"DOLOMITIZATION" RECONSIDERED

(1.1) "Pourquoi créer dès alors cette hypothèse gratuite de la dolomitisation des calcaires ? ... N'y a-t-il pas assez déja des mystères réels de la nature ?": Delanoüe (1854, p.493).

(1.2) The definition of diagenesis given by Walther (1894) included the following phenomena: compaction, increase in hardness, occurrences of concretions, desalination of marine sediments, disappearance of organic matter, newly formed minerals, displacement of the molecules, formation of accessory minerals, cementation, reduction of pore space, chemical changes directly or indirectly caused by organisms such as the formation of sulfides, phosphates, chemical concretions, manganese- and iron concretions, coloring by iron oxides, deposition of silica as a cement, formation of new minerals such as hornblende, gypsum, coelestine, anhydrite, processes in the formation of coal, deposition of calcium carbonate, formation of chert nodules, and certain processes in volcanic deposits: crystal growth in lava's and changes in tuffs, as well as the hardening and leaching of tuffs.

(1.3) "By metasomatic exchange is meant an interchange of substance, without necessarily involving, as does pseudomorphism, the preservation of the original form of the substance replaced or even of its orginal volume": Emmons (1886, p.565).

(1.4) "Diese Quellen haben den Dolomit gebildet, nicht dadurch, dass sie unmittelbar kohlensaure Magnesia, die sie in aufgelöstem Zustande aus der Tiefe heraufgebracht, abgesetzt haben, sondern dadurch, dass ihr kohlensaurer Kalk die Magnesiasalze des Seewassers decomponirt hat. Schon die Kugelform, welche der Faxödolomit immer annimmt, ist ein Beweis für die Bildung desselben durch Quellen": Forchhammer (1849, pp.57-58).

(1.5) "Combiniren wir alle diese Verhältnisse, so wird es sehr wahrscheinlich, daß Kalksteine, wenn sie wenig oder keine Silicate enthalten, aber reich an Magnesia sind, durch Auslaugen des grössten Theils ihres kohlensauren Kalks an Ort und Stelle in Dolomite umgewandelt werden können": Bischof (1855, Bd.II, Abth.2, p.1178) and concerning the formation of dolomite itself: "Dieser Neigung ist es auch zuzuschreiben, daß sich, wenn Magnesiacarbonat haltende Gewässer den Kalkstein in Dolomit umwandeln, die ausgeschiedene neutrale kohlensaure Magnesia mit dem kohlensauren Kalke zu diesem Doppelsalze verbindet, und dagegen Kalkcarbonat vom Wasser aufgenommen wird": Bischof (1855, Bd.II, Abth.2, p.1136).

(1.6) Hoppe-Seyler (1875) pointed out, that although Bischof (1855) had claimed dissolution of pre-existing limestones to be the main process of dolomite formation, the experiments by Von Gorup-Besanez (1872) had demonstrated this to be an impossibility ("... weder die Versuche von Sterry Hunt [1859, 1866], noch die Combinationen von G. Bischof [1855], noch endlich die Erwägungen von Th. Scheerer [1866] geben eine ausreichende Erklärung, und neuerdings hat Gorup-Besanez [1872] überzeugend nachgewiesen, daß an eine Bildung von Dolomit durch Extraction magnesiumhaltigen Kalksteins durch Bodenwässer, einen Process, den Bischof [1855] hauptsächlich zur Erklärung der Bildung von Dolomit aus magnesiumhaltigen Kalkstein benutzen zu können meinte, nicht zu denken ist": Hoppe-Seyler, 1875, p.497).

(1.7) "Kaum kann es einen bündigeren Beweis dafür geben, daß bei der Umwandlung des Kalksteins in Dolomit große Quantitäten Wassers das Gestein durchdrungen haben, als dieses Verschwinden der Kalkschalen im Gegensatze der Erhaltung derselben in Kalksteinen": Bischof (1855, II, 2.Abt., p.1143).

(1.8) After describing the dissolution process, Bischof (1855, II, 2.Abt., p.1143) continued: "Und so fordert es der Umwandlungsprocess, mag er durch Austausch gegen kohlensaure Magnesia oder durch blosses Auslaugen des kohlensauren Kalks vor sich gegangen sein".

(1.9) "Ich habe auch experimentell gefunden, dass mit Kohlensäure gesättigtes Wasser aus einem Thonmergel von Upsala mit ungefähr 18 % $CaCO_3$ und 1,3 % $MgCO_3$ nur Spuren des letzteren auslöste, während von dem ersteren beinahe die Hälfte ausgelaugt wurde": Högbom (1894, p.266).

(1.10) "The mechanism by which the dolomite is formed may need some explanation, since calcium exceeds magnesium in both the water-soluble salts and exchangeable cations. The soils of this area receive most of their precipitation during very short intervals of the year. Each year these soils become very dry, often to the extent that they show wide and deep cracks. During these periods of drought the salts are brought toward the surface by capillary rise of water. In the process of drying, much of the calcium salt is precipitated at lower levels, while the magnesium salt, owing to its higher solubility, remains in solution. At such periods the soluble magnesium may exceed the soluble calcium and thus create conditions favourable to the formation of dolomite by the action of magnesium sulphate on calcium carbonate": Sherman et al. (1947), pp.42-43.

(1.11) On more than one occasion this particular synthesis of dolomite has been attributed to Favre. However the text of Favre's (1849 B) paper is quite clear in pointing out, that it really was Marignac, who had conducted this experiment: "Cette note a pour objet des observations géologiques combinées avec une expérience que M. le professeur Marignac a bien voulu faire" (Favre, 1849 B, p.318).

(1.12) "Es ist wohl begreiflich, daß dieser Porphyr unter der bedeckenden Masse sich nur selten hervordrängen kann, daß er vielleicht an manchen Gebirgsreihen gar nicht hervorkommt, und sein Daseyn nur aus seinen Wirkungen geschlossen werden muß": Von Buch (1822 A, p.133).

(1.13) Von Buch (1822 A) was not quite sure, in what form the magnesium had been supplied from the augite porphyry to the pre-existing limestone. At one point he mentioned, that this magnesium would have been supplied as magnesium oxide ("Talkerde"), at another that the magnesium had possibly been supplied in the form of a vapor ("gasförmige Talkerde"). In a third case Von Buch proposed, that it had been in the form of magnesium carbonate (e.g.: "Diese vorausgehende Zerreissung und Zerklüftung ist es also, welche der kohlensaure Magnesia aus dem innern die Wege eröfnet, bis in das Tiefste und Verborgenste der Schichten des Kalksteins zu dringen, sich überall mit der kohlensauren Kalkerde zu verbinden, und eine neue Substanz, den Dolomit zu bilden...": Von Buch, 1822 A, p.116). No doubt could exist according to Von Buch (1822 A) as to the ultimate origin of the magnesium: it must have been supplied by the intrusion of porphyry ("... dieser Augith-Porphyr sey es eigentlich, der auf die Schichten des dunkelgefärbten, dichten Kalksteins einwirkend, sie entfärbt, Versteinerungen und Schichten vernichtet, mit Talkerde die Masse durchdringt, sie dadurch zu körnigem Dolomit umändert.", Von Buch, 1822 A, p.114). Even so Von Buch (1823) frankly admitted, that he did not know, how this conversion of a limestone into dolomite could have taken place: "Comment se fait-il que la magnésie puisse percer, traverser, changer la nature de couches calcaires qui ont plusieurs milliers de pieds de hauteur, pour en former une roche uniforme dans toute son étendue ? C'est une question que je me suis proposée dans toutes mes courses aux environs de la vallée de Fassa, sans en trouver la solution": Von Buch (1823, p. 296). Berzelius (1825) commented in his *Jahres-Bericht*, that the suggestion made by Von Buch concerning the conversion of pre-existing limestones into dolomite was nothing but speculation: "Ueber diese Vermuthung läßt sich kein Urtheil fällen, und sie gehört zu den Auswegen, die man bisweilen einzuschlagen verleitet wird, wenn man den Wegweiser der Erfahrung auf dem Felde der Speculation verliert, oder er zu weit abgeschieden steht" (Berzelius, 1825, p.253).

