CHAPTER TWO

SOLID SOLUTION OR SUPERLATTICE ?

MIXED CRYSTALS

When making an attempt to explain the formation of dolomite in the sedimentary environment, not only the chemical composition of the mineral should be known, but also its structure. In this second chapter both chemistry and structure of the mineral dolomite will be studied, once again placed in its historical perspective.

Numerous chemical analyses have become known, all of which describe dolomite as a compound with a composition of essentially $CaCO_3.MgCO_3$.[1] The chemical composition of dolomite is thus midway between that of calcite, $CaCO_3$, and magnesite, $MgCO_3$. The structural aspects of dolomite are somewhat more complex. Is dolomite part of a continuous series of mixed crystals with compositions in between that of calcite and magnesite? Calcite and magnesite are known to be isomorphic and both belong to the calcite group of rhombic carbonates. But what are the exact relations between calcite and magnesite with respect to the dolomite lattice? Is dolomite a solid solution or a superlattice? What arguments favor the superlattice, and what arguments exist to describe dolomite in terms of a solid solution between calcite and magnesite? The question is not at all only a theoretical one, since exactly this question was discussed for example between Ferrari (1929), who thought dolomite to be a solid solution, and Onorato (1930), who considered dolomite to be a superlattice. The whole discussion took place many years after Bragg (1914 A,B) had published his structural investigation of dolomite with the aid of the X-ray diffraction technique.

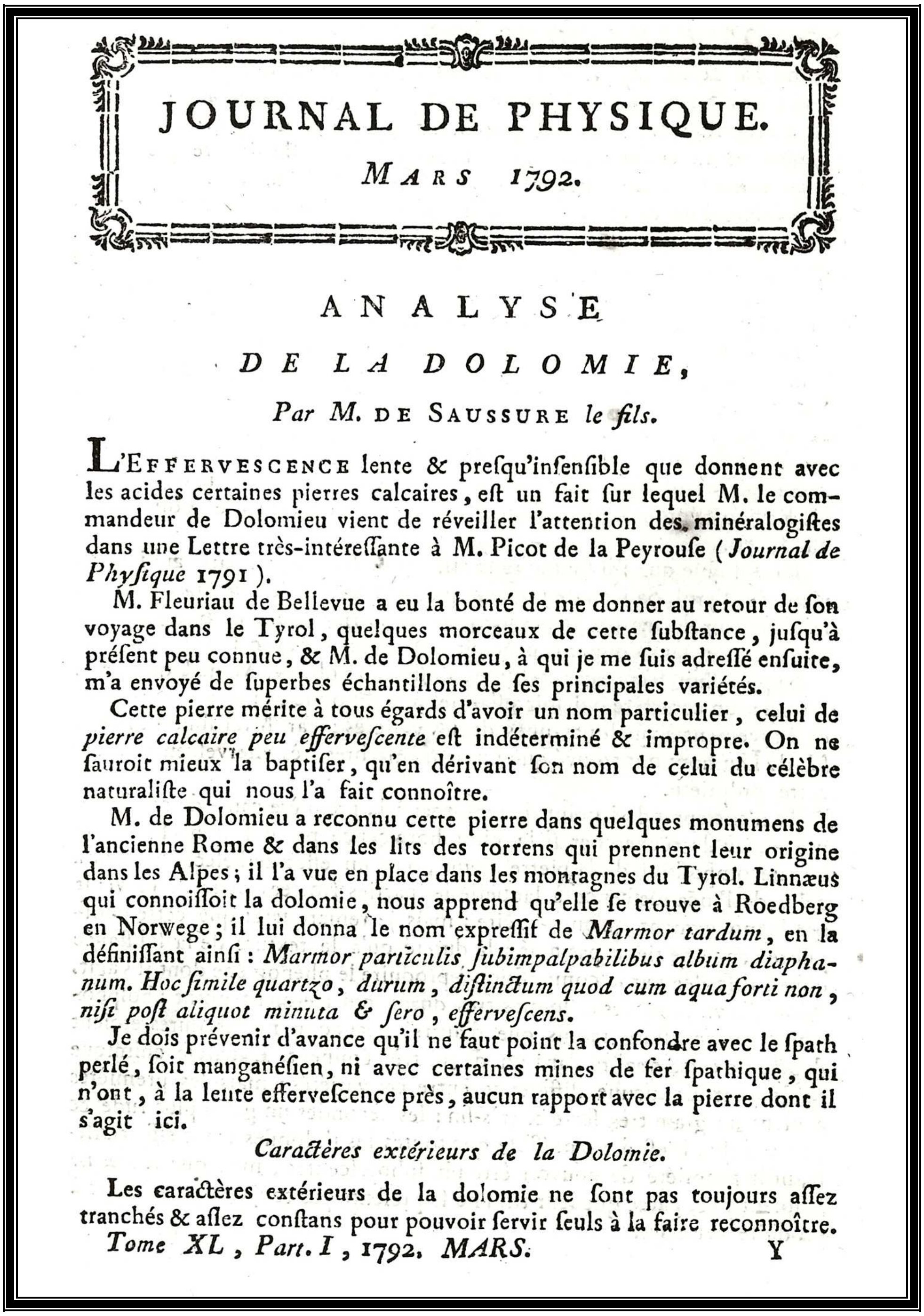
In order to avoid possible misunderstanding concerning the terminology used, the following definitions are given:

- *mixed crystal* is used here in its classical sense as defined by Lehmann (1889), i.e., a crystal made up from two (or more) components, that are also known as separate phases in the crystalline state;

- *solid solution* ("feste Lösung": Lehmann, 1889; Van 't Hoff, 1890) is a mixed crystal, exhibiting random distribution of the components.[2] Usually solid solutions are part of a continuous series of mixed crystals;

- *layer lattice* ("Schichtgitter") delineates according to Retgers (1889) a subdivision of the class of mixed crystals, that does not show a random arrangement, but possesses instead an ordered arrangement in the form of layers. Depending on the stacking sequence of such layers, two different types can be distinguished (Guggenheim, 1952): 1) the mixed-layer crystal, in which the two components show a random stacking sequence of the monolayers, and 2) superlattices, that possess a regular stacking sequence.

One year after the appearance of De Dolomieu's (1791) account[3] on the occurrences of the new mineral[4], a chemical analysis was published by De Saussure (1792) (Fig.1). After remarking that the mineral had previously been described by Linneaus (1768) as *marmor tardum*[5], De Saussure described the hardness, fracture, specific gravity, and the solubility of



JOURNAL DE PHYSIQUE.

MARS 1792.

ANALYSE

DE LA DOLOMIE,

Par M. DE SAUSSURE *le fils.*

L'EFFERVESCENCE lente & preſqu'inſenſible que donnent avec les acides certaines pierres calcaires, eſt un fait ſur lequel M. le commandeur de Dolomieu vient de réveiller l'attention des minéralogiſtes dans une Lettre très-intéreſſante à M. Picot de la Peyrouſe (*Journal de Phyſique* 1791).

M. Fleuriau de Bellevue a eu la bonté de me donner au retour de ſon voyage dans le Tyrol, quelques morceaux de cette ſubſtance, juſqu'à préſent peu connue, & M. de Dolomieu, à qui je me ſuis adreſſé enſuite, m'a envoyé de ſuperbes échantillons de ſes principales variétés.

Cette pierre mérite à tous égards d'avoir un nom particulier, celui de *pierre calcaire peu efferveſcente* eſt indéterminé & impropre. On ne ſauroit mieux la baptiſer, qu'en dérivant ſon nom de celui du célèbre naturaliſte qui nous l'a fait connoître.

M. de Dolomieu a reconnu cette pierre dans quelques monumens de l'ancienne Rome & dans les lits des torrens qui prennent leur origine dans les Alpes; il l'a vue en place dans les montagnes du Tyrol. Linnæus qui connoiſſoit la dolomie, nous apprend qu'elle ſe trouve à Roedberg en Norwege; il lui donna le nom expreſſif de *Marmor tardum*, en la définiſſant ainſi: *Marmor particulis ſubimpalpabilibus album diaphanum. Hoc ſimile quartzo, durum, diſtinctum quod cum aqua forti non, niſi poſt aliquot minuta & ſero, efferveſcens.*

Je dois prévenir d'avance qu'il ne faut point la confondre avec le ſpath perlé, ſoit manganéſien, ni avec certaines mines de fer ſpathique, qui n'ont, à la lente efferveſcence près, aucun rapport avec la pierre dont il s'agit ici.

Caractères extérieurs de la Dolomie.

Les caractères extérieurs de la dolomie ne ſont pas toujours aſſez tranchés & aſſez conſtans pour pouvoir ſervir ſeuls à la faire reconnoître.

Tome XL, Part. I, 1792. MARS. Y

Fig.1 – Reproduction of the first page of De Saussure's (1792) paper on the analysis of dolomite (reproduction by courtesy of the Bibliothèque Nationale et Universitaire, Strasbourg, France).

dolomite. Wet chemical analysis revealed that the composition of 100 "grains" of dolomite was:

"terre calcaire" ……………………………..	44.29 grains
"argile" …………………………………….	5.86
"magnésie" …………………………………	1.40
"fer" ………………………………………..	0.71
"acide carbonique" ………………………….	46.10
total…………………………………………	98.39

In all of the samples given to him by Fleuriau de Bellevue and by De Dolomieu, De Saussure had found considerable quantities of clay. As a result dolomite was interpreted by De Saussure (1792) to be a combination of calcium oxide, clay, and carbon dioxide.[6] This (mis-) interpretation of the chemistry of dolomite has been repeated by Haüy (1801). The latter author described dolomite as "*chaux carbonatée aluminifère*". The true character of dolomite as a magnesium-calcium double carbonate was first recognized by Tennant (1799)[7]. Subsequent analyses by for example Klaproth (1804), Von Buch (1823), Beudant (1832), Hirzel (1850), Roth (1852), Petersen (1867), Rumpf (1873 A), Des Cloizeaux (1874), Doelter (1875), Heddle (1878), Brun (1881), Haushofer (1881), Chester (1887), Williams (1887), Sella (1889), Buchdrucker (1891), Pfaff (1894), Vesterberg (1900), Arsandaux (1901), D'Achiardi (1901), Eisenhuth (1902), Loczka (1902), Knight (1904), Dürr (1909), Koller (1918), Reed (1918), Glatzel (1919), Harding et al. (1920), Rothrock & Shumaker (1920), Everman et al. (1921), Zsivny (1949), and Sanada & Miyazawa (1955), all have substantiated Tennant's analysis.

STRUCTURAL CHEMISTRY

Having established the chemistry of the mineral dolomite as a 1 : 1 combination of $CaCO_3$ and $MgCO_3$, the structural aspects need investigation. The first observations pertaining to this matter were made by Berthier (1806), who observed that calcite and magnesite can form mixed crystals ("*les carbonates de chaux, de magnésie, de fer et de manganèse peuvent se trouver en proportions variées dans la nature*": Berthier, 1806, p. 91). Wollaston (1812) drew attention to the fact, that the rhomb angles of crystals of calcite (105° 5'), dolomite (106° 15'), and siderite (107°) closely resemble each other, and stressed the view, that this phenomenon might be more than just coincidence. Isomorphism between calcite and magnesite was first recognized by Mitscherlich (1819, 1820), who had introduced the concept of isomorphism. A detailed investigation of the isomorphism between calcite and magnesite was published by Berthier (1823). Dolomite deserved, in the view of Berthier, a special position in the series of mixed crystals between calcite and magnesite. A different view was taken by De Sénarmont (1851 A), who stressed that various chemical analyses had shown the lack of a constant composition of the mineral dolomite, even to such a degree that it would be difficult to speak any longer of dolomite with $CaCO_3$ and $MgCO_3$ "*en proportions atomiques*".[8] This view was shared for example by Bischof (1855), who stressed the possibility for a wider range of compositions because of the isomorphism, that exists between calcite and magnesite.[9] Evidence in favor of a special position for dolomite was given by Tschermak (1881). Measurement of the angles between the crystal faces of calcite, dolomite, ankerite, and magnesite shows, that the rhomb angle of dolomite is not the simple arithmetic mean between the angles of calcite and magnesite. Tschermak's conclusion was supported, at least in his own view, by the observations of Jannetz (1879). In calcite maximum heat transport takes place along the *c*-axis of the crystal, but in dolomite maximum heat transport takes place in the *a-b*-plane.

The physicochemical relations between calcite, magnesite and dolomite were studied by Retgers (1891). As a working hypothesis Retgers used the idea of a continuous series of mixed crystals ranging from pure $CaCO_3$ up to pure $MgCO_3$. Much like $ZnSO_4$ and $MgSO_4$, known in every possible combination as mixed crystals, the two rhombic carbonates might represent the two end members of a continuous series. Apparently all three criteria in favor of Mitscherlich's concept of isomorphism were fulfilled: a) an analogy in morphology exists; b) an analogy in chemical composition is given; and c) the existence of at least one crystal with an intermediate composition. The data published up to 1891 on mixed crystals between $CaCO_3$ and $MgCO_3$ did not, in the view of Retgers, seem to fulfill the third requirement. No mixed crystal with a composition intermediate between that of dolomite and that of magnesite was known. Dolomite therefore held a rather unique status. And dolomite is a mixed crystal with a very constant Mg/Ca ratio of exactly one (hence Retgers' denomination *Normaldolomit*). On the basis of this special status of dolomite Retgers concluded, that no direct isomorphism could exist between calcite and magnesite.[10] More evidence was presented by Retgers, which underlined the singular status of dolomite. By way of combining measurements on the interfacial angles with data of specific gravity, diagrams were constructed showing the relations between the molar volumes of calcite, magnesite and dolomite. The diagrams did not show a simple linear relation. Optical methods were also used by Retgers to study the relations between calcite, magnesite and dolomite. The differences in physical properties between the cations Mg^{2+} and Ca^{2+} could possibly lead to optical anomalies, i.e., a discontinuity. Retgers used the light microscope as his main tool of research. Since its resolution is limited, no individual monolayers of calcite and magnesite could be seen. It must be remarked here, that Retgers' suggestion to examine mixed crystals with respect to their structure before performing any wet chemical analyses, was a clear attempt to distinguish in one way or another a solid solution from a superlattice.

