boundary values were mentioned by Chave (1954 A), who, much like Bøggild, had analyzed biogenic carbonates. The difference between the solid solution-type Mg-calcites and the aggregate-type Mg-calcites is not as much a difference in percentage of MgCO<sub>3</sub> incorporated, as it is a matter of structural chemistry.

Not only two different kinds of Mg-calcite mixed crystals appear to exist, even two essentially different types of disordered dolomite were seen to exist. A cation disordered or solid solution type of dolomite can be found only when ultra-high temperatures have been attained. Goldsmith & Heard (1961) have found in their tests that a minimum temperature of 1273 K must be reached before cation disorder takes place. The second type of dolomite, a dolomite with some disorder in the stacking sequence of the calcite and magnesite monolayers, is much

more common. The crystallographic criterion to distinguish cation disordered dolomites from the second type, has been discussed at some length by Goldsmith & Heard (1961). In those cases where the superstructure reflections in the X-ray diffractogram remain relatively sharp, even when these are perhaps of weak intensity, substitutional disorder is involved. In those cases where a disordered stacking sequence exists, the diffraction pattern shows a distinct smearing out of the reflections, which come from the planes normal or near normal to the c-axis.

The optical analysis of calcium-rich dolomites and stoichiometric dolomite by means of transmission electron microscopy<sup>22</sup> led Khan & Barber (1990) as well as Reeder (1992) to the conclusion, that an excess of calcium carbonate will be segregated into domains rather than substituting at random within the dolomite lattice. Using electron microscopy Schubel et al. (2000, p.860) came to the conclusion, that calcium-rich dolomite contains "…nanometer-scale microstructural heterogeneities" in the direction of the crystallographic c-axis. Such c-domains have been reported from various calcium-rich dolomites by for example Reeder & Wenk (1979), Van Tendeloo et al. (1985), Wenk & Zhang (1985), Reksten (1990), Wenk et al. (1991) and Reeder (1992). The conclusion seems inevitable, that as in the case of the magnesium calcites, an exception to Goldschmidt's Rule (Goldschmidt, 1926) does not exist with regard to dolomite, and that unmixing effects account for the observed microstructures of calcium-rich dolomites (and magnesium calcites).