(1.14) "Und darum führt uns Alles auf den Gedanken, daß der Dolomit in diesen Gegenden als ein wässeriger Niederschlag zu betrachten ist, dieses beweisen die Petrefakten, die ich aufgefunden habe": Zeuschner (1829, pp.408-409).

(1.15) "La roche calcaire appelée dolomie ne me paraît pas devoir son état magnésien à la présence des roches pyroxéniques. Je pense, au contraire, que cette roche calcaire était magnésienne lors de son dépôt...": Bertrand-Geslin (1834, p.8).

(1.16) "Wenn nun aber an so vielen Stellen der unmittelbare und allmähliche Uebergang des geschichteten petrefactenführenden Kalk in ungeschichteten Dolomit unseren eigenen geognostischen Beobachtungen sowie denen Anderer zu Folge nachgewiesen kann, ohne daß dabei Melaphyr irgend wie mit ins Spiel kommt (aus dem einfachen Grunde, weil keine vorhanden ist), so darf man wohl behaupten, daß die Dolomitisationstheorie auch ihre geognostische Begründung entbehre, dass vielmehr die Entstehung des Dolomits denselben Kräften und Ursachen wird zuzuschreiben sein, durch welche man den geschichteten Kalk entstanden sein läßt": Petzhold (1843, pp.242-243).

(1.17) On various occasions Von Morlot has attributed the idea of a reaction between limestone and a solution of magnesium sulfate giving rise to dolomite plus gypsum (or anhydrite) to Wilhelm Haidinger (see for example Von Morlot, 1847 A,B; 1848 A,B,C,D) and Von Morlot(1847 A) mentioned in particular Haidinger's paper "*On the parasitic* *formation of mineral species, depending upon gradual changes, which take place in the interior of minerals, while their external form remains the same*" (Transactions of the Royal Soc.Edinburgh, March 19. 1827). But in the Transactions of the Royal Society of Edinburgh for the year 1827 no such paper on dolomite by Haidinger can be found. Only when consulting Volume XI, 1831, of the Transactions of the Royal Society of Edinburgh (of which society Haidinger was a member) the mystery is solved: on pages 73 to 113 this particular paper by Haidinger was printed, as it was read on 19 March 1827. [The Catalogue of Scientific Papers (1800-1863) compiled and published by the Royal Society of London, Vol.III, 1869, reveals, that this very article not only has been published in the Trans.Roy.Soc.Edinb., Vol.XI, 1831, pp.73-113; but also in the Edinb.Jour.Sci., Vol.9, 1828, pp.275-292; in Froriep, Notizen, Vol.XXVI, 1830, col.17-25, pp.36-40; and in Schweiggert's Journ., Vol.LV (= Jahrb. XXV), 1829, pp.257-317] In it Haidinger called attention to the phenomenon of pseudomorphosis: minerals would show an external form not belonging to the substance. For example anhydrite would have been changed into gypsum, but still the original cleavage planes and crystal outlines would give the impression of anhydrite. After observing "Calcareous spar is one of those species which are very easily acted upon by atmospheric agents" (Haidinger, 1831, p.107), Haidinger suggested, that "... part of the carbonate of lime is replaced by carbonate of magnesia, so as to form in the new species a compound of one atom of each. How this change was brought about, is a difficult question to resolve, though the fact cannot be doubted, as we have in the specimen described a demonstration of it, approaching in certainty almost to ocular evidence"(Haidinger, 1831, p.108). How the transition of calcite into dolomite would take place was not explained. The word magnesium sulphate was not used in this context either. At the same time Haidinger (1831, p.108) declared: "I shall not enter into an inquiry respecting the probability of such changes in mountain masses, of such an enormous bulk as the dolomite of the Tyrol, to which Von Buch ascribed a similar origin."

(1.18) "Durch meinem verehrten Freund Wöhler wurde ich auf die Beobachtung, die auch Mitscherlich und L. Gmelin anführen, aufmerksam gemacht, daß man Dolomit in Pulverform künstlich zerlegen kann, wenn man eine Auflösung von Gyps durch denselben dringen läßt. Bittersalz wird gebildet und kohlensaurer Kalk bleibt zurück. Dieser Versuch erläutert wohle mit hinreichender Evidenz die Bildung des Kalkspathes aus Dolomit bei unserer gewöhnlichen Temperatur und atmosphärischer Pressung. Häufig beobachtet man in den vielen Gypsbrüchen der östlichen Alpen, z.B. zu Füllenberg bei Heiligenkreuz unweit Baden, zu Weidmannsfeld östlich von Bernitz, Ausblühungen von Bittersalz als Vollendung des Kreislaufes in der Bildung und Zerstörung von Dolomit": Haidinger (1844 A, p.250).

(1.19) "Ein von Wöhler schon 1843 eingeleiteter, von Hrn. von Morlot im verflossenen Winter durchgeführter Versuch wurde erläutert. Er beweist, daß die von der Theorie verlangte chemische Reaktion unter einem höheren Druck und bei 200^{o} R Wärme wirklich eintreffe, trotz dem daß bei gewöhnlicher Temperatur und unter dem einfachen Luftdruck der entgegengesetzte Prozess eintritt, so daß Dolomit durch eine Gypslösung zu Kalkstein bei Ausscheidung von Bittersalze umgewandelt wird. Dem letzteren Vorgang verdanken nach Hrn. Bergrath Haidinger die zelligen aus kohlensaurem Kalk bestehenden Rauhwacken ihren Ursprung": Von Morlot (1847 C, pp.393-394).

(1.20) "Haidinger hat zuerst die Vermuthung ausgesprochen, daß der Dolomit ein Zersetzungsproduct von kohlensauer Magnesia mit einer Nebenbildung von Gyps sey. Bei gewöhnliche Umstände, wie sie leicht eingeleitet werden können, findet indessen die umgekehrte Bildungsweise statt, indem eine Gypslösung durch feingepulverten Dolomit filtrirt eine Bittersalzlösung erzeugt. Unter höheren Druck und bei höheren Temperatur wird jedoch, wie dieses durch einen directen Versuch durch Von Morlot nachgewiesen ist, aus zwei Atomen Kalkspath und einem Atom Bittersalz, ein Atom Dolomit... und ein Atom Gyps gebildet": Sartorius von Walthershausen (1855, p.137).

(1.21) "Wenn man nämlich durch gepulverten Dolomit eine Auflösung von Gyps filtrirt, so entsteht die umgekehrte doppelte Zersetzung in der Art, daß Bittersalz aufgelöst durch's Filtrum geht, während kohlensaurer Kalk zurückbleibt": Von Morlot (1847 A, p.309).

(1.22) "Ich habe Chlormagnesiumlösungen von verschiedener Concentration mit Kreide angerührt anderthalb Jahre bei gewöhnlicher Temperatur stehen lassen und doch nicht eine Spur gegenseitiger Zersetzung entdecken können": Liebe (1855, p.431).

(1.23) "Viele Mühe habe ich mir gegeben, eine Zersetzung des Magnesiumcarbonats durch Kalkcarbonat zu bewirken. Kohlensaure Magnesia, volkommen kalkfrei, wurde in Wasser, durch welches anhaltend Kohlensäure strömte, aufgelöst und zur klar von der rückständigen kohlensauren Magnesia abgegossenen Flüssigkeit kohlensaure Kalkerde, die ganz magnesiafrei war, gesetzt. Nachdem das in einem verschlossenen Glase aufbewahrte Gemeng über Nacht theils in gewöhnlicher Temperatur, theils in ganz gelinder Digestionswärme gestanden hatte, wurde die flüssigkeit abfiltrirt und der kohlensaure Kalk so lange ausgewaschen, als das Abwaschewasser noch auf Magnesia reagirte. Allein es enthielt weder die abfiltrirte Flüssigkeit kohlensauren Kalk, noch der ausgewaschene kohlensaure Kalk kohlensaure Magnesia. Diese Beimischungen hätte man aber finden müssen, wenn das Magnesiacarbonat halbgebundenen Kohlensäure an den kohlensauren Kalk abgetreten und denselben in löslicher Kalkbicarbonat umgewandelt hätte": Bischof (1855, p.1120).