The conclusions reached by Retgers were: 1) calcium and magnesium are chemically and physically much too different for any isomorphism between their anhydrous carbonates. 2) From chemical analyses it became clear, that although calcites containing $MgCO_3$ and dolomite were known, no continuous series of mixed crystals between $CaCO_3$ and $MgCO_3$ existed. 3) The double carbonate dolomite cannot be considered to be a simple mixture of calcite and magnesite. 4) The constant chemical composition of dolomite in combination with its specific physical properties (specific gravity, heat transport, optics) excluded the possibility of isomorphism.

Retgers' (1891) conclusions were questioned by Brauns (1892), who stated that the physical properties and the chemical composition of dolomite itself were without significance for the question whether or not a continuous series of mixed crystals existed between calcite and magnesite. In his answer Retgers (1892) stated, that Brauns apparently could not change the basic fact, that no mixed crystals with a composition in between that of dolomite and magnesite were known. There was no truly continuous series of mixed crystals, ranging from calcite to magnesite. The experiments had shown, that dolomite could not be described as being part of a continuous series of mixed crystals.[11] The physical differences between magnesium and calcium were such that isomorphism between calcium carbonate (calcite) and magnesium carbonate would be excluded.

The work of Retgers was later also commented on by Foote & Bradley (1914), who stressed the possible importance of the temperature for the composition of the reaction products. In order to study this temperature dependence to the full, it would be necessary to analyze mixed crystals, which had been formed at a high temperature from a melt consisting initially of calcite

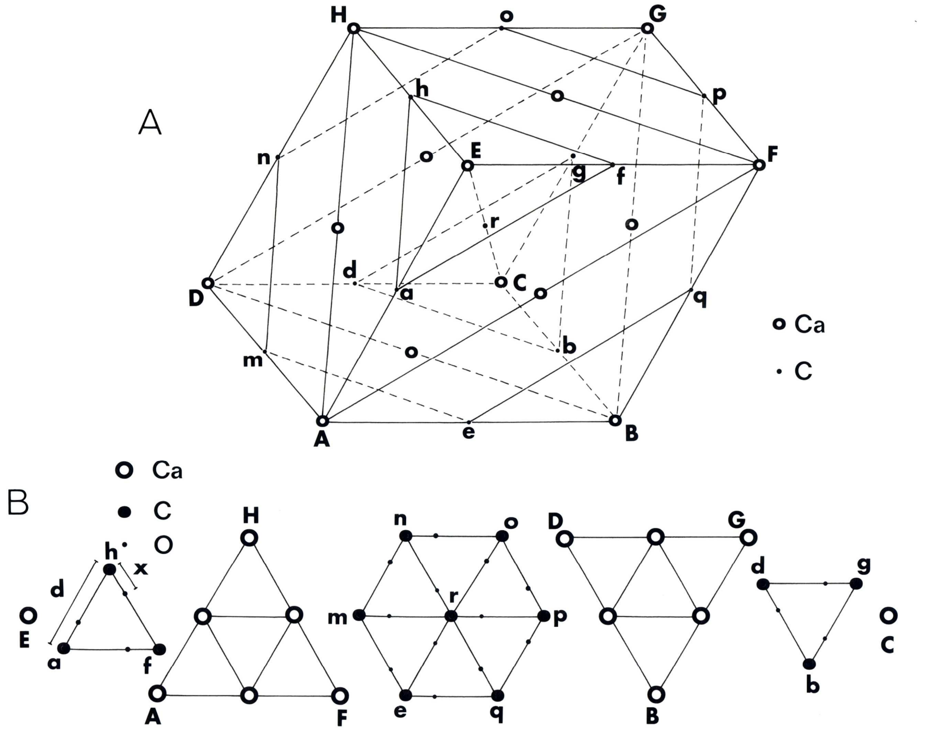


Fig.2 – Structure of calcite proposed by Bragg (1914 B) based on X-ray diffraction analyses.

and dolomite. Such mixed crystals were not available, but crystals of dolomite overgrown with calcite, crystals of calcite overgrown by dolomite, and intercalations of dolomite and calcite were available to Foote & Bradley (1914). Chemical analyses showed, that calcite overgrowths on dolomite contained about 1 % $MgCO_3$ and that the dolomite overgrowths on calcite contained markedly more calcium than that present in pure dolomite.[12] But individual dolomite crystals studied by Foote & Bradley, contained $CaCO_3$ and $MgCO_3$ in the ideal ratio of 1 : 1 , as had been suggested by Retgers (1891).

X-RAY ANALYSIS

In one of the very first papers on X-ray analysis, Bragg (1914 A) reported on the crystal structure of calcite. In this early investigation Bragg employed the method of Von Laue (Friedrich et al., 1912): a pencil of white X-radiation was scattered by a well-oriented thin-section of a crystal. Regarding the orientation of the thin-sections of calcite, Bragg remarked, that not the edges of the rhombohedron should be chosen as the X, Y and Z axes, but instead the three diagonals of the rhombohedron faces meeting in an obtuse corner. In a second paper Bragg (1914 B) reported further analyses of the structure of calcite as well as the structure of sodium nitrate, dolomite, manganese carbonate, and iron carbonate. Here Bragg had used the "ionization spectrometer" developed by Bragg & Bragg (1913) instead of the Laue method. For the second time the structure of calcite was analyzed. In calcite, as in dolomite, rhodochrosite and siderite, the carbonate anion groups would be arranged in planes parallel to (111). The structure of calcite as proposed by Bragg (1914 B) has been summarized here in the diagram of Fig.2. In a few words the structure of calcite can be characterized by "... perpendicular to the trigonal axis the planes are evenly spaced and contain alternately calcium atoms and groups of the composition CO_3" (Bragg, 1914 B, p.469).

The possibilities to distinguish a solid solution (with a random distribution of components A and B) from a superlattice (with alternating monolayers of A and B) were explained in detail by Bragg (1914 B). In the case of a solid solution the planes of the lattice can be regarded as containing both A and B atoms. In a superlattice these planes will be alternately populated by either A or B atoms. The diffraction pattern of the superlattice differs from that of a solid solution not only in the intensities of the X-ray reflections, but also in the possible presence of a new set of reflections. These extra lines denote the distances A-A and B-B typical of the superlattice compared to the constant AB-AB spacing of the solid solution. Knowing the Ca-Ca distance in the lattice of calcite, Bragg tried to find diffraction peaks corresponding with the Mg-Mg distance in the diffractograms of dolomite. These extra lines were not found ("No trace of such a spectrum has yet been found, but it would be easy to miss it": Bragg, 1914 B, p.489). Nevertheless other arguments in favor of the superlattice structure remained (such as the extra reflections), and therefore Bragg concluded, that in dolomite a periodic alternation between monolayers of calcite and magnesite existed in the direction of the *c*-axis. *"It is tempting to consider that in dolomite the arrangement of planes perpendicular to the trigonal axis may be Ca -* CO_3 *- Mg -* CO_3*"* (Bragg, 1914 B, p.488).

The structural model presented by Bragg has been confirmed in publications by Wyckoff & Merwin (1924), Wasastjerna (1924), Gross (1924), Bradley et al. (1953), Howie & Broadhurst (1958), Steinfink & Sans (1959), Beran & Zemann (1977), and Althoff (1977). The model was not accepted by Feigl (1927) and Halla (1935). According to Feigl (1927) the reaction, or rather the lack of any reaction, between dolomite and di-phenyl carbazide showed, that the magnesium cations were "masked" in the form of magnesium carbonato acid, and dolomite would be the calcium salt of that acid. Halla (1935) concluded on the basis of a hypothetical redox reaction involved in the low-temperature formation of dolomite, that the mineral must consist of a highly disordered and inhomogeneous lattice.

Although dolomite is closely related to calcite in its structure, as shown in X-ray diffraction, it is different from both calcite and magnesite (Wyckoff & Merwin, 1924). The difference between calcite (crystal class $\bar{3}m$, space group R $\bar{3}c$ - $D^6_{3}d$ according to Schiebold, 1919 and Wyckoff, 1920) and dolomite (crystal class $\bar{3}$, space group R $\bar{3}$ - C^2_{3i} according to Wyckoff & Merwin, 1924) consists essentially of the presence of three vertical planes of symmetry.

In dolomite the Ca - O distances are somewhat larger than those in calcite. Beran & Zemann (1977) measured 23.81 nm for Ca - O in dolomite, and compared it to the Ca - O distance for calcite published by Chessin et al. (1965): 25.36 nm. The C - O distances in dolomite (of 12.86 nm: Beran & Zemann, 1977) are virtually identical to those measured in calcite (of 12.83 nm: Chessin et al., 1965). The carbonate groups in dolomite can be considered to be planar in the *a-b* direction. Beran & Zemann (1977) found, that the C-atoms rise by only 0.17 nm above the oxygen plane of the CO_3 groups into the direction of the Mg^{2+} plane. Effenberger et al. (1981) revised this value to 0.18 nm. Measurements showing, that the carbonate groups possess a slight aberration from the horizontal plane, have been published by Steinfink & Sans (1959) and Althoff (1977).

It might be thought, that the planes of the carbonate groups would be nearer to the (small) magnesium cations than to the (larger) calcium cations. Gross (1924) had stated, that the carbonate groups would be arranged in planes virtually midway between the Ca^{2+} and the Mg^{2+} layers. Such an arrangement would be required, according to Gross, by the symmetry elements of the dolomite lattice. Evidence that the plane formed by the Mg^{2+} ions is in fact nearer to the CO_3^{2-} plane has been put forward by Althoff (1977), Beran & Zemann (1977), and Effenberger et al. (1981). The difference in distances between cation and oxygen atoms was quite pronounced. Effenberger et al. (1981) gave the Ca-O distance in dolomite as 23.822 nm and the Mg-O distance as 20.877 nm (compare the Mg-O distance of 21.018 nm in magnesite and the Ca-O distance of 23.598 nm in calcite). In other words the Mg-O distance in dolomite is shorter than that in magnesite, and the Ca-O distance in dolomite is longer than that in calcite.

DIFFRACTION SIGNAL

Identification of the precipitates formed in a multitude of laboratory experiments aimed at the low-temperature synthesis of dolomite, magnesite and huntite, took place with the aid of modern X-ray diffraction equipment. This type of equipment has been developed by amongst others Le Galley (1935), Friedman (1945) and Parrish & Gordon (1945) on the basis of the "ionization spectrometer" of Bragg & Bragg (1913). The main difference between the "ionization spectrometer" and the X-ray diffractometer is to be found in the use of a Geiger-Müller tube (Geiger & Müller, 1928) instead of the ionization chamber filled with sulfur dioxide as designed by Bragg & Bragg (1913).

Modern powder diffraction techniques for routine identification possess noticeable advantages over photographic techniques. In many instances crystals with a size suited for single-crystal X-ray diffraction techniques are not to be found in the fine-grained powders, which form in laboratory experiments. Another considerable advantage is the lack of any time-consuming preparation techniques in the case of powder X-ray diffraction. Measurement of the resulting diffraction maxima (or peaks) on the paper of the recorder is relatively rapid and easy to perform. (In the latest type of diffraction equipment on-line computer analysis is incorporated, rendering superfluous paper chart recordings.) The position of the various peaks can be used to calculate interplanar spacings of the crystal lattice under investigation, and so lead to successful identification. But more information can be deduced from the recorded signal of the powder, notably from the nature of the profiles of the various diffraction maxima.

The interference theory of Von Laue (1912) has been found useful in calculating the exact location of the maxima in X-ray photographs, but it failed to predict the intensity of those maxima. Darwin (1914 A) thought, that in this respect the approach of Bragg (1912) based on the diffraction of the Röntgen radiation, would turn out to be more rewarding. The comparison between X-ray phenomena and optics would be able to supply the required theoretical basis for calculations of the intensities of the measured maxima. The first observation made by Darwin (1914 A) concerned the influence of the exponential degree of absorption of X-rays penetrating a (crystalline) solid. As a consequence the image of a fine line of the incident beam of X-rays will become, after reflection/diffraction by a crystal, an asymmetrical band. On the side of this band where the X-rays of the shortest route converge, it is quite sharp. But the other side of the same peak is weaker, not so sharp, because of the absorption encountered deeper inside the crystal, and on the way out again after reflection.

Because of the approach in terms of reflection by planes of atoms, the question could be asked, whether the reflected beam of X-rays could ever possess a higher intensity than the incident beam. Darwin (1914 A) answered this question with calculations on the width of the reflected bundle of X-rays. According to theory the reflected bundle had to be extremely narrow (only 5"), but in practice much wider bundles were measured. This discrepancy had to find its origin in interacting atoms, giving rise to a spreading out of the reflected bundle into a broader pattern. Electrons had to be the cause of this dispersion of the electromagnetic energy. In some instances an extra degree of scattering had been measured, notably upon the reflection of X-rays at small angles by an amorphous substance (Barkla & Ayres, 1911; Crowther, 1911). There were two other factors causing scattering: in the first place the heat movement of the atoms is responsible for deviations from the strictly flat plane required for ideal reflection. The second factor responsible for the broadening of the reflected bundle had been found by Debije (1913): atomic displacements in directions other than within the reflecting plane such as the displacements of the different kinds of atoms in mixed crystals.

In his second paper on the theory of X-ray reflection Darwin (1914 B) stressed the importance of "a considerable amount of distortion" in almost all crystal lattices. This had to be the main cause of the higher degree of reflection actually measured, when compared to the theoretically calculated reflected intensity. Mathematical treatment of the reflected intensities was hampered by uncertainty, because of the lack of quantification of the imperfections of crystals ("The irregularity of a crystal is of necessity a rather indefinite matter, which it would be perhaps difficult to discuss with rigour": Darwin, 1914 B, p.685).

Ehrenberg & Von Susich (1927), discussing the width of X-ray emission lines coming from calcite crystals, gave several possible explanations for the phenomenon of line broadening. In the first place the crystal itself might possess small-scale irregularities in the lattice (the so-called *Mosaikfehler*). The size of the crystallites used in powder diffractograms would influence line width, as would alignment and adjustment of the sample and its holder in the diffractometer.[13] The temperature of the sample was another factor, and the voltage on and current through the X-ray tube had to be taken into consideration. In practice factors such as voltage and current are kept strictly constant, and an attempt must be made to keep the instrument settings such as alignment and adjustment as constant as possible (checks have to be made from time to time). Temperature is room temperature in most instances, and by far not approaching the melting points of the substances being studied. Therefore of the factors mentioned by Ehrenberg & Von Susich (1927), grain size and imperfection (mosaic structure) remain of interest. Other factors influencing the intensity of the reflected beam are Lorentz factor, the absorption factor, and the structure factor. Because these factors are characteristic for each crystalline substance, they can be left out of consideration, when restricting the choice of samples to only one category of compounds such as the anhydrous Mg/Ca carbonates.

Publications by Ewald (1917), Darwin (1922), Bragg et al. (1926) and James (1934) have provided more details on the significance of X-ray diffraction for the recognition of imperfect crystals. "In an extreme case of this, we may find an apparently single crystal to consist of several separate crystals, each fairly perfect, but differing from the others in orientation": James (1934, p.297). Large-scale imperfections are usual in most natural crystals, and consequently the reflected intensities usually do not form very narrow peaks, but rather broad ones. But, as James (1934, p.307) observed: "It appears that calcite although not an ideally perfect crystal is far from being irregular enough to be classed as a mosaic".

STACKING FAULTS

In dolomite the two different cations, magnesium and calcium, are separated into alternate layers. Möller & Rajagopalan (1972) published calculations showing, that this separation into individual monolayers is a necessity. Random substitution of calcium cations by the much smaller magnesium cations would lead to insurmountable disturbances in the lattice. A calcium position occupied by a magnesium cation would, through its enhanced Coulomb attraction, initiate rotation and tilting of the neighboring carbonate anion groups. An arrangement of the two different cations separated into two individual monolayers is energetically favored over a situation, in which the two types of cations replace each other at random. The mean bonding energy in the first case is considerably higher than in the second situation (Koss & Möller, 1974). Similarly Althoff (1977) concluded from her single crystal X-ray analyses, that the interatomic bond lengths and the angles of the atomic structure of dolomite are to be preferred from a viewpoint of the bonding forces above those found in calcite and magnesite. Crystallographic considerations led Zemann (1981) to much the same conclusion concerning the necessity to separate calcium and magnesium cations into separate monolayers.[14]

From calculations using the cluster variation method Burton & Kikuchi (1984) drew the conclusion, that calcium and magnesium cations will tend to separate into monolayers (or sub-lattices) in the case of dolomite. Using computer simulations Wright et al. (2002) noted how dolomites containing less than 50 mol % $MgCO_3$ will tend to incorporate the excess calcium cations in the form of stacking faults (the δ-structure of Reeder, 1992) rather than substitution of magnesium by calcium (the γ-structure of Reeder, 1992).

Considerations on bonding energies make the separation of calcium and magnesium cations into monolayers relatively easy to understand. A different matter would be the exact sequence of these monolayers. The chemical composition of dolomite requires equal amounts of $CaCO_3$ and $MgCO_3$ to be present. In theory at least an alternation of these two components different from the sequence ABAB... might be envisaged. And in fact many dolomites seem to possess such an irregular stacking sequence of calcite and magnesite monolayers. The peaks of *c*-axis reflections in X-ray diffractograms of synthetic dolomites and certain natural dolomites are according to Graf et al. (1957) often found to be asymmetric, when compared with the peaks of *a*-axis reflections. This asymmetry is proof of the fact, that an irregular stacking sequence of calcite and magnesite monolayers in the direction of the *c*-axis exists (Graf et al., 1957): mixed layer effects exist in these dolomites.

Mixed layer effects are known from the clay minerals. Therefore a comparison can be made between the phyllosilicates and dolomite. Such a comparison was made for example by Lippmann & Johns (1969). In calculations involving the *c*-axis dimensions only of calcite, magnesite and dolomite, it became clear, that especially the refined structure of dolomite published by Bradley et al. (1953) and Steinfink & Sans (1959) justified the description of dolomite as a regular interstratification of calcite and magnesite-like layers. In the view of Lippmann & Johns (1969) these alternating layers are not true calcite and magnesite monolayers: the oxygen atoms of the CO_3-groups of dolomite are rotated by as much as 6.5^o away from the *a*-axis. But Lippmann & Johns (1969) did agree on the description of dolomite as a regular interstratification of "calcite-like and magnesite-like layers".

Evidence of a more direct character than that obtained in X-ray analysis, has been supplied by the electron microscope. Barber (1977) reported stacking faults disrupting the regular ABAB... sequences in metamorphic dolomite, and Barber et al. (1977) reported such stacking faults from synthetic dolomite produced under shear stress at 1073 K. More evidence on the existence of mixed-layering in dolomites came from Reeder & Wenk (1979), Reeder (1981), Reeder & Nakajima (1982), Wenk & Zenger (1983), Van Tendeloo et al. (1985), Wenk & Zhang (1985), Reeder & Prosky(1986) and Carballo et al.(1987). Electron microscopy of thin foils of dolomite revealed in electron diffraction new superstructure reflections, that indicate a doubling of the unit cell dimension *a*. This doubling of the *a*-axis parameter is most likely caused by cation stacking disorder, disrupting the Ca-Mg-Ca-Mg... sequence. The "tweed texture" reported by Reeder & Wenk (1979) is probably the result of the disturbed regular stacking sequence in dolomite. According to calculations by Chen et al. (1979) the "tweed texture" is caused by a certain degree of mismatch between the lattices of the two co-precipitated carbonates. Modulated structures had previously been recognized during electron microscopy of ordered non-stoichiometric metal alloys such as Ni - Mo (Van Tendeloo et al., 1974), Au - Mn (Van Tendeloo & Amelinckx, 1981) and Pt - Ti (Schryvers et al., 1983).

The dolomites that show evidence of an irregular stacking sequence are invariably calcite-rich: extra calcite monolayers had to be accommodated, and the ideal dolomite lattice could not provide the required extra space. The result is an "out of step" sequence. Reeder (1981) stressed the observation, that stacking faults (= mixed-layer effects) are found only in dolomites formed at elevated temperatures. Reeder & Nakajima (1982) estimated that this kind of disorder in dolomite would require a minimum temperature of 1373 to 1423 K. The studies on the ultra-structure of dolomite by Reeder (1981) and Reeder & Nakajima (1982) give extra support to the work of Graf et al. (1957), since these authors were the first to observe the existence of disordered stacking sequences in dolomite.

A variety of microstructures found in Ca-rich dolomites has been described by Reeder (1992): modulations (this pervasive microstructure shows in transmission electron microscopy as an almost regular pattern of alternating contrast between dark and light), coherent ribbon-like intergrowths (ribbon-like defects observed in a variety of dolomite with curved crystal faces: see also Barber et al., 1985), and ordered superstructures (recognized only by way of electron diffraction). The same microstructures were found to a lesser degree in calcite, but no such microstructures could be detected by Reeder (1992) in pure (i.e., stoichiometric) dolomite. Except for the occasional dislocation (which can be found in virtually every crystal), no forms of modulations, ribbon-like intergrowths or similar microstrucures were found at all in stoichiometric dolomite. In other words: in dolomite with exactly 50 mol % $CaCO_3$ and 50 mol % $MgCO_3$ no inhomogeneities on the atomic level are to be found. Similarly Wenk et al. (1993, p.772) concluded: "Ordered dolomite precipitates are coherent overall." Reeder (1992) considered his observations as proof of the conclusion reached by Goldsmith (1983), that any anhydrous Mg/Ca carbonate other than stoichiometric dolomite would be metastable. Much the same situation was found to occur in the system $CaCO_3$ - $FeCO_3$. There a variety of microstructures can be found in the mixed crystals with excess calcium carbonate, but no lattice disturbances occurs in the double carbonate $CaCO_3.FeCO_3$ itself, provided it possesses a stoichiometric composition (Barber & Khan, 1987; Reeder & Dollase, 1989; Khan & Barber, 1990; Reksten, 1990 A). From the combined observations on the systems $CaCO_3$ - $MgCO_3$ and $CaCO_3$ - $FeCO_3$ Khan & Barber (1990) as well as Reeder (1992) drew the conclusion, that it was the excess calcium carbonate that must be held responsible for the formation of microstructures in these mixed crystals.

STOICHIOMETRY

After chemical analyses of samples of dolomite Tennant (1799, p.306) stated, that "Upon examining the composition of this substance ... it was discovered to contain three parts of pure calcareous earth, and two of magnesia" [i.e., wt.% CaO : wt.% MgO = 3 : 2 or 53.4 wt.% $CaCO_3$ and 41.8 wt.% $MgCO_3$; compare the 54.3 wt.% $CaCO_3$ and 45.7 wt.% $MgCO_3$ composition of pure dolomite as given for example by Scheerer, 1866]. In 1804 Klaproth realized, that dolomite does not always exhibit the composition given by its formula $CaCO_3.MgCO_3$. In other words Klaproth (1804) advanced the view, that dolomite would not conform to what has become known as the Law of the Multiple Proportions of Dalton (1808). Klaproth's observation was based on chemical analyses of four different samples of dolomite, revealing a noticeable divergence from the ideal composition (see Table II / Appendix). The first sample analyzed by Klaproth (1804) came from Campo Longo (Switzerland),[15] and it was found to contain 52 wt.% $CaCO_3$, 46.50 wt.% $MgCO_3$, 0.50 wt.% Fe_2O_3 and 0.25 wt.% MnO . The second sample of dolomite analyzed by Klaproth (1804) came from Castelmare (Italy) and contained as much as 59.0 wt.% $CaCO_3$ and 40.5 wt.% $MgCO_3$. A third sample had been collected in Kärnten (Austria), and it was analyzed to contain 52 wt.% $CaCO_3$ and 48 wt.% $MgCO_3$. The fourth sample of dolomite came from a piece of "antique sculpture" (analyzed because De Dolomieu, 1791 had pointed out, that dolomite had been a favourite rock among the classic sculptors), and its analysis gave 51.50 wt.% $CaCO_3$ and 48.0 wt.% $MgCO_3$. From these analyses Klaproth (1804) concluded, that the question had to be asked, in how far the name dolomite could be of practical use in geology.[16] But not all geologists could agree with that point of view. For example Von Buch (1822 B) stated, that perhaps dolomite might be intermingled with calcium carbonate, but at least the amount of magnesium carbonate in dolomite would not vary to any marked degree.[17] It is important to note here, that Von Buch (1822 B) expressed his doubts concerning the pureness of the samples of dolomite he had analyzed. A fundamental question indeed, but virtually impossible to answer. In this section even the eldest mineralogical determinations will be respected, because ever since the first description of dolomite by De Dolomieu (1791) properties such as crystal habit, color, hardness, refraction index, and specific gravity all have contributed to successful determination as much as chemical analysis. Numerous authors publishing analyses have taken the trouble to point out, that they had carefully chosen only pure samples of dolomite.[18] In this way the discussion concerning the nomenclature of "dolomitic limestones" with its inherent maximum and minimum percentages dolomite contained in a limestone, as performed for example by Forchhammer (1852), Rammelsberg (1875) and Doelter & Hoernes (1875) may be avoided. The word dolomite will be used to define the mineral only. At the same time it is of interest to note, how Karsten (1848) emphasized the need to establish the mineralogical relations between $CaCO_3$ and $MgCO_3$ before conducting any chemical analyses.[19] From dolomitic limestones crystallites of pure dolomite could best be recovered, according to Karsten's (1848) description, by way of dissolving the sample in dilute acetic acid kept at temperatures below 273 K.

Early analyses for example those of Gmelin (1826) showed, that the amount of calcium carbonate present was virtually equal to that implied by the stoichiometry of dolomite (54.54 wt.% $CaCO_3$ found and 54.27 wt.% calculated), but the amount of magnesium carbonate was less than expected for the pure crystal (42.80 wt. % $MgCO_3$ found and 45.73 wt.% calculated). Karsten (1828), after analyzing some ninety samples of dolomite, had not found any compositions all too different from that of the usual chemical composition of dolomite. But Karsten (1828) warned for samples consisting of mixtures of dolomite and limestone. In Karsten's (1828) interpretation crystalline dolomites would possess the composition of dolomite, and noncrystalline dolomites could have any composition.[20] Beudant (1832) reported to have found among other analyses 54.1 wt.% CaCO and 38.3 wt.% $MgCO_3$ in one instance and 62.1 wt.% $CaCO_3$ plus 35.5 wt.% $MgCO_3$ in another. After repeating a number of chemical analyses published by others, Rammelsberg (1841) concluded, that the amounts of calcium carbonate and magnesium carbonate did vary to a considerable extend, but in "the purest forms of dolomite" these amounts were invariably found to be of "simple proportion". Petzhold (1843) claimed to have found in his analyses of dolomite percentages of calcium carbonate ranging from 53.00 wt.% to 54.79 wt.% and amounts of magnesium carbonate ranging from 44.5 to 46.96 wt.% . Von Morlot (1849) measured 54.7 wt.% $CaCO_3$ combined with 42.5 wt.% $MgCO_3$.

As more and more analyses of dolomite became known, the confusion increased. For example Doelter & Hoernes (1875) wondered whether to consider the mineral dolomite as being a double salt or an isomorphic mixture. Undoubtedly calcite and magnesite were isomorphic carbonates, but did the two form a real double salt in the case of dolomite? Numerous aberrations from the ideal composition had become known, and for example $MnCO_3$ could replace part of the $MgCO_3$ of dolomite. The fact that Von Gorup-Besanez (1872) had found equimolal amounts of calcite and magnesite in the residue of dolomite dissolved in CO_2 saturated water was interpreted by Doelter & Hoernes (1875) as proof of the fact, that at least in that particular case dolomite must have been a double salt. And such dissolution experiments had to be performed in each and every chemical analysis of dolomite samples. Unless such an analysis had taken place, there was no need to describe dolomite as a double salt of stoichiometric composition. Dissolution experiments have been conducted for example by Hoppe-Seyler (1875), Haushofer (1881) (both of whom concluded, that dolomite consisted of an isomorphic mixture of $CaCO_3$ and $MgCO_3$), and Vesterberg (1900) (who was convinced, that dolomite was not a mixture but a real double salt).