(1.24) "Die Bildung von Dolomit aus schwefelsauer Magnesia und kohlensaurem Kalk beruht auf einem Process, welcher dem bei gewöhnlicher Temperatur stattfindenden fast gerade entgegengestezt ist. Ich habe nun versucht, die Temperatur zu bestimmen, bei welcher diese Umkehr erfolgt, aber derselbe nicht sicher ermittelt; sie scheint bei oder nahe über 100^{o} [= 373 K] zu liegen": Hoppe-Seyler (1875, p.505).

(1.25) Pfaff Sr. (1894, p.487) noted: "Da nun bekannt ist, dass Gyps sich mit kohlensauer Magnesia umsetzt und schwefelsaure Magnesia neben kohlensaurem Kalk bei gewöhnlicher Temperatur liefert...". His son has confirmed the observation, and illustrated it with the following experiment: "Man kann sich von dieser Umsetzung sehr leicht überzeugen, wenn man feingepulverten Gips und Dolomit miteinander mischt, diese Salze in einen Trichter, dessen Rohr mit Baumwolle verstopft ist, bringt und Wasser aufgießt. Im abtropfenden reinen Filtrat wird man die Magnesia in bedeutenden Mengen stets nachweisen können": Pfaff Jr. (1907, p.563).

(1.26) "Bis heute haben wohl tausendfach variierte Versuche durch Einwirkung von Meerwasser oder von Lösungen der Chloride oder Sulfate des Magnesiums auf Kalziumkarbonat keinen Dolomit zu erzeugen vermocht": Linck (1937, p.281).

(1.27) The original electrochemical series as given by Berzelius (1836, Vol.5, pp.61-62) is as follows: oxygen, sulfur, nitrogen, fluorine, chlorine, bromine, iodine, selenium, phosphorous, arsenic, chromium, vanadium, molybdenum, tungsten, boron, carbon, antimony, tellurium, tantalum, titanium, silicon, hydrogen - gold, osmium, iridium, platinum, rhodium, palladium, mercury, silver, copper, uranium, bismuth, tin, lead, cadmium, cobalt, nickel, iron, zinc, manganese, cerium, thorium, zirconium, aluminum, yttrium, beryllium, magnesium, calcium, strontium, barium, lithium, sodium, and potassium (whereby oxygen is the most electronegative element and potassium the most electropositive). Some of the elements meanwhile have been allocated a slightly different position, but the overall sequence as such has remained much the same. (Berzelius, 1836 excused himself at beforehand, because to him not all facts were known at that moment.)

(1.28) For a much more complete account of the history of electrochemistry the reader is referred to *Elektrochemie: Ihre Geschichte und Lehre* (a book of 1151 pages !) by Wilhelm Ostwald (1896).

(1.29) "Jede chemische Wirkung ist also, ihrem Grunde nach, ein elektrisches Phänomen..": Berzelius (1836, Bd.5, p.71) and "Werden die Körper nach ihren elektrischen Dispositionen geordnet, so entsteht ein elektrochemisches System, welches, nach meiner Meinung, am besten von allen sich eignet, eine Idee von der Chemie zu geben": Berzelius (1836, Bd.5, p.60).

(1.30) "... diess zeigt, dass das, was wir Vereinigungs-Verwandschaft, chemische Verwandschaft nennen, eine nothwendige und unveränderliche Beziehung mit den elektrochemischen Erscheinungen habe": Berzelius (1836, Bd.5, p.59).

(1.31) But that is not all: Morrow & Ricketts (1986) called attention to their low-temperature syntheses of $BaMg(CO_3)_2$ and $PbMg(CO_3)_2$, because as they put it "... the more readily precipitated mineral analogues of dolomite, $BaMg(CO_3)_2$ and $PbMg(CO_3)_2$, may provide insight into the precipitational environment of dolomite itself" (Morrow & Ricketts, 1986, p.408). And what to think of the problem raised by Hausmann (1854): if a sample of dolomite is known to contain $FeCO_3$, at what moment would this iron have been introduced into the pre-existing limestone; before or after the introduction of magnesium carbonate?

(1.32) On this occasion Baron (1960) did not consider the possible role played by the addition of relatively large amounts of carbon dioxide in this particular experiment. Only a few pages before describing this experiment ("expériment H" as found on p.45), Baron (1960) had observed, that the presence of carbon dioxide had prevented the formation of nesquehonite or magnesium hydroxide carbonate, and that instead mixed anhydrous Mg/Ca carbonates had been formed ("La présence de CO_2 dans les systèmes d'équilibre étudiés conduit dans toutes les expériences à la formation d'un carbonate mixte de calcium et de magnésium. En particulier il n'y a plus ni de nesquéhonite $MgCO_3.3\ H_2O$, ni d'hydromagnésite $4MgCO_3.Mg(OH)_2.\ 4\ H_2O$ comme nous l'avions observé lors des séries précédentes dans l'étude du système Cl^- , CO_3^{--} , Ca^{++} , Mg^{++} , Na^+ , H_2O ": Baron, 1960, p.40). What would be needed to corroborate Baron's conclusion on the effects of solid state diffusion, would be a duplication of this experiment with nitrogen instead of carbon dioxide. And in fact Michard (1960) stated, that Baron had performed such tests with nitrogen instead of carbon dioxide, and that no dolomite at all formed in those tests. Baron (1960, p.22) did mention the use of nitrogen gas, being bubbled through a solution of calcium chloride mixed with magnesium chloride, to which sodium carbonate was being added drop by drop. But those were low-temperature tests (298 K), carried out without any increase in pressure. At the same time it should be noted, that Baron's conclusion, that the presence or absence of the salt solution had no effect on the conversion of the magnesium calcite into dolomite, can be doubted. When looking at the diffractograms of this particular experiment (Expériment H) on page 44 of Baron's (1960) paper, little or no difference can be detected between the first and the second diffractogram (H sec and H + H_2O), but the more so between the first and the third (H sec and H + solution mère). It is curious to find, that Baron (1960) did not mention the second experiment of this series (H + H_2O) in the text of his paper.

(1.33) Even so Sorby (1879, p.85) was not quite sure: "That some chemical replacement did occur admits of no doubt; but it might be going further than the evidence warrants to conclude that the whole rock was entirely altered by true replacement, without any direct chemical precipitation of magnesia."

(1.34) After Ch. Martins had read in the name of A. Favre "... une note sur l'origine des dolomies du Tyrol" at the meeting of the *Societé de Géologie de la France* on 5 March 1849, several objections were raised against the newly proposed theory. Coquand considered the theory totally inadmissible, because volcanic eruptions could never have raised the temperature of the sea water to 473 K. If such temperatures would have been attained, all of the animals living in it would have been destroyed. Moreover there was no need for any high temperatures, because a supply of magnesium would have been sufficient to form dolomite in the sedimentary way. Most dolomites would have formed in this manner ("M. Coquand considère comme sédimentaires la plus grande partie des dolomies, quoiqu'il reconnaisse plusieurs exemples de dolomies métamorphiques": Bulletin Soc. Géol. France, Volume 6, 1849, p.322). In addition Coquand had observed, how limestones in Toscane (Italy) had been changed into dolomite near the contact with serpentine, but that the contact between dolomite and these limestones was but a gradual one. Boubée added, that he distinguished two different types of dolomites: the first had in general a compact appearance and was of a sedimentary origin. The second type was cavernous and had to be of metamorphic origin. Delesse had also recognised sedimentary dolomites in the Jura mountains of France.