As a consequence the more or less general conviction has established itself, that dolomite never occurs in its stoichiometric composition (e.g., "The typical dolomite, $CaCO_3.MgCO_3$, 54.35 per cent $CaCO_3$ and 45.65 per cent $MgCO_3$, possibly never occurs in nature; but one or the other, or both, of the constituents are replaced by various other substances": Rothrock & Shumaker, 1920, p.29). After performing their high-temperature syntheses of "protodolomite", which often showed an excess of $CaCO_3$ over $MgCO_3$, Goldsmith & Graf (1958 B) set out to find such dolomites in nature. After a thorough search Goldsmith & Graf (1958 B) found a large number of "Ca-rich" or "non-ideal" dolomites in samples from for example the Ordovician Galena-Platteville Formation, Illinois (USA) (with 53.3 mol % $CaCO_3$); from the Cretaceous Cogollo Formation, Venezuela (with 52.5 mol % $CaCO_3$); from the Eocene Avon Park Formation, Florida (USA) (with 55.2 mol % $CaCO_3$); from various depths of the Funafuti core samples (with a maximum of 56.6 mol % $CaCO_3$); from the cores of Kita Daito Jima (with 56.0 mol % $CaCO_3$ at maximum); and from the Eniwetok cores (with as much as 55.6 mol % $CaCO_3$). Because their analyses based on X-ray diffraction could be undermined by substitution of Mg by Fe or Mn, Goldsmith & Graf (1958 B) also performed spectrographic analyses to measure the Fe and Mn contents of the dolomites studied. For the mainly Fe- and Mn-free dolomites percentages between 53 and 56.5 mol % excess $CaCO_3$ were found. But in addition to the dolomite samples enriched in calcium carbonate, other samples had been found, that were enriched in magnesium carbonate ("Eight dolomites from evaporative environments have compositions ranging from 49.2 to 50 mol per cent $CaCO_3$. These dolomites may well have crystallized in Mg-rich environments ...": Goldsmith & Graf, 1958 B, p.688). But the variations in magnesium carbonate and calcium carbonate content could even occur within one and the same crystallite of dolomite: diffuse satellites in the basal reflections indicated compositional variations "... even within a single crystal" (Goldsmith & Graf, 1958 B, p.688). From these observations the conclusion was drawn, that mere recrystallization would not suffice to change the metastable Ca- or Mg-rich dolomites into stoichiometric dolomite. And moreover: "The *mechanism* by which recrystallization could effect a closer approach of dolomite to ideality is unknown, however": (Goldsmith & Graf, 1958 B, p.692).

Füchtbauer & Goldschmidt (1965) claimed, that the possible relation between salinity and stoichiometry of sedimentary dolomites hinted by Goldsmith & Graf (1958 B), had been proven in the laboratory experiments by Siegel (1961). Further evidence was thought to be supplied by the fact, that in the humid climate of Florida the (modern) dolomite showed a calcium carbonate content of 58 to 67 mol % ; whereas in the semi-arid climate of Bonaire the dolomite held 54 to 56 mol % calcium carbonate, and in the arid climate of the Persian Gulf dolomites formed with only 54 mol % $CaCO_3$. From core samples the relation between dolomite stoichiometry and porosity could be established: a decrease in porosity was accompanied by a decrease of the calcium carbonate content of the dolomite. Or in other words an increased porosity led to the formation of a dolomite with more $CaCO_3$ in its lattice. It was therefore clear to Füchtbauer & Goldschmidt (1965), that secondary changes will influence dolomite stoichiometry.

Schmidt (1965) performed chemical analyses on 745 different samples from a Jurassic limestone formation of northwestern Germany and found the $MgCO_3$ content of the dolomites to vary between 41 and 47.5 mol %. Schmidt (1965, p.143) concluded from his observations: "Incompletely dolomitized rocks document that the dolomitization process had been interrupted". In his extensive study on Devonian and Permian dolomites from the Eifel region (Germany) Richter (1974 B) measured calcium carbonate contents of up to 56 mol % . Dolomites with the least excess $CaCO_3$ occurred in the centre of the Devonian deposits of the Eifel; near the boundaries of the Devonian formations the dolomites possess a higher content of excess calcium carbonate. Land (1980) explained the variations in the substitution of calcium for magnesium in Holocene dolomites, in comparison with older dolomites to be the result of "... a process of stabilization from very Ca-rich dolomite to less Ca-rich dolomite" (Land, 1980, p.92): in fact a new name for the old theory of replacement. Lumsden & Chimahusky (1980) analyzed 290 different Paleozoic (well ordered) dolomite samples, and observed, that dolomite non-stoichiometry was *not* related to insoluble residue of the samples, to porosity, rock type, percentage of crinoid fragments, recrystallization or percentage dolomite in the carbonate fraction of the limestone. Nor could any large-scale trend towards increased stoichiometry with increasing age of the samples be detected.[21] The conclusion reached by Lumsden & Chimahusky (1980) was, that larger dolomite crystal ("crystalline dolomite") tended to be more nearly stoichiometric than the finer grained varieties of dolomites ("dolomicrites"). On the basis of X-ray diffraction of 55 samples of different dolomitic limestones Sperber et al. (1984) were able to conclude, that a relation exists between the amount of dolomite in a carbonate sediment and dolomite stoichiometry. Especially in the Paleozoic dolomites stoichiometric dolomite was found, but the dolomite from the dolomitic limestones of the same era was more calcium-rich. Fine-grained dolomites from evaporitic settings were more stoichiometric than the dolomite from normal marine settings.

Two different sorts of modern dolomite in the sediments from Sugarloaf Key (Florida, USA) were recognized by Carballo et al. (1987). The vast majority of the dolomite rhombs showed, when studied with the scanning electron microscope, sharp outlines and smooth crystal faces. The crystals measured several micrometer in diameter: a small part of the dolomite

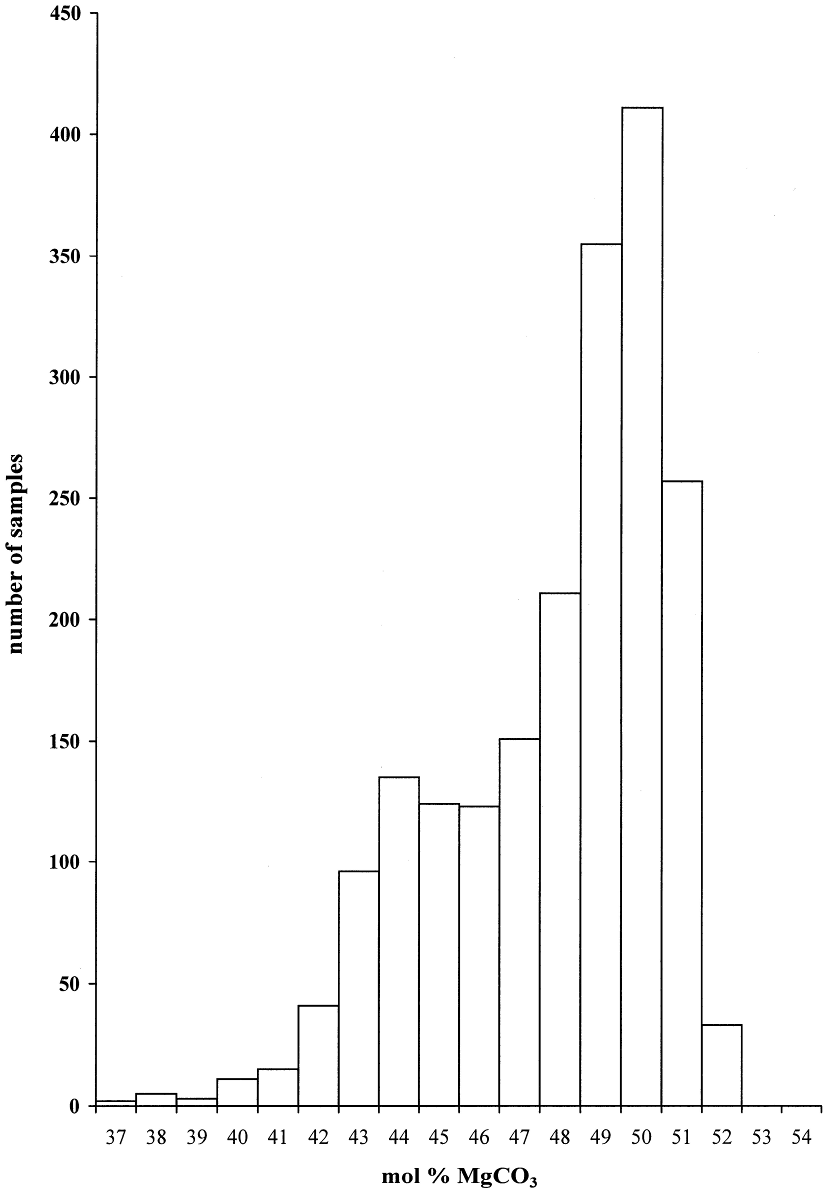


Fig.3 – Histogram of mol percentage magnesium carbonate in dolomite plotted against the number of analyses (in total 1871 different analyses performed by electron probe or by way of chemical analyses) (graph based on data from Searl, 1994).

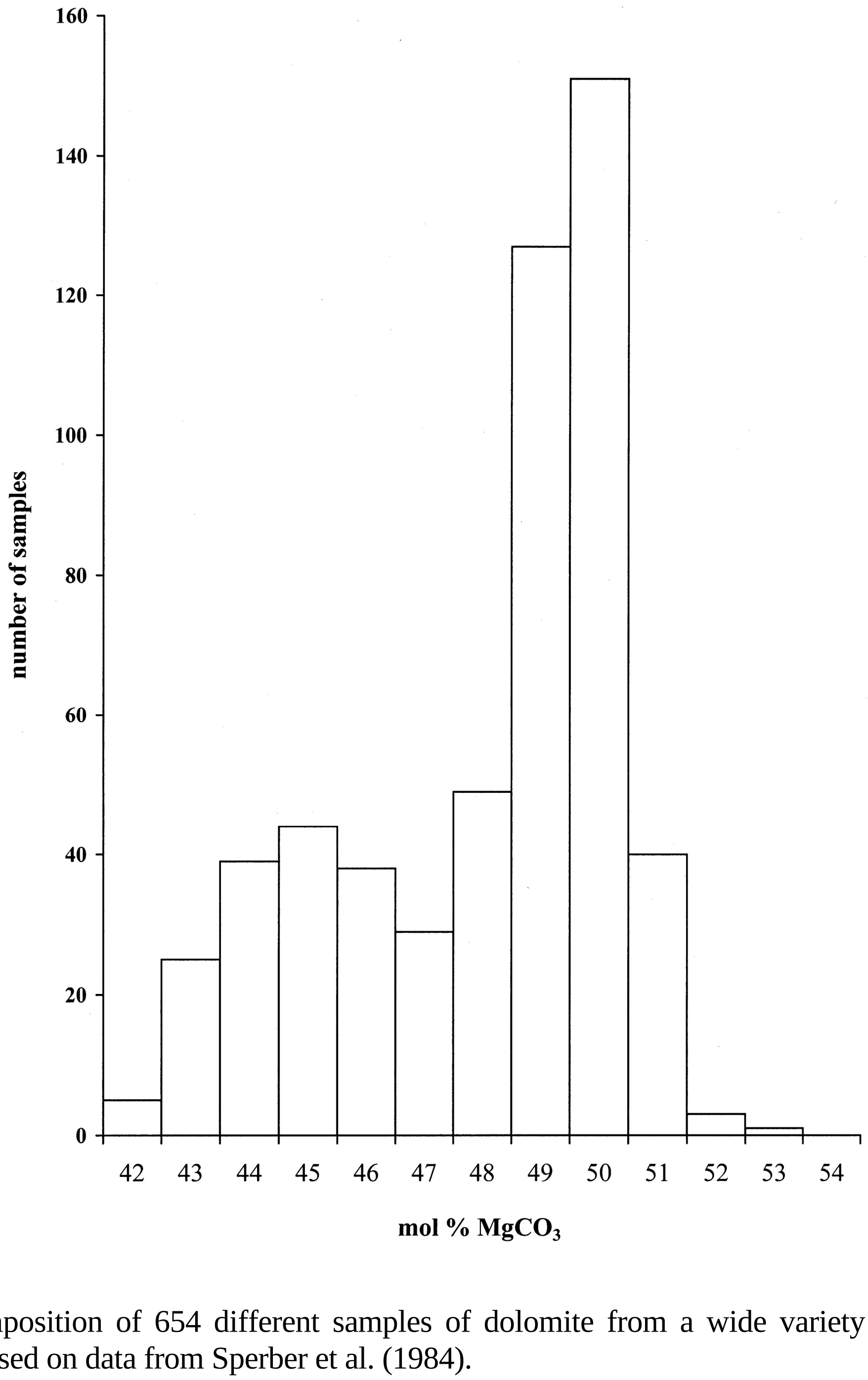


Fig.4 – Composition of 654 different samples of dolomite from a wide variety of ages and locations. Based on data from Sperber et al. (1984).

crystals consisted of subrounded microcrystallites, some 0.1 to 0.3 micrometer in size. The latter crystallites were interpreted as representing the initiation of the process of dolomite formation. X-Ray diffraction showed clearer superstructure reflections in samples of the smooth faced crystals than in those coming from samples of predominantly microcrystalline dolomite. X-Ray data combined with microprobe analyses proved the latter type of dolomite crystals to contain more calcium carbonate ($Ca_{0.60}$ $Mg_{0.40}$) than the samples of the smooth-faced dolomite (composition $Ca_{0.57}$ $Mg_{0.43}$). In transmission electron microscopy modulated structures, such as those described by Reeder (1981), were observed. Carballo et al. (1987) postulated that the less ordered, microcrystalline variety of dolomite would inevitably be replaced by the more nearly stoichiometric, smooth-faced dolomite.