(1.35) At the start of his paper on the first ever synthesis of dolomite Von Morlot (1847 A) pointed out, that at room temperature dolomite powder reacted with a solution of gypsum to give calcium carbonate plus a solution of magnesium sulphate. But Haidinger (1844 A,B) had suggested, that although under atmospheric pressure and normal temperature dolomite would change into calcite, the reverse reaction would be taking place in the deeper realms of the earth, where higher temperatures and pressures existed. The application of Haidinger's (1844 A,B) theory of *anagenous* and *katogenous* metamorphism would thus explain the change of calcite into dolomite. Von Morlot (1847 A) gratefully acknowledged Haidinger's suggestion to perform experiments aimed at the synthesis of dolomite at elevated temperatures and high pressure in the laboratory of the *k.k. Hrn. General-Landes- und Haupt-Münz-Probirers* A. Löwe (Vienna) in the winter of 1846.

(1.36) Commenting on this fact, Pfaff (1851, p.468) concluded: "Es ist damit also die ganze Theorie von einer Dolomitisirung überhaupt als eine ganz und gar unstatthafte zurückgewiesen."

(1.37) Mere rhetorics were used for example by Doelter & Hoernes (1875) to convince their readers of the necessity to develop a wide variety of theories of dolomitization: "Gleich hier möge bemerkt sein, daß die Entstehung des Dolomites in verschiedenen Gegenden auf sehr verschiedene Weise erfolgt sein mag, und daß lediglich genaue geologische Beobachtung uns die bezügliche Erklärung für den speciellen Fall zu liefern im Stande ist" (Doelter & Hoernes, 1875, p.295), and "Bereits früher haben wir darauf hingewiesen, wie unrichtig es wäre, für ein Gestein wie der Dolomit eine einzige universelle Hypothese für seine Bildung aufzustellen, wie das von Manchen gethan wurde" (Doelter & Hoernes, 1875, p.307). But then it should be realized, that at the same time Doelter & Hoernes (1875) found it difficult to give a chemical definition for dolomite: "So schwierig die petrographische Definition des Dolomites ist, so schwierig ist auch die chemische" (Doelter & Hoernes, 1875, p.297). [Compare the strikingly similar remarks by Land, 1980, p.88: "There is clearly no unique environment necessary for the formation of dolomite ... The "dolomite problem" must ultimately be reduced to particular cases. No single, simple, all embracing model exists ... The second point I wish to emphasize is that "dolomite" is a complex mineral".] But how could they know at beforehand, at a time when not one low-temperature synthesis of dolomite had been performed?

(1.38) The concept of "de-dolomitization" was introduced by Von Morlot (1848 A), to delineate the reaction between a solution of calcium sulfate and dolomite powder (leading even at room temperature to calcium carbonate plus a solution of magnesium sulfate). Von Morlot stressed the observation, that this very reaction takes place under conditions of low temperature and atmospheric pressure, and that only under conditions of high temperature and elevated pressure a solution of magnesium sulfate reacts with calcium carbonate to give dolomite plus gypsum.

(1.39) The "de-dolomitization" concept used by Teall (1903) was clearly restricted to metamorphic reactions only.

(1.40) "Most dolostones are formed by replacement of pre-existing calcium carbonate sediments, but dolostones may revert back to calcium carbonate rocks by the process of dedolomitization": Friedman & Sanders (1967, p.269).

(1.41) The absence of any noticeable ionic diffusion in the carbonates at room temperature inevitably leads to another conclusion: Tammann & Sworykin (1928) warned, that no true equilibrium can possibly exist between any mixed crystal lacking measurable diffusion in the solid state and its mother solution. As a consequence it will not be possible to define any "solubility" of mixed crystals such as the magnesium calcites. "Berücksichtigt man, daß die Diffusion von Salzen bei gewöhnlicher Temperatur im Laufe von Jahren nicht nachzuweisen ist, so sieht man ein, daß die atomistische Bedingung des Gleichgewichtes für Mischkristalle mit den Lösungen, aus denen sie entstanden sind, nicht erfüllt ist. Infolgedessen darf man auch von einer isothermen Löslichkeitskurve nicht sprechen, wenn man mit dem Worte Löslichkeit einen Gleichgewichtszustand bezeichnen will": Tammann & Sworykin (1928, p.240).

II. SOLID SOLUTION OR SUPERLATTICE ?

(2.1) In this book I will follow the example of Schaffgotsch (1839), Karsten (1861), Von Gorup-Besanez (1872), Halenke (1872), Ostwald (1919) and Mitchell (1923) and will represent dolomite by the chemical equation $CaCO_3.MgCO_3$. In chapter 3 it will be shown, that there are good reasons for doing so because of the structural chemistry of the mineral.

(2.2) De Dolomieu (1791) made a considerable point of the phosphorescence exhibited by the new mineral, when struck with a piece of metal or another piece of the same rock. But not more than one year later Gillet-Laumont (1792) observed, that this phosphorescence was not a property exclusive to the newly described limestone, that would not effervesce with dilute acid, and thus questioned the observations made by De Dolomieu ["... je conclus... Que la phosphorescence n'est reservée exclusivement aux pierres calcaires des montagnes primitives (mêmes à celles à lente effervescence), mais qu'il y a en France beaucoup de pierres calcaires dans les montagnes primitives, secondaires & tertiaires douées de la vive effervescence & de la phosphorescence": Gillet-Laumont, 1792, p.99.]

(2.3) According to Klaproth (1795, *Beiträge zur chemischen Kenntnis der Mineralkörper*, Bd.I, p.304) the first description of the mineral dolomite should be attributed to Woulfe (1779). From that paper, in particular from the section headed *"Of a set of spars whose properties were not hitherto known, and experiments made on one of them"*, it can be seen that Woulfe (1779) had indeed analyzed a carbonate ("spar") "... whose properties were not hitherto known", and that that carbonate not only contained calcium oxide, but also "some other oxide" (as Woulfe, 1779, p.32 put it: ".. judged from the foregoing experiments that this spar was composed of calcareous earth, some iron, and a portion of some other earth, which, with acid of vitriol, forms a soluble salt"). It will be difficult to maintain, that Woulfe had indeed discovered dolomite: his descriptions of the crystal are rather vague (and restricted to its colour and rhombohedral form) and his chemical analysis is obviously wanting.

(2.4) "Marmor tardum - Marmor particulis subimpalpabilibus album diaphanum. Hoc simile quartzo durum, distinctum quod cum aqua forti non, nisi post aliquot minuta & fero, effervescens": Linnaeus (1768, Tomus III, p.41). [translation: Slow marble - Marble, white and transparent with barely discernible particles. This is as hard as quartz, but it is different in that it does not, unless after a few minutes and later, effervesce with "aqua forti".]

(2.5) "... la dolomie n'est autre chose qu'une combinaison proprement dite, de l'acide carbonique avec l'argile & la terre calcaire": De Saussure (1792, p.169).

(2.6) In his own words: "An analysis of this substance was lately given in the *Journal de Physique*, but this is probably erroneous; for, upon examining three specimens, they were found to consist of magnesia and calcareous earth, like the magnesian limestone; so that it ought, no doubt to be considered as the same species of stone, but in a state of greater purity": Tennant (1799, p.310), and: "The crystallized structure which may generally be observed in the magnesian limestone, seems to shew that it has not been formed by the accidental union of the two earths, but must have resulted from their chemical combination": Tennant (1799, p.310).

(2.7) "La dolomie en proportions atomiques existe-t-elle comme espèce minérale définie ? On doit presque en douter, aujourdhui que l'analyse nous montre les carbonates de magnésie et de chaux associés en proportions à peu près indéterminées. On peut tout au plus admettre que la composition de ces unions complexes oscille de préférence autour de certains points de stabilité maximum": De Sénarmont (1851 A, p.149).

(2.8) "Da beide Basen isomorph sind, so können sie sich innerhalb gewisser Grenzen in sehr verschiedenen Verhältnissen vereinigen, und doch denselben krystallisirten Körper darstellen": Bischof (1855, p.1103).

(2.9) "Durch diese Thatsache war eine directe Isomorphie zwischen $CaCO_3$ und $MgCO_3$ wenn nicht unmöglich, so doch bedenklich geworden": Retgers (1891, p.133).

(2.10) "Die Versuche lehren uns nichts anderes, als daß in der Mitte der Reihe ein physikalisches nicht-additives Doppelsalz auftritt": Retgers (1892, p.213).

(2.11) "... a somewhat surprising excess of calcium above the dolomite ratio and the excess is variable": Foote & Bradley (1914, p.344).

(2.12) At this point it must be remarked, that the question whether a broadened peak is the result of small individual grains or the result of the occurrence of an enhanced *Mosaikstruktur* (the occurrence of a strong domain structure in the crystal's lattice) is not really of importance. The main problem in the low-temperature nucleation of dolomite in laboratory tests was in fact the creation of a very clear, high and sharp main diffraction peak at 28.8 nm. Only in that case any hope could exist to find the required superstructure reflections at 40.3 , 25.4 and 20.6 nm. Finding these superstructure reflections is, according to a criterion stipulated by Graf & Goldsmith (1956), necessary to distinguish real dolomite from "protodolomite".

(2.13) "Geometrisch ist auch ein gewisses Verständnis dafür zu erhalten, daß bei diesen Überstrukturen des Calcit-Typs nur *zwei* unterschiedlich große Kationen, und zwar im voll geordneten Zustand im Verhältnis 1 : 1 vorkommen. Soll in den Koordinationspolyedern um die Kationen die 3zählige Achse erhalten bleiben, so *müssen* innerhalb einer Karbonatschicht alle CO_3-Gruppen in selben Sinn gedreht werden. Verlangt man zusätzlich für die Kationen Punktsymmetrie 3 , so entstehen notwendigerweise Schichten mit größeren und kleineren Oktaedern im Verhältnis 1 : 1 ": Zemann (1981, p.106).

(2.14) Klaproth (1804) gave the name of this dolomite deposit in Switzerland as Campo Longo; Linck (1907) described the same as Campolongo, and Mühlenthal (1922) referred to it as Campolungo.

(2.15) "Endlich stelle ich den Gebirgsforschern anheim, ob die Bennennung Dolomit, nach den Resultaten vorstehender Untersuchungen, in der Geognosie noch brauchbar bleiben...": Klaproth (1804, p.130).

(2.16) "La dolomie peut être mêlée avec de la pierre calcaire; mais elle-même contiendra une proportion detérminée de magnésie qui ne change point": Von Buch (1822 B, p.263).

(2.17) To give only a few examples: "Dolomit aus dem Asbest des Greiners im Zillerthal; krystallisirt, ausgezeichnet klar und wasserhell ..." (Haushofer, 1881, p.221); "Dolomitspath von Pfitsch, Tirol. Aus dem Mineraliensammlung der Universität Uppsala. Spaltungsrhomboëder mit glasklaren Spaltebenen. In kleinen Stückchen fast wasserhell und durchsichtig.." (Vesterberg, 1900, pp.110-111); and "Dolomit vom Greiner. Ein 4 cm großes wasserhelles Spaltungsstück..." (Eisenhuth, 1902, p.584).

(2.18) "Es genügt also nicht, durch eine chemische Untersuchung die Menge der kohlensaure Bittererde in irgend einem Kalkstein zu bestimmen, sondern es muß zugleich der Verbindungszustand der beiden kohlensauren Erden ermittelt werden, wenn die Lagerungsverhältnisse des Gesteins über seine Bildungsweise nicht schon einem unzweifelhaften Aufschluß zu geben vermögen": Karsten (1848, pp.573-574).

(2.19) "Ein anderes bestimmtes Verhältniß zwischen der kohlensauren Kalk- und Bittererde, als das gewöhnliche, habe ich niemals gefunden. Bei nicht krystallisirten Dolomiten sind unzählige Verhältnisse möglich und kommen auch wirklich vor. Aber diese lassen sich erweißlich auf den Zustand eines bloßen Gemenges von Dolomit mit kohlensaurer Kalkerde führen": Karsten (1828, p.82).

(2.20) The multitude of analyses performed by Lumsden & Chimahusky (1980) has provided evidence against the theory, that all Recent dolomites would be non-stoichiometric and only very old dolomites would ever attain a stoichiometric composition (e.g., "Such a stochiometry is characteristic of most ancient dolomites, whereas reported occurrences of Recent, authigenic dolomite from a number of sedimentary environments are of non-stochiometric, calcium-rich phases": Hardie, 1968, p.1292).

(2.21) Karsten (1807 B) had found in a serpentinite rock near Aggsbach, Austria a large quantity of a white crystalline mass, which upon chemical analysis was found to consist of 70.50 wt. % calcium carbonate and 29.50 wt. % magnesium carbonate. John (1814) had analyzed a bladder stone from a horse and had found it to contain 80 wt. % calcium carbonate plus 10 wt. % magnesium carbonate.

(2.22) It is often thought, that Chave (1952) would have been the first to coin the "magnesium calcite" concept. In this regard it is perhaps interesting to realize, that Damour (1851) had described deposits of "calcaire magnésien" of biogenic origin, that Hunt (1859, p.184) reported "a double carbonate of lime and magnesia"; that it was Scheerer (1866, p.12), who spoke of "Krystalle von Kalk-Magnesia Carbonat"; and that Linck (1909 A) described laboratory syntheses of mixed crystals denoted as "Kalzium-Magnesiumkarbonat" and "Magnesiumkalziumkarbonat". From the context it can be concluded, that all four authors mentioned, meant to describe mixed crystals between $CaCO_3$ and $MgCO_3$ different from dolomite. If only Chave (1952) would have taken the trouble to read the paper by Steidtmann (1911 A), which appeared in the same *Journal of Geology* in which Chave's paper was printed, he would have learned, that observations on the same subject by Forchhammer (1852) and Högbom (1894) preceded his own.

(2.23) The postulated linear relationship between percentage $MgCO_3$ and the position of certain diffraction peaks implies, that only $CaCO_3$ and $MgCO_3$ should be present. Magnesium calcites containing any other cations cannot be used in this type of X-ray analysis. According to Chave (1952) trace element concentration in the samples used would not be responsible for the noted deviations from Vegard's Law, but he did not give chemical analyses.

(2.24) The mathematical calculations used by Zen (1956) to illustrate his rejection of "Vegard's Law" were based on a binary solution, in which the volume effects of the two different components are additive (i.e., the volume of the mixed crystal or "solid solution" is not changed by mixing the two components of it). V_1 and V_2 denote the molal volumes of these two components, and N denotes the mole fraction of component 1. The volume of the mixed crystal is therefore given by

$$V = N.V_1 + (1 - N).V_2$$

$$\text{or} \quad V = N.(V_1 - V_2) + V_2 . \qquad \text{(eq.1)}$$

Provided that the two components, as well as the mixture itself, crystallize in the cubic system, and after replacing the molar volumes by the dimensions of the two unit cells with edge R_1 and R_2 respectively, the preceding equation changes into

$$R^3 = R_2^3 [1 - \frac{(R_2^3 - R_1^3)}{R_2^3}.N], \quad (eq.2)$$

from which it follows, that

$$R = R_2.(1 - [1 - \left(\frac{R_1}{R_2}\right)^3].N)^{1/3} \quad (eq.3)$$

The last equation must be reconciled with "Vegard's Law". This can be done after defining the molar volume of component 1 as

$$\alpha = \frac{R_2^3 - R_1^3}{R_1^3}$$

and the molar volume of component 2 as

$$= \frac{R_1^3 - R_2^3}{R_2^3}.$$

For now "Vegard's Law" gives the unit cell edge R of a mixed crystal with intermediate composition as:

$$R = R_2 (1 + \text{ß} . N) , \qquad (eq.4)$$

(which is tantamount to the prior statement, that the volume effects of the two end-members are additive). In the latter formulation the unit cell edge of a mixed crystal with intermediate composition is proportional to the mole fractions; whereas in equation (3) R is proportional to the cube root of the mole fraction. "This problem can be formulated in a slightly different way. Writing $\alpha = (R_1/R_2)^3 - 1$ in equation (3) and expanding the cube root in a series, we get

$$R = R_2 (1 + 1/3.\alpha.N - 1/9.\alpha^2.N^2 + ...) \qquad (eq. 5).$$

Comparing with (4), we see that ß = $1/3.\alpha$, and the two expressions can be reconciled only when terms higher than the first power in α are negligible, i.e., if

$$(\frac{V_1}{V_2} - 1) << 1,$$

which means that the pure end-members do not have very different molar volumes. The fact is intuitively obvious, but equation (5) expresses it analytically and gives a precise relation between allowable difference in end-member volumes and any desired degree of approximation to linearity for the solution (when other conditions are also satisfied)": Zen (1956, p.524).