Gregg et al. (1992) applied X-ray analyses to modern dolomite (younger than 3000 years) from Ambergris Cay, Belize, and found that most of the ordering of the high-magnesium calcites (with 40 to 46 mol % $MgCO_3$) took place in the upper 15 cm of the section studied. But at the same time "No relationship was observed between increasing stoichiometry and depth" (Gregg et al., 1992, p.149). Contrary to for example McKenzie (1981), who had noted an increase in cation ordering, in stoichiometry and crystal size with increasing depth in the dolomite deposits from the sabkha at Abu Dhabi.

From about 2000 different spot tests made with electron microprobe analyses, Searl (1994) obtained results distinctly different from those made with X-ray diffraction. The histogram of the number of analyses plotted against mol % $CaCO_3$, does not show a continuous change in composition. Instead a polymodal distribution pattern was found by Searl (1994). Much of the difference with X-ray diffraction data of others must have been caused by the impossibility to measure the nanometer heterogeneity, which can be seen (and measured) in electron microscopy (Searl, 1994). Plotting the mol percentages $MgCO_3$ instead of mol % $CaCO_3$ (as Searl,1994 has done), leads to a clear conclusion with regard to the structural chemistry of magnesium calcites and dolomite (Fig.3). Most of Searl's samples are seen to contain 50 mol % $MgCO_3$; some samples contain less than 50 mol %, but little or no of these dolomite samples contain more than 50 mol % $MgCO_3$. The same phenomenon becomes clear in the histogram of 654 analyses of dolomites published by Sperber et al. (1984). When plotting the mol % $MgCO_3$ instead of the mol % $CaCO_3$ (as Sperber et al., 1984 did), as done in Fig.4, much the same asymmetry results as that seen in Fig.3. These two histograms of the $MgCO_3$ percentages of a multitude of dolomite samples appear to confirm the observation made by Retgers (1891): mixed crystals with compositions in between those of calcite and dolomite are known, but there is no continuous series of mixed crystals with compositions between that of dolomite and that of magnesite.

MAGNESIUM CALCITES

In 1791 Bouvier described chemical analyses of *Corallina officinalis* Linn., and reported finding 2.3 % *magnésie* (in the form of carbonate). The presence of magnesium carbonate and calcium carbonate in one and the same mineralogical specimen has been confirmed for example by Karsten (1807 B), John (1814)[22] , Laugier (1826), and Kühn (1846). Later Damour (1850), Forchhammer (1852) and Högbom (1894) measured $MgCO_3$-contents in the skeletons of calcareous marine organisms such as *Porites*, *Millepora*, *Oculina*, and especially *Lithothamnium* (the latter species contained up to 10 wt. % $MgCO_3$). Branner (1904) reported the chemical composition of coral from living reefs in the sea along the coast of Brazil as 82.19 (wt.) % $CaCO_3$ and 12.98 % $MgCO_3$. Bütschli (1908) described the calcite deposited by

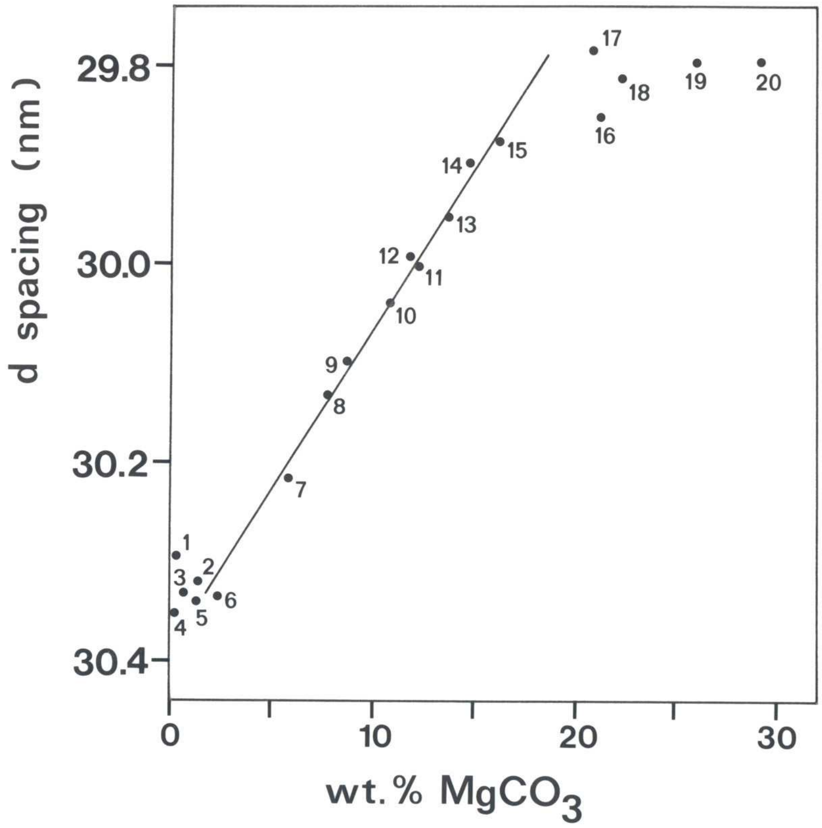


Fig.5 – Relations between weight percentage $MgCO_3$ incorporated and the position of the main diffraction peak of magnesium calcites of various origin. Samples were: 1) pelecypod, Bermuda; 2) pelecypod, Alaska; 3) pelecypod, Bermuda; 4) Iceland spar, unknown origin; 5) pelecypod, Bermuda; 6) barnacle, Japan; 7) sponge, California; 8) echinoid, California; 9) echinoid spines, Bermuda; 10) echinoid, Bermuda; 11) echinoid, Guam; 12) foraminifera, Bermuda; 13) coral, Bermuda; 14) algae, Bermuda; 15) starfish, Florida; 16) algae, Guam; 17) algae, Palau; 18) algae, Bermuda; 19) algae, Florida; and 20) algae, Florida (redrawn after Chave, 1952).

marine organisms (such as *Echinus esculentus*, *Stichopus* sp., *Corallium rubrum*, and *Melobesia* sp.) containing up to 12.3 % $MgCO_3$. Lemoine (1911) analyzed various calcareous algae, and found percentages $MgCO_3$ of 10 to 13 % in *Lithothamnium calcareum* and even 16 % $MgCO_3$ in a sample of *Lithothamnium craspedium* from Tahiti. Jourdy (1914) found up to 29 wt.% $MgCO_3$ in Miocene calcareous algae. The point of view that especially marine calcareous organisms will concentrate magnesium carbonate, has become widespread, even though Klähn (1928 A,B) found magnesium-containing calcites precipitated in lakes, as the result of CO_2 uptake by plants such as *Potamogeton*. Köhler (1928) analyzed 105 different samples from the Zechstein bryozoan reefs of Thuringia (Germany) and measured magnesium concentrations, which varied between traces and amounts equal to that found in dolomite. Mägdefrau (1933) found 2.5 to 6.2 wt.% $MgCO_3$ in the calcareous alga *Lithophyllum expansum*. Schroeder et al. (1969) have found extremely high magnesium contents in parts of the sea urchins *Diadema antillarum* and *Lytechimus variegatus*: compositions up to $Ca_{57}Mg_{43}(CO_3)_{200}$ were measured. Schroeder and co-authors demonstrated, that the entire range of chemical compositions varying from that of pure calcite up to pure dolomite can be found in marine organisms. Ali-Zade et al. (1978) reported on fossil sea urchins (*Echinocorys* and *Micraster* sp.), containing as much 52 mol % $MgCO_3$.

Not only because of the problem of the structural chemistry of the magnesium calcites as such, but especially because of their possible significance in the nucleation of dolomite the magnesium calcites deserve more attention. Current explanations of the structure of the Mg-calcites tend to follow the solid solution model proposed by Chave (1952).[23] Through the combination of chemical analyses of both Recent and fossil calcareous organisms with X-ray diffraction data, Chave (1952) was led to postulate the existence of a solid solution between calcite and dolomite (Fig.5). At the same time Chave (1952) suggested, that these mixed crystals would be unstable under all near-surface conditions "... except within the biological environment which produced it" (Chave, 1952, p.192). The solid solution model with its random distribution of calcium and magnesium cations over the cation sites is however not the only model available. As a basis for his conclusions on the nature of the magnesium calcites Chave (1952) had used Vegard's Law: a linear relation would exist between the weight percentage of $MgCO_3$ (as measured in wet chemical analysis) and the d-spacing of the crystallographic planes parallel to the main cleavage direction (at least for $MgCO_3$ percentages between 2 and 16 wt. %).[24]

The linearity between the lattice parameters found in X-ray diffraction and the percentages of the individual components of a solid solution was first noted by Vegard (1921) in ionic crystals, and Vegard & Dale (1928) observed the same relation in metal alloys. Later it was found, that this linearity cannot be found in many metallic solid solutions ("... in the great majority of alloys there are deviations from the law": Hume-Rothery, 1950, p.58). Similarly Vegard's Law appeared to hold true for ionic lattices in only a limited number of instances (e.g., aluminium oxide and chromium oxide: Spriggs & Bender, 1962).

Serious objections against "Vegard's Law" have been formulated by Zen (1956). The linear relation between the length of the unit cell edge and the composition of mixed crystals, and applied by Chave (1952) to the magnesium calcites, could not withstand critical re-examination. Only in those cases where the two different components of the mixed crystal have a comparable molar volume, a linear relation will result. In all other instances no linearity can be found at all.[25]

It is the very diagram presented by Chave (1952), that shows, how in the case of the magnesium calcites Vegard's Law does not hold true. From Chave's diagram (reproduced here as Fig.5) it can be seen, that only 9 out of 20 samples show a linear relation between d-spacing and the percentage of incorporated $MgCO_3$. The majority of the samples analyzed by Chave do not show such a linear relation. The obvious discrepancy between the disordered solid solution

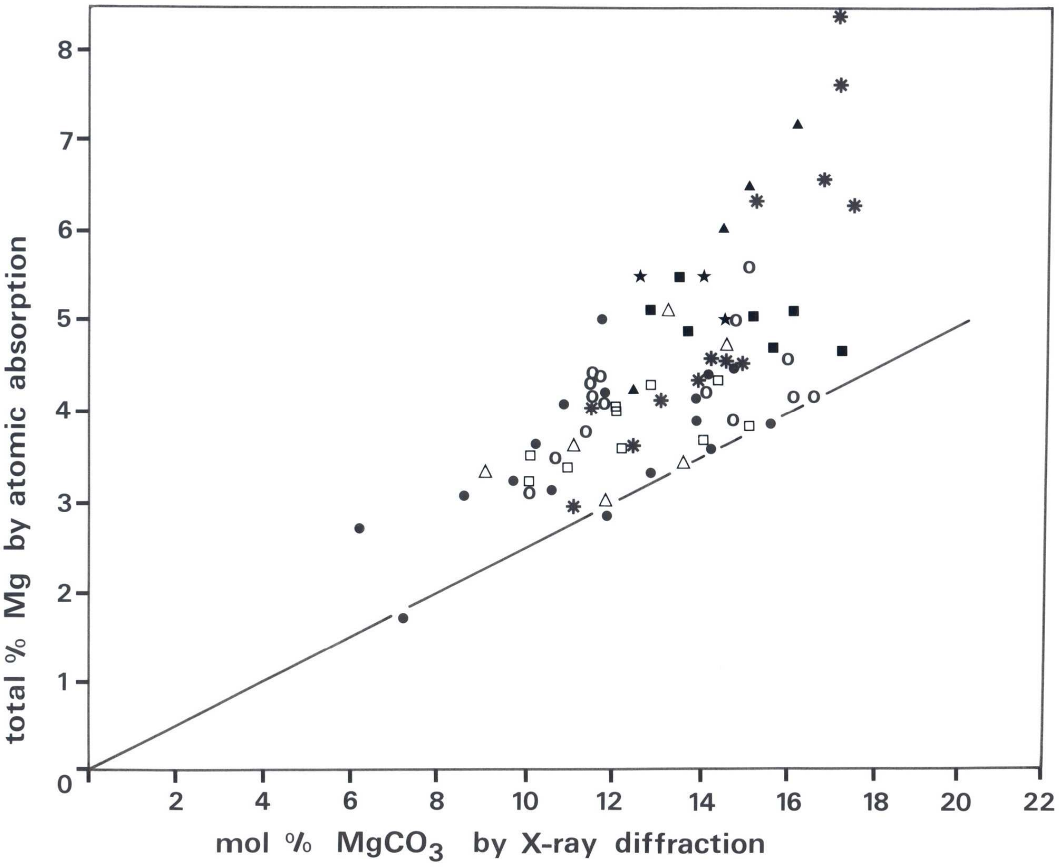


Fig.6 – Relations between mol % $MgCO_3$ as determined by X-ray diffraction (using the graph of Goldsmith & Graf, 1958 A) and percentage of $MgCO_3$ measured in atomic absorption spectrophotometry (after Milliman et al., 1971) (□ = Janita sp.; Δ = Corallina; ★ = Amphoroa; ● = Lithothamnium; **o** = Lithophyllum; ■ = Goniolithon; ▲ = Porolithon; * = others).

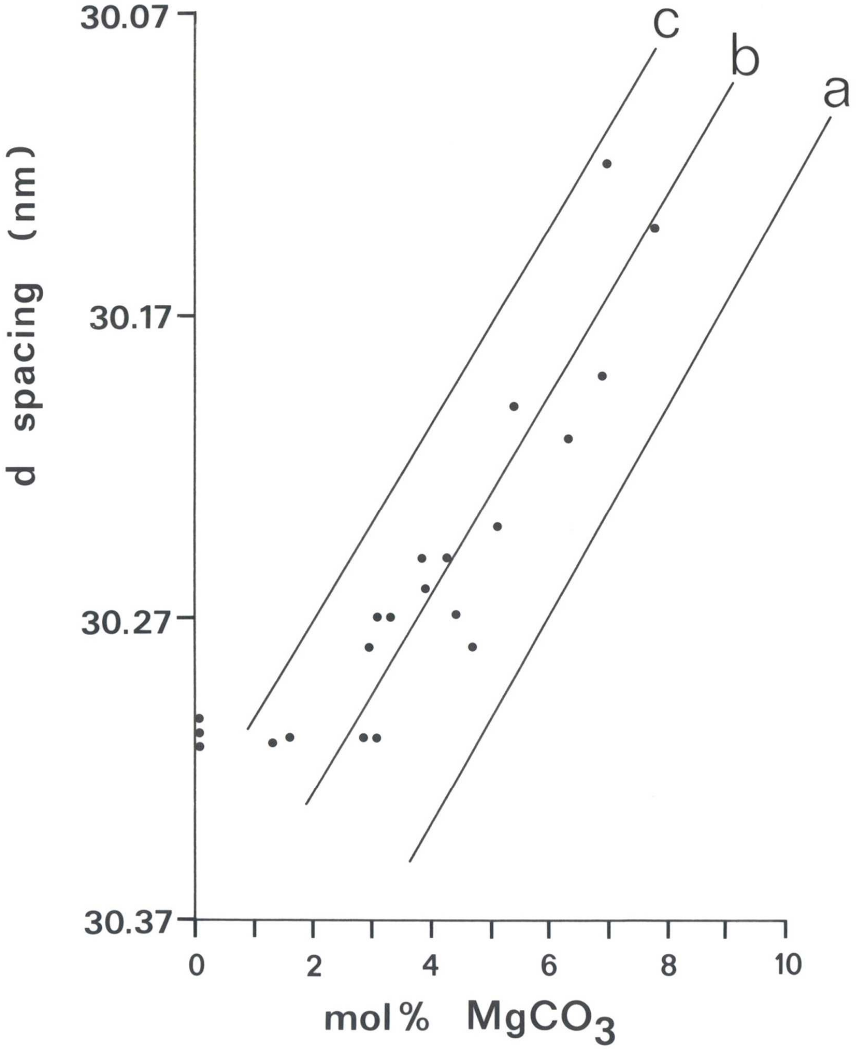


Fig.7 – Relations between mol percentage $MgCO_3$ incorporated in magnesium calcites and position of the main diffraction in X-ray analysis. Lines represent the linear relationships suggested by Chave (1952) (= A), Goldsmith et al. (1955) (= B), and Goldsmith & Graf (1958 A) (= C). Points represent analyzed samples of natural magnesium calcites (after Arnaud & Herbillon, 1973).

and the deviation from Vegard's Law must have crystallographic implications. In fact Harker & Tuttle (1955, p.277) have pointed out, that it is impossible "... to use the straight line between calcite and magnesite .. to determine the compositions of dolomite". The underlying crystallographic reason was, in the explanation of Harker & Tuttle (1955), that dolomite has at least two superstructure reflections and therefore belongs to space group $R\ \bar{3}$ and not to space group $R\ \bar{3}c$, as did calcite and magnesite. Dolomite has a crystallographic arrangement different from that of calcite and magnesite. This very same argument has been used by Goldsmith et al. (1955) to reject the use of the solid solution concept for the structure of the magnesium calcites by Chave (1952).[26]

Of special interest to the structural chemistry of the magnesium calcites is the observation made by Dodd (1967), that not all magnesium present in calcareous skeletons needs to be in the form of magnesium carbonate. Magnesium in the form of $Mg(OH)_2$ had been reported by Schmalz (1965) and Weber & Kaufman (1965) in the calcareous alga *Goniolithon*. "The presence of brucite in *Goniolithon* was suspected on the basis of the discrepancy between the Mg/Ca ratio in the crystal lattice as demonstrated by X-ray diffraction and the chemically determined Mg content. Such a discrepancy has commonly been noted....": Dodd (1967, pp.1314-1315). The same comparison between chemical analyses (in this case by way of atomic absorption spectrophotometry) and the percentages of $MgCO_3$ as measured by peak shift in X-ray diffraction has been made by Milliman et al. (1971). From a total of 59 samples of coralline algae between 76 and 83 % were found to contain more magnesium than that indicated by extrapolation of the X-ray data on the basis of the linear relationship postulated by Goldsmith & Graf (1958 B) (Fig.6). In addition Milliman et al. (1971) pointed out, that five different "linear relations" between peak shift and percentage $MgCO_3$ had been published: those of Chave (1952), Goldsmith et al. (1955), two by Goldsmith & Graf (1958 A) and one more by Goldsmith et al. (1961). The differences were considerable: for example a measured main peak (211) at 29.9 nm for a magnesium calcite, would give calculated percentages of $MgCO_3$ between 14.0 and 17.4 mol %, depending on which one of the "linear relationships" were used. The conclusions reached by Milliman et al. (1971) have received support from measurements made by Arnaud & Herbillon (1973); the latter two authors added an illustrative diagram (reproduced here as Fig.7). By way of combining data from X-ray analyses with microprobe analyses of 36 different dolomite samples Reeder & Sheppard (1984) found, that the assumed linear relationship between composition and lattice parameters breaks down in the case of dolomites with a nearly stoichiometric composition. In addition Reeder & Sheppard (1984) found X-ray diffraction unsuitable for the analysis of mixtures of crystals with different compositions. Reeder (1992, p. 386) observed: "Unfortunately, many dolomite compositions reported in the literature have been estimated from unit cell dimensions as determined by powder XRD. No independent calibration relating unit cell dimensions to composition has yet been established, and such correlations are made on the basis of assumptions." (As a consequence I will no longer use percentages $MgCO_3$ of magnesium calcites calculated by way of extrapolation from X-ray diffraction.)

More evidence concerning the discrepancy between the random model of a solid solution and the actual distribution pattern of $MgCO_3$ in Mg-calcites can be found in chemical analyses. In microchemical tests Dodd (1965), Weber (1969), and Macqueen et al. (1974) have shown, that the $MgCO_3$ content of biogenic magnesium calcites is not at all homogeneous. Additional observations by Towe (1967), who used electron microscopy to study Mg-calcite from echinoids, have revealed, that these magnesium calcites were not monocrystals, but consist of "... highly oriented polycrystalline aggregates". Towe argued, that mere examination with the light microscope will create the false impression that these Mg-calcites consist of a single crystal. But the markedly increased resolution of the electron microscope is capable of revealing the true nature of these mixed crystals. Moberly (1968, 1970) found inhomogeneities in microprobe analyses of the magnesium calcite of coralline algae on a micrometer scale, and attributed these inhomogeneities to changes in water temperature at the moment of formation. Mackenzie et al. (1983), using microprobe analysis, also detected a domain microstructure in biogenic Mg-calcites (from *Amphiroa* sp. and *Lithothamnium* sp.). In their electron microprobe studies Bischoff et al. (1983) noted domains (of about 10,000 nm width) containing markedly more $MgCO_3$ than the bulk of their biogenic Mg-calcite samples. By contrast Blake & Peacor (1981) could not find any such clear inhomogeneities in the columnals of the crinoid *Neocrinus blakei* when using microprobe analysis, but their single-crystal X-ray diffraction analyses of the same material indicated the existence of a mosaic texture of about 1 nm in size. Van Tendeloo et al. (1985) studied Mg calcite in electron microscopy and with electron diffraction, and found evidence of “ordered superstructures”. The composition of the magnesium calcite (54 mol % $CaCO_3$ + 46 mol % $MgCO_3$) was explained to have its origin in “… layers of additional Ca intercalated in the dolomite structure” (Van Tendeloo et al., 1985, p.333). In electron microprobe analyses of authigenic magnesium calcites from the Kattegat (Denmark) Jørgensen (1991) noted, that within individual crystallites the percentage $MgCO_3$ was not constant: the crystallites apparently were inhomogeneous. After using scanning electron microscopy, transmission electron microscopy and electron diffraction, Ma et al. (2008) concluded, that the magnesium calcite making up the teeth of a sea urchin (*Paracentrothus lividus*) consists of a polycrystalline assembly of misoriented nanocrystals (with a size of 10 to 20 nm). At the same time Ma et al. (2008, p.1556) found, how “… the lattice images of the single crystals do not show any obvious imperfections.”

Raman spectroscopy was applied by Bischoff et al. (1985) to magnesium calcites of two different origins; one set of samples was of biogenic origin, the others had been produced in high temperature / high pressure experiments (as described by Bischoff et al., 1983). Distinct differences in Raman spectra were found between these two groups: the biogenic Mg-calcites would show more positional disorder of the carbonate anion groups than the synthetic Mg-calcites. After subjecting inorganically precipitated Mg-calcite to scanning Auger microanalysis Mucci & Morse (1985) found inhomogeinity (or "patchiness") in the composition of the outermost layer and attributed it to an irregular growth process.

There are more examples of X-ray studies, which have supplied evidence on the inhomogeneous nature of the Mg-calcites. Although West (1937) had concluded, that the Mg-calcite of an echinoid spine would be a monocrystal, Garrido & Blanco (1947) and Nissen (1963) concluded from X-ray diffraction, that the magnesium calcite samples they had studied, consisted of an almost parallel array of tiny crystallites. Donnay & Pawson (1969) concluded from their X-ray diffraction studies, that various skeletal elements (such as plates, scales, valves, spines and ossicles) of a number of echinoids, sea cucumbers, sea stars and sea lilies were in fact single crystals with magnesium substituting for calcium in a homogeneous manner. But echinoid teeth and the teeth and the calcareous ring of a sea cucumber were seen to consist of a magnesium calcite in the form of a polycrystalline aggregate. Arnaud & Herbillon (1973) concluded from the "... broad and often asymmetrical peaks", that their Mg-calcite samples did not contain a constant amount of $MgCO_3$, but variable amounts instead. At the same it must be realized that anomalous X-ray diffraction phenomena such as exhibited by certain magnesium calcites, do not supply unequivocal evidence in support of a definite microstructure. Even so its significance to distinguish between solid solution and mixed crystal remains. As Fontaine (1966) pointed out, there are two theories to explain the occurrence of satellite reflections: the first theory postulates a periodic variation of composition about the mean c_o, with a wave length much greater than the mean interplanar spacing in the direction of

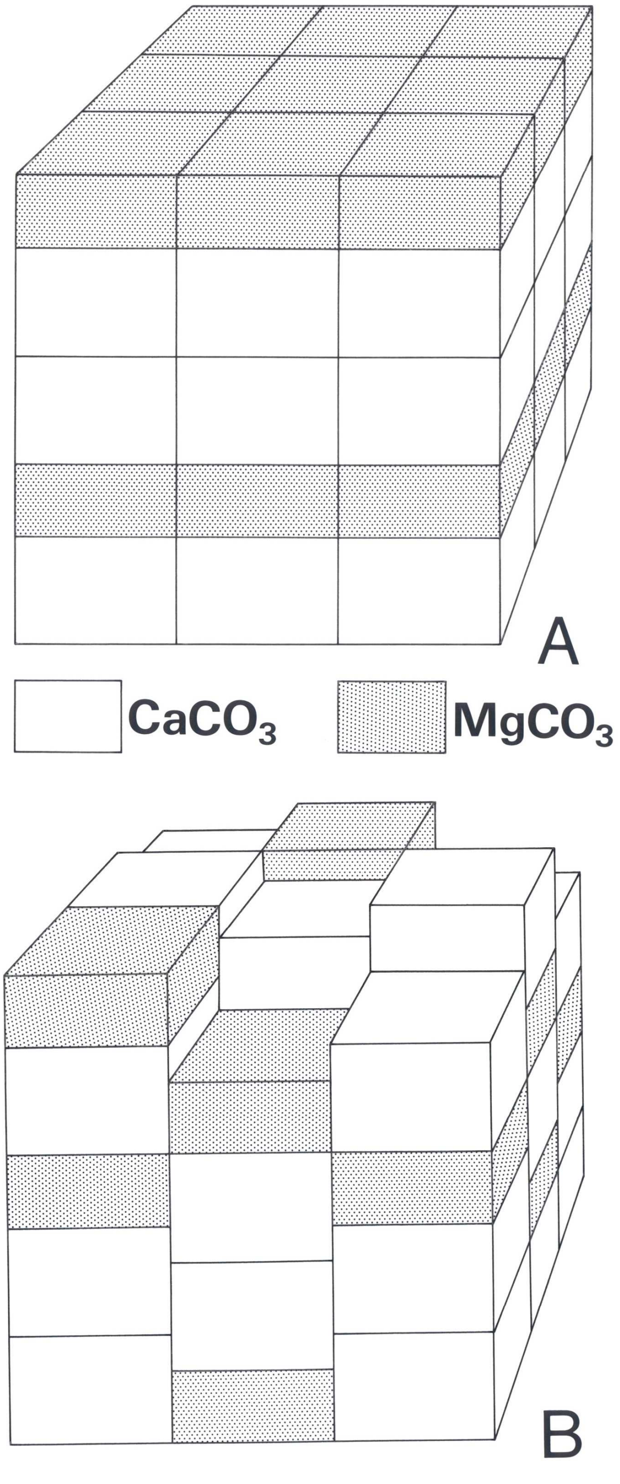


Fig.8 – Two different models of the structural chemistry of the magnesium calcites: A - stacking sequence of homogeneous layers of calcite and magnesite; B – “domain” structure consisting of an aggregate of highly oriented individual crystallites. (N.B. White and grey blocks are though to represent units larger than one molecule calcite or magnesite.)

the fluctuation (Daniel & Lipson, 1943, 1944; Hargreaves, 1951; Tiedema et al., 1957; Biedermann, 1960). The second theory explains anomalous diffraction by the occurrence of isolated fluctuations of composition, distributed at random in the untransformed matrix (Guinier, 1955; Hillert et al., 1961). In the view of Guinier (1964) peak broadening, without affecting the position of the peak itself, can only be explained by the occurrence of stacking faults in the lattice.