(2.25) "Chave's use of the expression "solid solution between calcite and dolomite" is misleading; compositionally, this expression is permissible, but structurally it fails to take into account the ordered nature of dolomite, and the fact that this ordering does not exist when there is significant deviation from a 1 : 1 Ca : Mg ratio": Goldsmith et al. (1955, p.212/ FOOTNOTE).

(2.26) "The calcite-dolomite solid solution is unstable. Analyses of fossil materials show that the magnesium content falls to 1 or 2 per cent often within a few of millions of years. The magnesium is replaced by calcium. The forms richest in magnesium seem to be changed first. This suggests that the solid-solution series is unstable under all near-surface conditions, except within the biological environment which produced it": Chave (1952, p.192). But compare the observation made by Bischof (1855, p.1125) on the $MgCO_3$ content of biogenic calcites: "Auch diese Erde kann daher nur durch organische Thätigkeit aus dem Meerwasser abgeschieden werden, wie diese auch der Magnesiagehalt in den von Seethieren gebildeten Kalksteinen zeigt."

(2.27) The definition of a "mineralogical species" as given by Haüy in his *Traité de Minéralogie* (1801, Vol.1, p.162) reads: "... une collection des corps dont les molécules intégrantes sont semblables, et composées des mêmes éléments unis en même proportion", and Haüy added, that "... chacune des espèces est distingée de toutes les autres par une forme de molécule intégrante qui lui appartient exclusivement".

(2.28) "Die vom Herrn Inspektor Werner im gedachten Aufsatz ebenfalls beschriebene sechsseitige Kalkspatkristallisationen aus Arragonien ... können ... also nur als Abänderung des gewöhnlichen Kalkspats angesehen werden, welche Abänderung nicht in einer Verschiedenheit der Bestandtheile, sondern blos in einer abweichenden Zusammenfügung der gleichartigen Theile, ihren Grund hat": Klaproth (1788, pp.299-300).

(2.29) "Der Arragonit enthält nämlich außer kohlensaurem Kalk noch *kohlensauren Strontian*, in einem constanten Verhältniß mit ersterem *chemisch* verbunden, und muß als eine wahre natürliche *Tripelverbindung* der Kohlensäure mit Kalk und Strontian betrachtet werden. Die Menge des in dem Arragonit mit dem kohlensauren Kalk verbundenen Strontians beträgt zwischen 3 und 4 Procent": Stromeyer (1813, p.232).

(2.30) The possible significance of strontium towards the mineralogy of sedimentary carbonates, originating in this very publication by Stromeyer (1813), is apparently still being discussed today (more than 170 years after Mitscherlich, 1819 introduced the concept of polymorphism!). Papers on the occurrence of strontium in calcium carbonate, such as for example those by Kulp et al. (1952), Siegel (1960), Stehli & Hower (1961), Holland et al. (1964), Dodd (1967), Green (1967), Bausch (1968), Kinsman (1969), Kinsman & Holland (1969), Katz et al. (1972), Veizer & Demovic (1974), Mucci & Morse (1983), Baker et al. (1982), and Pingitore & Eastman (1986) document the unabated interest.

(2.31) Rose (1868) has documented the events leading to the discovery of isomorphism by Mitscherlich in 1819.

(2.32) The artificial sea water used by Vetter (1910) contained in 1 dm^3 water 27.90 g NaCl , 2.34 g $MgCl_2$, 1.85 g $MgSO_4$, 1.56 g $CaSO_4$, 1.55 g KCl , and 0.52 g NaBr.

(2.33) Although Chave (1954 B, p.594) used the term "low-magnesian aragonite", he refrained from giving a definition or an analysis of such a mixed crystal. The concepts of "low-magnesian calcite" and "high-magnesian calcite" have been defined by Chave(1954 B, p.594) in the following way: "... high-magnesian calcite (i.e., calcite with more than 4 per cent magnesium carbonate in solid solution)". The use of the concepts "low-magnesian aragonite" and "high-magnesian aragonite" by Friedman (1968) must be regarded to be confusing, the more since the maximum $MgCO_3$ content of the so-called "high-magnesian aragonite" was only 5.8 ‰ (*promille*) (Friedman, 1968, Table 5, p.912).

(2.34) "Man hat somit vom Calciumcarbonat zum Magnesiumcarbonat eine isomorphe Reihe mit sehr beschränkter Mischbarkeit, wie sie im Mineralreiche so häufig sind": Redlich (1917, pp.52-53).

(2.35) But there was more, that Searl (1994) concluded from his more than 2000 microprobe analyses of dolomite. The measured bimodal distribution of mol % $CaCO_3$ in various dolomites could not have been caused by precipitation from two different solutions. The uptake of magnesium (and calcium) during crystal growth might well be controlled largely by surface geometry (as Paquette & Reeder, 1990 and Dickson, 1991 had proposed), and therefore the often suggested role of the Mg/Ca ratio of the solution must be rather limited.

(2.36) On the basis of their measurements on the manganese contents of various dolomites Lumsden & Lloyd (1997) thought it necessary to distinguish five different kinds of dolomite: group A dolomite, group B dolomite, group O dolomite, protodolomite and metamorphic dolomite. "Group A dolomite, typical of dolomitic limestones and some dolomicrites, is calcian (> 53 % Ca) and has a low manganese partitioning rate (MnPR < 25), a small crystal size (< 0.05 mm) .... Group B is nearly stoichiometric (< 52 % Ca), has a high MnPR (> 50), large crystal size (0.1 - 0.5 mm) ... Group O dolomite, common in evaporite-related dolomicrites, is stoichiometric (49 - 52 % Ca), and has a low MnPR (10 - 25) and a compact unit cell (*c* axis 16.01 - 16.04 Å)": Lumsden & Lloyd (1997, p.391).

(2.37) "Despite the fact that complete chemical reorganization has taken place, the c-axis orientation of the replacement product, as determined by optical properties, appears to be identical with that of the original alga": Land & Epstein (1970, p.197).

(2.38) "The discrepancies between solubilities obtained from precipitation versus dissolution experiments remain as yet unexplained": Mackenzie et al. (1983, p.118), and "Dissolution experiments, which have been performed exclusively with biogenic materials, are fraught with difficulties of sample preparation (grain size distribution, crystal strain owing to grinding, annealing) and microarchitectural effects (skeletal crystal size, surface morphology). Because the magnesian calcites contain hydroxyl or molecular water as demonstrated, heating procedures aimed at annealing biogenic samples in which water is lost, could conceivably affect the dissolution rates and solubility. Furthermore, the problem of interpretation of dissolution reaction data has not yet been resolved": Mackenzie et al. (1983, p.143).

(2.39) "Berücksichtigt man, daß die Diffusion von Salzen bei gewöhnlicher Temperatur im Laufe von Jahren nicht nachzuweisen ist, so sieht man ein, daß die atomistische Bedingung des Gleichgewichtes für Mischkristalle mit den Lösungen, aus denen sie entstanden sind, nicht erfüllt ist. Infolgedessen darf man auch von einer isothermen Löslichkeitskurve nicht sprechen, wenn man mit dem Worte Löslichkeit einen Gleichgewichtszustand bezeichnen will." (Tammann & Krings, 1923, p.240).