In particular calcareous algae appear to contain amounts of magnesium that will not show in X-ray diffraction (Goldsmith et al., 1955; Milliman et al., 1971). Comparison of wet chemical analyses with X-ray data of numerous Mg-calcite samples led to the conclusion, that these crystals may contain inclusions of very-high-magnesium calcite or even amounts of brucite (Schmalz, 1965; Weber & Kaufman, 1965; Milliman et al., 1971). Such comparisons show, like the direct observations by electron microprobe, that the mixed crystals known as magnesium calcites are by no means homogeneous as would be expected of solid solutions. Therefore doubt must be expressed concerning the claim, that magnesium calcites would consist of "... a single phase" (as Chave, 1952, p.190 had claimed). Because of the extent of these inhomogeneities, Bischoff et al. (1983) suggested, that X-ray data on Mg-calcites should be accompanied by atomic absorption measurements (or wet chemical analyses) giving the $MgCO_3$ content. The existing diagrams relating $MgCO_3$ percentages to d-spacings, were found not to give reliable results in the case of biogenic magnesium calcites.

After realizing, that the solid solution model can no longer be used to explain the structural chemistry of the Mg-calcites, a new model should be devised. That new model should not only account for the need to separate calcium and magnesium into monolayers (because of the size difference between the two cations), but it should also adequately explain the observed optical phenomena and the data from electron microscopy.

An irregular stacking sequence of calcite and magnesite monolayers leads to asymmetrical X-ray diffraction peaks. Not only in dolomites such asymmetrical peaks have been found (for example by Graf et al., 1957; Barber, 1977; Reeder & Wenk, 1979; and Reeder, 1981), but also in biogenic magnesium calcites (Milliman et al., 1971). Such an irregular stacking sequence of otherwise complete monolayers of calcite and magnesite (Fig.8 A) cannot explain the ultra small-scale variations in $MgCO_3$ content detected in microprobe analysis. Therefore a second structural model, featured here in Fig.8 B, is perhaps more adequate in explaining all of the details of the magnesium calcites. This second model consists in fact of a large number of individual crystallites, arranged into a ".. highly oriented polycrystalline aggregate". Model B of Fig.8 possesses in metallurgical terms a domain structure. The difference between the two models of Fig.8 is to be found in the arrangement of the calcite and magnesite layers in the *a-b* plane; an irregular stacking sequence in the direction of the crystallographic *c*-axis is shared by both. The proposed model (Fig.8 B) possesses *unit-cell order* but at the same time *lattice disorder* (in the definition of Megaw, 1960).

There are more aspects to the magnesium calcites that need revision. For example the direct relation between biological activity and nucleation of Mg-calcite suggested by Chave (1952) must be reconsidered.[27] Low-temperature syntheses of magnesium calcites in exclusively inorganic laboratory tests by Glover & Sippel (1967) make the suggestion untenable. In addition a large number of magnesium calcites has become known, that must have formed in nature in an inorganic manner. Eisenhuth (1902) described $MgCO_3$-containing calcites, occurring in metamorphic rocks. Recent Mg-calcites of inorganic origin have been found in deposits from the intratidal and supratidal environments by Friedman (1968), Lucia (1968), Alexandersson (1969), and Shinn (1969). Magnesium calcites of inorganic origin from beach rock deposits have been described for example by Friedman & Gavish (1971), Moore (1971), Moore & Billings (1971), Schmalz (1971), Taylor & Illing (1971), and Tietz & Müller (1971). Inorganic Mg-calcite occurring as a micritic cement in lithified carbonate sediments dredged from the deep sea has been described by among others Friedman (1964, 1968), Gervitz & Friedman (1966), Milliman (1966, 1971), Russell et al. (1967), Fischer & Garrison (1967), and Marlowe (1971 A).

CALCITE, ARAGONITE AND DOLOMITE

The question should be raised, why the incorporation of considerable amounts of $MgCO_3$ is restricted to calcite only and does not take place in the case of the two other polymorphs of calcium carbonate, aragonite and vaterite. This aspect of the polymorphism of calcium carbonate will be approached here by way of developing the historical perspective.

The definition of "a mineralogical species" by Haüy (1801) as a chemical compound with a molecular arrangement, that would distinguish itself from all other compounds,[28] led to a more or less general conviction among the mineralogists of that era, that one and the same chemical substance could occur only in one crystallographic form. However there were two substances, calcium carbonate and titanium dioxide, that showed a behavior contradicting the postulated "uniqueness of every chemical compound". In particular the chemical composition of aragonite, as compared to that of calcite, gradually became the subject of lengthy discussions.

Aragonite (or as it was originally named *arragonite*: see for example Dana, 1844) had been described by Romé de l'Isle (1783) as a mineral from the Aragon region in Spain. Chemical analyses by Klaproth (1788) showed the aragonite to consist of carbon dioxide and calcium oxide. Klaproth (1788) was quite explicit regarding his observations: the analyses had shown, that aragonite was different from calcite only in its crystallographic form, not in its chemistry.[29] In other words the first basic knowledge of the phenomenon of polymorphism had been gathered by Klaproth in 1788 on the aragonite-calcite system. The all too obvious differences between the chemical analyses of Klaproth (1788), which received support in the form of analyses by various other scientists, and the dogma of the *molécules intégrantes* of Haüy inevitably had to lead to a serious controversy. Based on additional analyses, numerous mineralogists (among them De Fourcroy & Vauquelin, 1804; Proust, 1806; and Thenard & Biot, 1807) all had to arrive at the conclusion reached by Klaproth: aragonite and calcite were in fact one and the same chemical substance. This conclusion, clearly formulated for example by Berthollet (1803), was rejected by Haüy (1808). The presence of strontium, magnesium, iron oxide, and manganese oxide in aragonite was according to Haüy convincing evidence against the suggested parallel with calcite. Stromeyer (1813) stated to have found in his analyses, that aragonite always contained a certain amount of strontium carbonate.[30] This strontium carbonate would be responsible for the crystallization of calcium carbonate in the form of aragonite instead of calcite.[31] Even very low concentrations of strontium would lead to the formation of aragonite. The suggestion was contradicted to a certain extent by the discovery of Laugier (1814) and Bucholz & Meissner (1815), that strontium-free and strontium-containing aragonites were fully comparable, if not identical. Vauquelin (1814) remarked, that strontium was present in aragonite presumably only as an impurity. The description of the crystal form of strontium carbonate by Gehlen (1814) added a new aspect to the discussion: strontianite was found to be crystallographically identical with aragonite. The discussion as such was to come to an end soon after the discovery of the general principle of polymorphism by Mitscherlich (1819, 1820, 1821). In experiments Mitscherlich had been able to show, that one and the same chemical compound could crystallize into two (or even more) different crystal forms.[32]

After Mitscherlich had shown the existence of polymorphism in well-defined laboratory tests, such experiments were also carried out with calcium carbonate. Rose (1837) demonstrated, that calcite precipitates from a pure calcium bicarbonate solution when the solution is cold (or at room temperature), and that aragonite crystallizes from such a solution at a temperature of 333 K or higher. Numerous scientists have studied the effect of temperature on the calcium bicarbonate solution. The observations of Rose (1837) were essentially confirmed by Vater (1899), Foote (1900), and Faivre (1946). The observation made by Rose (1861) on the simultaneous deposition of aragonite and calcite in one and the same calcium bicarbonate solution being heated (aragonite would float the surface, and calcite would be seen to adhere the walls of the glass beaker), cannot be explained in terms of temperature alone. Perhaps a role is being played by the nature of the substratum. The tests of Vetter (1910) could not reveal any possible influence of the substratum. In those experiments air was bubbled through calcium bicarbonate solutions kept at temperatures between 273 and 291 K. In all these tests calcite would nucleate, even when small amounts of aragonite crystallites had been added. Only when the calcium bicarbonate solutions were heated to at least 302 K, aragonite would nucleate. A somewhat different temperature for this boundary for the nucleation of pure calcite has been reported by Kohlschütter & Egg (1925): in their paper the transition temperature was given as 294 K.

Obtaining calcite from a calcium bicarbonate solution is not only dependent on the temperature. Rose (1860) noted that the concentration of the solution is a factor of importance too. From dilute calcium bicarbonate solutions calcite was seen to nucleate, and from the more concentrated solutions mainly aragonite would form. Enhanced removal of carbon dioxide, by way of stirring or by bubbling air through the solution, increases the yield of calcite (Stumper, 1935). Crystallization of calcite from a calcium bicarbonate solution at 298 K could best be attained, according to Radcewski et al. (1940), by lowering the pressure above the solution.

The nucleation of $CaCO_3$ polymorphs depends as well on the presence of certain cations in the solution. Observations on the phenomenon, in this case of strontium ions favoring the nucleation of aragonite, were made by Stromeyer (1813), Rose (1837), and Credner (1870). It has been noted by Cornu (1907), Leitmeier (1909, 1910 A) and Vetter (1910), that the presence of magnesium chloride or magnesium sulfate leads to aragonite nucleation. The presence of potassium carbonate in solution also favors the nucleation of aragonite (Johnston et al., 1916; Bäckström, 1921; Buchan, 1927). Much the same influence is exerted by lead salts in solution (Credner, 1870), and by barium salts in solution (Bauer, 1890). Concerning the possible effects of calcium sulfate on the formation of calcium carbonate polymorphs, the views are somewhat diverging. Becquerel (1852) as well as Credner (1870) stated that the presence of gypsum would facilitate aragonite nucleation, but Vetter (1910) maintained that it would exert little or no influence. The same would be true for small amounts of sodium chloride, potassium chloride, ammonium chloride and ammonium sulfate according to Vetter (1910). But a mixture of salts resembling in its composition the dissolved salts of sea water,[33] would certainly favor aragonite crystallization at temperatures of 293 K and more (Vetter, 1910). At temperatures between 273 and 291 K a bicarbonate solution on the basis of that artificial sea water would give rise to calcite, vaterite, or even $CaCO_3.6\ H_2O$.

The relations between polymorphism and crystal growth are of special interest with regard to the low-temperature nucleation of dolomite. The mineral dolomite consists of an alternation between calcite and magnesite monolayers. It seems likely therefore, that dolomite will nucleate under conditions favoring the nucleation of calcite. If aragonite or vaterite would be formed, no incorporation of major amounts of magnesium carbonate can take place. No incorporation of $MgCO_3$ into aragonite or into vaterite is known to such an extent as to create a mixed crystal. Of special interest in this regard is the observation made by Waskowiak (1962) on the distribution of $MgCO_3$ in shells of lamellibranchiata of the genus *Mytilus*. These shells are dimorphous, containing layers of calcite alternating with layers of aragonite. In the calcitic prism layer the magnesium carbonate content was found to be 10 to 30 times as high as that in the mother of pearl layers consisting of aragonite (Waskowiak, 1962). In laboratory cultivation of *Mytilus edulis* Lorens & Bender (1980) noted, how the magnesium calcite of its shell will incorporate the more Mg^{2+} the higher the magnesium content of the medium. But after reaching a maximum concentration, no more Mg calcite will be formed: from then on only aragonite is being precipitated in the shell.

In numerous studies in which chemical analyses of aragonite were made, significant amounts of incorporated $MgCO_3$ have not been measured. Clarke & Wheeler (1922), after analyzing numerous skeletal carbonates, concluded that in contrast to calcite, aragonite usually contains less than 2 mol % $MgCO_3$. Similarly Bøggild (1930) had found little or no $MgCO_3$ in the aragonite of mollusc shells. Much the same observation has been made by Linck (1937), not based on the analysis of natural carbonates, but on laboratory tests. All of these observations have essentially been confirmed by Chave (1954 A), who could not measure more than 1.5 mol % $MgCO_3$ in aragonite of biogenic origin. But Krinsley (1960) claimed to have found "magnesium aragonite". The magnesium content of the aragonite in certain gastropods would be quite high during the lifetime of these organisms, and the magnesium would disappear rapidly from the calcium carbonate as soon as the organism had died. It is significant to note, that the aragonite of the living gastropods contained a maximum of only 780 ppm $MgCO_3$ (Krinsley, 1960). Because of these extremely low amounts,[34] it may well be concluded, that "... most natural aragonites are practically free from magnesium" (Lippmann, 1973, p.197).

Lacroix (1898) had introduced the word *ktyptéit* for a possible third polymorph of calcium carbonate. Vater (1902), while studying the *Sprudelsteine* from Karlsbad (the present-day Karlovy Vary, Czech Republic) noted, that not only aragonite was present in these spherulites, but that a third modification of $CaCO_3$ could be discerned. But Vater (1902) hesitated to describe the unknown phase as *ktyptéit*. It was Meigen (1911), who defined the new mineral, and named it after H. Vater. The discovery of this third polymorph of calcium carbonate in nature has been confirmed for example by Johnston et al. (1916), Rinne (1924), Heide (1924), Von Olshausen (1925), McConnel (1960) and Bentor et al. (1963). Papers describing vaterite (e.g., Meigen, 1911; Johnston et al., 1916; Rinne, 1924; Heide, 1924; Von Olshausen, 1925; Mayer & Weineck, 1932; and Flörke & Flörke, 1961) have not revealed any incorporated $MgCO_3$. Especially the observations by Vater (1897), on the formation of vaterite in a calcium bicarbonate solution containing 0.085 g $MgCO_3$ per dm^3 , are noteworthy in this respect. No $MgCO_3$ at all was found by Vater (1897) upon chemical analysis of the thus formed third modification of $CaCO_3$.

DISCUSSION

Dolomite is not only a mixed crystal containing approximately equal amounts of $CaCO_3$ and $MgCO_3$, but it is also a crystal with a layer lattice. Monolayers closely resembling calcite alternate with monolayers closely resembling magnesite in a 1 : 1 sequence in the direction of the crystallographic *c*-axis. Numerous authors have confirmed Bragg's (1914 A,B) model for the structure of dolomite. The interpretation of dolomite as a superlattice was established not only by way of X-ray diffraction. In direct optical observation by way of high-resolution microscopy this fundamental model for the lattice of dolomite has been confirmed. It is surprising to note, that dolomite unites in its lattice two such contrasting compounds as calcite and magnesite. Investigations by Retgers (1891) have shown, that it will be difficult to maintain, that dolomite is part of a continuous series of mixed crystals ranging in composition from that of calcite up to that of magnesite. As Retgers pointed out, the differences between calcium and magnesium are such, that the existence of a continuous series of mixed crystals will be effectively excluded. Redlich (1917) stressed the observation that although calcite and magnesite are isomorphic, only a limited miscibility exists between the two.[35] In other words there is no real solid solution between calcite and magnesite at low temperatures; not in the case of dolomite, and not in the case of the magnesium calcites. Chemical analyses performed on magnesium calcites have shown that no simple linear relation exists between the percentage of incorporated $MgCO_3$ and the position of the main diffraction peak of such magnesium calcites (Milliman et al., 1971; Arnaud & Herbillon, 1973). The theory claiming linearity between lattice parameters measured in X-ray diffraction and the percentage of $MgCO_3$ has been refuted on crystallographic grounds (Zen, 1956). Because of the structural relationship between dolomite and the magnesium calcites, the same conclusion must be drawn for dolomite. Essene (1983) as well as Reeder & Sheppard (1984) have stressed, that there is no longer any justification for "reading" the percentage $MgCO_3$ from a line drawn between the d-spacing of calcite and the corresponding one of dolomite.[36] For magnesium calcites as well as dolomite the percentage of $MgCO_3$ should be measured in a direct way by chemical analysis, and not in an indirect manner such as X-ray diffraction. Alternatively Reeder & Sheppard(1984) suggested to calculate lattice parameters after X-ray analysis of dolomite samples: "... better precision is obtained by refining lattice parameters since random error is minimized by the least-squares method and calculated standard errors give an indication of the uncertainty of the measurement" (Reeder & Sheppard, 1984, p.526). After plotting a multitude of electron microprobe analyses of various dolomite samples into a histogram, Searl (1994) observed the absence of any continuous gradient; yet another proof of the non-existence of a solid solution. The histogram of mol percentage magnesium carbonate found in the analyses by Sperber et al. (1984) shows much the same discontinuity. Behavior according to the solid solution model would imply a continuous range of compositions. Even in samples of calcite with only small amounts of $MgCO_3$ the solid solution model could not be found: there too the discontinuous mode of compositions was measured. The discontinuous distribution pattern found may well be related to strain release upon the formation of evenly spaced monolayers of calcium and magnesium cations. Intralayer cation ordering will increase dolomite stability even at intermediate levels of $CaCO_3$ - $MgCO_3$ stoichiometry. Searl (1994) claimed, that calculations had shown the impossibility of replacement.[37] The overall distortion associated with the substitution of Ca^{2+} into Mg^{2+} sites, would exceed by far the energy of ordering (Searl, 1994).

The crystallographic structure of dolomite forms a convincing argument against any theory of "dolomitization", based as it is on the supposed replacement of calcium cations by magnesium. During such an assumed secondary conversion of calcite specific calcium cations would have to be exchanged, and others not. The process would have to involve an atomic selection mechanism not yet known. The model calculations performed by Möller & Rajagopalan (1972) illustrate, that the separation of Ca^{2+} and Mg^{2+} into individual monolayers in between sheets of carbonate anion groups is a structural necessity. Random substitution of calcium by magnesium is not possible, because the small magnesium cation would initiate rotation and tilting of neighboring carbonate groups. Such a disruption of the calcite lattice will not take place, when an arrangement in the form of layers has been attained. In dolomite this layer arrangement has reached a superstructure status: calcite and magnesite alternate in individual monolayers. Another anhydrous Mg/Ca carbonate that possesses such a layer lattice is huntite. Considering dolomite as the 1 : 1 superlattice, huntite would be the 1 : 3 superlattice of calcite and magnesite. Such a superlattice with a higher zone number would in general possess a lower stability than the superlattice with the lower zone number (Hume-Rothery & Raynor, 1962).

The question could be raised, why dolomite crystallizes in each and every instance with the exact 1 : 1 ratio between calcite and magnesite. When trying to answer this question, it must be realized, that only an anhydrous Mg/Ca carbonate with exactly this 1 : 1 superlattice can ever be recognized as being dolomite. By definition any other Mg/Ca carbonate that lacks the 1 : 1

superlattice (and its inherent extra superstructure reflections in X-ray diffraction) cannot be described as dolomite. Close inspection of dolomite does indeed show evidence, that not in all cases the strict 1 : 1 ratio need be maintained. In a multitude of chemical analyses it has been found, that deviations from the composition of "pure dolomite" do occur. Even when accepting the determinations of "pure dolomite" given in early papers (and as stated before the definition of the mineral dolomite is not founded solely on chemical analysis), the variations in amounts of $CaCO_3$ and $MgCO_3$ remain undeniable. To dolomites with amounts of calcium carbonate and magnesium carbonate other than that present in pure dolomite, $CaCO_3.MgCO_3$, Dalton's Law of Multiple Proportions (Dalton, 1808) cannot be applied. Prerequisite is, that the chemical compound under discussion is *homogeneous*. Before applying stoichiometry to chemical compounds, it is necessary to verify the homogeneous character of the compound involved, as for example Richter (1792) and Berthollet (1803) have pointed out. Retgers (1891) investigated this requirement in the case of the structural chemistry of the anhydrous calcium-magnesium carbonates, but the optical analyses of his time were restricted to light microscopy.

Inhomogeneity in dolomites has been revealed by Graf et al. (1957), who described stacking faults in dolomite on the basis of X-ray analysis. Direct evidence on stacking faults has meanwhile been obtained in electron microscopy. The electron microscope has made it possible to follow up Retgers' (1891) suggestion to use optical means to study the structure of a mixed crystal and so determine, whether the random arrangement typical of a solid solution, the alternating monolayer arrangement characteristic of a superlattice, or a mixed crystal with domain structure (typical of unmixing effects) exists. The solid solution model does not apply to the anhydrous Mg/Ca carbonates, as for example Retgers (1891) and Zen (1956) have noted. Application of electron microscopy has revealed inhomogeneities on a nanometer scale; but such inhomogeneities were found to be restricted to magnesium calcites and those varieties of dolomite, that are known as calcium-rich dolomite or "protodolomite". It was Reeder (1992), who made the fundamental observation, that stoichiometric dolomite is devoid of all of the microstructures, which are found in the calcium-rich dolomites and the magnesium calcites. Only in the case of a regular superlattice the conditions favor a stoichiometric composition of the crystal as a whole. In a mixed anhydrous Mg/Ca carbonate with domain structure amounts of calcium carbonate and of magnesium carbonate can be found, that are different from the molar fractions in pure $CaCO_3.MgCO_3$.

The basic observation made by Retgers (1891), that calcium and magnesium cations are much too different to form a solid solution, equally applies to the structure of those mixed crystals, which are known as the magnesium calcites. The publication by Chave (1952) actually shows that a linear relation between the percentage $MgCO_3$ and the d-spacings of the lattice does not exist (contrary to the suggestion of Chave himself). The absence of such a linear relation finds its origin in the fact that the magnesium calcites do not consist of a solid solution. All too often the structural model of a solid solution for mixed crystals postulated by Vegard & Shelderup (1917) on the basis of early X-ray studies is still being followed. In (micro-) chemical analyses the inhomogeinity of mixed crystals such as the magnesium calcites has meanwhile been demonstrated. Papers by Towe (1967), Moberly (1968, 1970), Blake et al. (1982, 1984), Bischoff et al. (1983), Given & Wilkinson (1985), Humphrey & Radjef (1991), Tsipursky & Buseck (1993), and Ma et al. (2008) have revealed the significance of the claims of Garrido & Blanco (1947) and Nissen (1963), that Mg-calcites consist of "... highly oriented polycrystalline aggregates" (as Towe, 1967, p.1048 defined it). Through the use of X-ray diffraction, electron microprobe analysis and high-resolution transmission electron microscopy on spines and skeletal plates of two species of sea urchins (*Strongylocentrotus franciscanus* and *Strongylocentrotus purpuratus*) Tsipursky & Buseck (1993) gathered evidence on the existence of mosaic structures in magnesium calcite. Numerous coherent and complex incoherent boundaries between slightly misoriented mosaic blocks were observed. "Most of these defect zones contain dislocations that relieve stresses in the structure": Tsipursky & Buseck, 1993, p.781).

In calcium ankerites, mixed crystals that are comparable to the magnesium calcites in that part of lattice sites of magnesium is occupied by iron (II), rod-shaped variation within the crystallites has been found (Reksten, 1990 A). The elongated domains within the lattice were interpreted by Reksten (1990 A) to be the result of the growth process itself. "From a crystallographic point microcellular growth is a reasonable model. The rods are normal to the $\{10\bar{1}4\}$ growth bands, which are really fossil growth surfaces, and which occur commonly on crystals of dolomite": Reksten (1990 A, p.500). Even in virtually pure calcite crystals containing only very small amounts of Fe, Mg, or Mn, such superstructures have been found (Reksten, 1990 B).

The model presented here as an alternative explanation for the structural chemistry of the magnesium calcites, is presumably somewhat more complex than outlined. For, as Fouke & Reeder (1992) pointed out, growth surfaces may well lead to differences in the degree of incorporation of cations such as Mn^{2+} , Fe^{2+} , and Mg^{2+} . In transmission electron microscopy as well as in cathodoluminiscence microscopy such differences have been detected: different growth rates on the different faces of zones $\{10\bar{1}4\}$ and $\{10\bar{1}1\}$ must have been responsible for differences in the amount of cations other than Ca^{2+} . The phenomenon of sector zoning ("Sectoral zoning results when elements are incorporated in different concentrations on nonequivalent faces during crystal growth": Fouke & Reeder, 1992, p.4015) has been described from dolomite (Reeder & Prosky, 1986; Searl, 1994) as well as calcite (Reeder & Paquette, 1989; Paquette & Reeder, 1990). According to Morse & Bender (1990) cation partitioning finds its origin in differences among the growth rates of the different zones of a crystal; in general nonequivalent zones possess different growth rates and therefore the adsorption of cations other than calcium also varies. "These observations raise the interesting idea, although speculative, that the nature of the growth mechanism may be an important factor controlling the range of Ca:Mg ratios observed in dolomite": Fouke & Reeder (1992, p.4023).[38]

The structural model for the magnesium calcites as mosaics or polycrystalline aggregates may well be the only one to explain the observations on dolomite/Mg-calcite intergrowths by Land & Epstein (1970). In skeletons of red algae from a reef in Jamaica, dolomite was found intergrown with Mg-calcite in such a way, that the orientation of the *c*-axes of both dolomite and Mg-calcite was identical. Not as much as an assumed replacement reaction changing Mg-calcite into dolomite,[39] but instead the similarities between the lattices of dolomite and that of the Mg-calcites within the *a*-*b*-plane are responsible for this type of paragenesis. It is the stacking sequence within the direction of the crystallographic *c*-axis, which distinguishes dolomite from the magnesium calcites. Only in dolomite monolayers are to be found. In the magnesium calcites out-of-step domains have formed in order to accommodate the excess of calcium carbonate over magnesium carbonate. It is this structural relationship, which governs the close mineralogical relations between Mg-calcite and dolomite. A comparable observation has been made by Richter (1974 A) on dolomite occurring in the magnesium calcite of echinoid skeletons in Recent carbonate sediments of Greece. Lohmann & Meyers (1977) described micron-sized dolomite crystallites in crystallographic continuity with the surrounding calcite crystals. Using single crystal X-ray diffraction, Blake et al. (1982) observed alternations on a micro-scale between dolomite and magnesium calcite in fragments of fossil crinoid spines. In this case too the intergrowth was such, that the two were in "... perfect crystallographic registry" (Blake et al., 1982, p.61), i.e., the intercalations between dolomite and magnesium calcite took place in the direction of the crystallographic *c*-axis. Using various techniques of electron microscopy Wenk et al. (1993) observed how ordered dolomite occurred intergrown on a submicron scale with a disordered calcium magnesium carbonate. The calcium magnesium carbonate had a composition of 70 mol % $CaCO_3$ and 30 mol % $MgCO_3$ and showed a heterogeneous microstructure, much like the ordered dolomite ($Ca_{0.54}Mg_{0.46}CO_3$). The latter revealed in electron microscopy "... a well-developed, planar, modulated structure" (Wenk et al., 1993, p.770); electron diffraction showed it to be ordered. But the magnesium calcite was seen to be "grading into" the dolomite: within the magnesium calcite spherical domains (of about 2 to 10 nm in diameter) of dolomite were detected (in electron diffraction the ordering of this dolomite was established). Somewhat surprisingly Wenk et al. (1993) found most of the magnesium calcite from the Abu Dhabi sabkha sediments to be fairly homogeneous, but "... in some areas there are considerable distortions due to internal strain and misorientations of small domains" (Wenk et al., 1993, p.772): in those instances a mosaic structure was found.

Much like Graf et al. (1967), Müller & Wagner (1978), and Nordeng & Sibley (1994), Drits et al. (2005) had to conclude, that non-stoichiometry of dolomite cannot be explained in terms of “a solid solution”, instead a mixed-layer model with random stacking sequences was proposed.[40]

The structure of the Mg-calcites as polycrystalline aggregates implies, that these mixed crystals, in so far that these can be recognized as individual crystals, are by no means homogeneous. As a consequence it will be virtually impossible to assign to these crystals one definite value for their "solubility" (or "activity"). The observation made by Doelter & Hoernes (1875), that the dissolution behavior of dolomite reflects the structural chemistry, can be applied equally to the magnesium calcites. The difficulties encountered, when trying to explain the low-temperature dissolution behavior of magnesium calcites in terms of a homogeneous solid solution,[41] have been illustrated in the discussion between Thorstenson & Plummer (1977, 1978), Lafon (1978), Garrels & Wollast (1978), Berner (1978), Lahann & Siebert (1982), Lippmann (1982), and Koenigsberger & Gamsjäger (1992). Perhaps the problems described, will be placed in a different light when realizing, that the magnesium calcites should be considered as polycrystalline aggregates lacking a constant chemical composition. Even when considering magnesium calcites simply as mixed crystals, no definite solubility can be attributed. As Tammann & Krings (1923) stated, the absence of any measurable degree of diffusion between the two different components of such a mixed crystal prohibits the possibility to define equilibrium between the solution and these two components. As a consequence the definition of a specific "solubility" cannot be applied to the magnesium calcites.[42]