III. NEODOLOMITE RE-EXAMINED

(3.1) In their 1955 paper on dolomite - magnesium calcite relations at elevated temperatures and CO_2 pressures Graf & Goldsmith observed, how in several runs of the high temperature & high pressure experiments equilibrium apparently had not been reached. That is to say from the calcite and magnesite mixtures or the co-precipitated Ca-Mg carbonates used as a starting material "... a phase was obtained that had spacings equivalent to, or near, those of dolomite but with somewhat diffuse reflections. The ordering reflections in such cases were weak or absent": Graf & Goldsmith (1955, p.124). This phase was originally given the name *neodolomite* (Graf & Goldsmith, 1955, p.124).

(3.2) Goldsmith & Heard (1961) noted, that three order reflections can be distinguished in powder diffractograms of dolomite, and claimed that "... many more are seen in single-crystal pictures" (Goldsmith & Heard, 1961, p.57).

(3.3) To give only one example of the confused state of things regarding "protodolomite": Hein et al. (1979) described the magnesium calcium carbonate found in cores from the Deep Sea Drilling Project as "protodolomite" and added, that "... X-ray reflections of ordered dolomite are present but of low intensity and broadened" (Hein et al., 1979, p.691).

(3.4) The term "superstructure reflection" is to be preferred over "order reflections", because Bragg (1914 A) did not use the word "order reflection" quite unambiguously to distinguish between reflections resulting from the multiples of $n.\lambda$ (as in 2nd, 3rd ... order reflections) and reflections based on geometrical order (for example in the case of crystallographic planes in sodium chloride containing only sodium atoms or only chlorine atoms).

(3.5) As expressed by Nix & Shockley (1938, p.2): "... the conclusive evidence of ordered arrangements, of superstructures, or superlattices as they are called, is furnished by the presence of "superstructure lines" on X-ray diffraction patterns".

(3.6) "Isomorphe Mischbarkeit in erheblichem Ausmaße und bei Temperaturen, welche nicht sehr nahe den

Schmelzkurven liegen, tritt ein, wenn die Radien der betreffenden Bausteine um nicht mehr als etwa 15 % (in Prozenten des kleinsten Radius) voneinander verschieden sind": Goldschmidt (1926, p.83). It must be remarked here, that Vegard (1921) had already hinted the fact, that the two different kinds of atoms making up a mixed crystal of the solid solution type should not be too different in size ("... die einander ersetzenden Atome müssen sich im Mischkristall auf annähernd denselben Atomdurchmesser einstellen": Vegard, 1921, p. 22).

(3.7) Puhan (1984) even showed scanning electron photomicrographs of dolomite crystallites in perfect register with the crystallographic threefold axis within a host crystal of exsolved magnesium calcite. These samples were from high grade metamorphic marbles found in Namibia.

(3.8) It is this two-step decompostion of dolomite being heated, that forms the basis for a number of industrial processes intended to extract magnesium (oxide) from the mineral dolomite. For example in the process patented by the *Steierische Magnesit-Industrie A.G.* (1922/1924) the magnesium carbonate content of dolomite starts its decomposition at a temperature of 773 to 873 K, whereas the calcium carbonate content remains intact unless temperatures above 973 K are reached. Comparable processes based on partial calcination have been described by for example Eitel (1925), Heinrich (1925) and patented by DuBois (1932) (see also the reviews on the separation of magnesia from dolomite by Platzmann, 1937 and Seil et al., 1943).

(3.9) Bischof (1855) stated, that analyses of (pure) magnesite by Döbereiner (1815), Berthier (1822), and Stromeyer (1827) had revealed a maximum of only 0.3 (wt.) % $CaCO_3$. Analysis by Rumpf (1873 B) of magnesite from Mariazell (Steiermark, Austria), had shown, that it contained only 1.58 wt.% $CaCO_3$. Six other samples of magnesite analyzed by Rumpf (1873 B) were found to contain between 0.86 and 2.42 wt.% $CaCO_3$. Only 0.17 wt.% $CaCO_3$ were found by Garrels et al. (1960) in magnesite from Oberdorf, Austria. As early as 1827 Stromeyer had concluded from his chemical analyses, that magnesite would not contain any calcium carbonate. [Stromeyer, 1827 had analyzed samples of crystalline $MgCO_3$, but wanted confirmation of his observations. Therefore four different samples of *Magnesitspath* from the Zillertal, from the Fassatal, from Hall in Tyrol (Austria), and from the St. Gotthard (Switzerland) were sent by Stromeyer to Prof. Mohs in Vienna to be analyzed. The analyses by Mohs confirmed his own: the samples of magnesium carbonate did contain iron carbonate, manganese carbonate, and even a small amount of coal, but no calcium carbonate at all.]

(3.10) In his textbook on chemical and physical geology Bischof (1855) observed, on the basis of the analyses of dolomite published by Karsten (1828), how dolomites might well contain more than the stoichiometric amount of $CaCO_3$, but never more than the stoichiometric amount of $MgCO_3$: " Aus allen Analysen ergab sich, daß in den Dolomiten, deren Zusammensetzung sich der von (I) [i.e., 1 At. $CaCO_3$ = 54.18 wt.% + 1 At. $MgCO_3$ = 45.82 wt.%] nur nähert, die kohlensaure Magnesia nie mehr, sondern stets weniger als 45,82 Proc. beträgt, daß dagegen die kohlensaure Kalkerde 54,18 Proc. immer übersteigt": Bischof (1855, Bd.II, Abth.2, p.1104).

(3.11) "This latter sample contains 62.9 mole % Mg by titration and 58 % by its X-ray spacing. It was prepared by adding 3.75 g of $NaHCO_3$ in 75 ml of water to a solution of 80 g $MgCl_2.6\ H_2O$, 1.12 g $CaCl_2.2\ H_2O$ and 30 g NaCl in 75 ml of water at 35^{o}C. The precipitate was filtered from the solution after 70 hr": Glover & Sippel (1967, p.608).

(3.12) "Although no experimental work has been carried out on this portion of the system, it might be expected that less Ca would be substituted in $MgCO_3$ than Mg in $CaCO_3$. The difference in ionic size of Ca^{++} and Mg^{++} is considerable (1.06 Å vs. 0.78 Å, Goldschmidt values), and extensive substitution of the larger atom for the smaller one should be less likely than the reverse": Graf & Goldsmith (1955, p.127). And the comparable observation: "This difference reflects, in part, the relative difficulty of substituting a rather large cation (Ca^{2+}) on a small site (in magnesite) compared with substituting a small cation on a larger site (as in the magnesian calcites)": Reeder (1983, p.18).

(3.13) Kitaigorodsky (1984), in a description of the same phenomenon occurring not in ionic crystals but in metals, coined it picturesquely with the term "hanging loose".

(3.14) "Protodolomite entstanden nur dann, wenn sich das Gleichgewicht bei zu kurzer Reaktionsdauer noch nicht eingestellt hatte": Usdowski (1967, p.34).

(3.15) In more or less comparable experiments on the hydrothermal synthesis of dolomite Sibley et al. (1987) could distinguish only two different stages: an induction stage (during which no detectable products form) and a nucleation-growth stage.

(3.16) "The disturbed layer sequence in these materials may represent a two-phase intergrowth on an exceedingly fine scale": Goldsmith & Heard (1961, p.62).

(3.17) "The term protodolomite is suggested for single-phase rhombohedral carbonates which deviate from the composition of the dolomite that is stable in a given environment, or are imperfectly ordered or both, but which would transform to dolomite if equilibrium were established": Graf & Goldsmith (1956, p.184).

(3.18) "If superstructure reflections are truly absent, however, then these materials are not dolomites": Reeder (1983, p.36).

(3.19) "Products without ordering peaks are considered HMC": Sibley (1990, p.740) (HMC = high magnesium calcite).

(3.20) "HMC and nonstoichiometric dolomite both formed smooth-faced rhombs. The surface of the stoichiometric dolomite appeared heavily pitted and corroded": Nordeng & Sibley (1994, p.193).

(3.21) Backscatter scanning electron microscopy was used by Searl (1989) to study the compositional zoning in samples of what was described as "saddle dolomite". (The subject "saddle dolomite" as such will be disregarded in the present book, because morphology has little to do with structural chemistry.)

IV. REGIONAL ASPECTS OF DOLOMITE FORMATION

(4.1) The reader may well wonder about a statement such as that by Philippi (1907, pp.408-409): "Wir dürfen mit Sicherheit annehmen, daß die primäre Dolomitbildung in großem Maßstabe auch in den heutigen Meeren vor sich geht."

(4.2) "These multicyclic modern dolomite rhombs and rhomb clusters may be the future nuclei for epitaxial precipitation of further dolomite, either on the modern sea floor or later, during burial": Bone et al. (1991, p.28).

(4.3) In 1920 Gignoux had asked attention for the fact, that the protozoan *Trichosphaerium* consisted entirely of "carbonate de mangésie", and that this fact might have some significance for the formation of dolomite.

(4.4) As early as 1834 Ehrenberg described, how he had found the sediment of the Red Sea near Ras Muhammed to consist of a mixture of quartz and feldspar grains cemented by dolomite: "Die Küsten des rothen Meeres bestehen auf der arabischen Seite zuweilen aus Mergel und Gyps, wie bei Hamam Faraun im Norden und bei el Gisan im Süden, zuweilen aus Sandsteine, wie bei Nakuhs, oder aus einem Sandsteinartigen Conglomerat von Quartz und Feldspath mit Dolomit-Cäment, wie bei Ras Muhammed..." (Ehrenberg, 1834, p.45).

(4.5) The difference between the vadose zone and the phraetic zone has been explained by for example Davis & DeWiest (1966) as follows: the groundwater that occurs in the phraetic zone (i.e., zone of saturation) forms the deepest part of the groundwater, and it will enter freely into wells. Groundwater above the water table changes into the water of the vadose zone. This vadose water, also known as suspended water, is in downward motion under the influence of gravity.

(4.6) For identification purposes the geographic location will be given in degrees latitude and longitude for the islands mentioned (Pacific atolls or otherwise):

Atiu (Cook Islands)	19^o 99’ S	158^o 10’ W
Bikini (Marshall Islands)	11^o 35’ N	165^o 20’ E

Christmas Island	2° 00’ N	157° 30’ E
Clipperton	10° 18’ N	109° 13’ W
Eleuthra (Bahamas)	25° N	76° 30’ W
Eniwetok	11° 30’ N	162° 10’ W
Eua (Tonga)	21° 23’ S	174° 55’ W
Fangataufa (Tuamotu Archipelago)	22° 12’ S	221° 20’ W
Funafuti (Ellis Islands)	8° 30’ S	179° 12’ E
Guam (Marianas Islands)	13° 30’ N	144° 40’ E
Jarvis Island (Line Islands)	0° 23’ S	160° 02’ W
Kambara (Fiji Islands)	18° 57’ S	178° 58’ W
Kapingamaragni	1° 1’ N	158° 8’ E
Kita-daito-jima	25° 27’ N	141° 16’ E
Lau (Fiji Islands)	20° 7’ S	178° 7’ W
Lifou-Lifou (Loyalty Islands)	21° S	167° 20’ E
Makatéa (Tuamotu Archipelago)	16° 10’ S	148° 14’ W
Mangaia (Cook Islands)	21° 9’ S	157° 9’ W
Mango (Pacific Islands)	20° 20’ S	174° 53’ W
Metia	17° 87’ S	148° 7’ W
Midway (Hawaiian Islands)	28° 13’ N	177° 22’ W
Minamidaitó Zima	26° N	131° E
Mururoa	21° 50’ S	138° 47’ W
Namuka-Iki (Tonga)	20° 06’ S	174° 46’ W
Nauru	0° 31’ S	166° 55’ E
Niau Atoll (Tuamotu Archipelago)	16° 09’ S	146° 20’ W
Niue (Cook Islands)	19° 02’ S	169° 51’ W
Ouvea / Uvea (Loyalty Archipelago)	20° 30’ S	166° 25’ E
Tenia	22° 01’ S	165° 56’ W
Tongatábu/Tongatapu (Tonga)	21° 10’ S	175° 10’ W
Vatu Vara (Fiji Islands)	17° 25’ S	179° 34’ W
Vavau/Vava’u (Tonga)	18° 40’ S	174° W
Yathala (Figi Islands)	17° 15’ S	179° 33’ W

(4.7) Dana (1872, p.353) mentioned the Feejee reefs, but at present the name of these islands is usually given as Fiji. However, there is much more confusion surrounding the nomenclature of Pacific atolls. For example *Makatéa* is not only the name of one specific atoll, it is at the same time a concept. For as Hoffmeister & Ladd (1935, p.658) explained: The *makatea* is supposed to represent an elevated barrier reef...". Similarly Fairbridge (1950, p.385) stated: "Marshall (1930) carried out field tests on the *makatea*, or raised coral rim, of Atiu in the south Pacific...". Another example of the confusion was given by Dana (1872), who proclaimed the names of Metia and Aurora to be identical.

(4.8) On various other atolls no dolomite has (yet) been found. These include for example Niue, Vavan, Tongatabu, Niau and Guam (Skeats, 1918 B); Pearl and Hermes Reef (Thorp, 1936); Kapingamarangi (McKee, 1958); Kure and Midway (Gross et al., 1969).

(4.9) "Examination of specimens from upraised coral-islands, such as Christmas Island, the Fiji's, etc., led me to the conclusion that the formation of dolomite can proceed in quite shallow waters": Skeats (1905, p.133).

(4.10) At present such high rates of subsidence of the sea level are not as "unlikely" as it might have seemed in the year 1918: Vatu Vara is a coral reef built on top of a volcanic core. After his discovery of some 160 "curious, flat-topped peaks ... in the Pacific Basin", Hess (1946) provided the following explanation: guyots are originally volcanic peaks with flat tops caused by erosion. Some of the guyots, but not all, are overgrown by reefs and ultimately have developed into atolls. Carsola & Dietz (1952) proved the guyots to consist of extinct volcanoes.

(4.11) According to Ohde & Kitano (1982) "beautiful protodolomite" covers about three-quarters of the island of Minami-daito-jima (near Kita-daito-jima; some 370 km east of Okinawa). But no protodolomite was found in the centre of the west coast of the island. Ohde & Kitano (1982) suggested, that possibly water circulation in the (former) lagoon of Minami-daito-jima had been responsible for this pattern in geographical distribution.

(4.12) "The high degree of correlation between magnesium content and gamma counts ... suggests that deposition of radio-active elements in samples accompanied dolomitisation": Schofield & Nelson (1978, p.42).

(4.13) In Lotze's (1957) textbook on salt deposits the name Kara Bogaz Gol or Karabugas is used in a rather restricted sense, in that it would denote the narrow channel coming from the Caspian Sea, and streaming into the salt flat named Adshi-darja. Here I will follow the Russian authors mentioned, and apply the name Kara Bogaz Gol to both channel and the large salt sea..

(4.14) Degrees Beaumé is a scale for density measurements. For solutions heavier than water 0 ^{o}Bé corresponds with a specific gravity of 1.000 , and 66 ^{o}Bé equals a specific gravity of 1.842 . Therefore 18.8 ^{o}Bé is equivalent with a specific gravity of 1.240 (see for example Weast, 1973).

(4.15) Murray & Irvine (1895) gave the following explanation for the laminations between black mud and calcareous layers: the chemistry of the water in the deeper parts of the Black Sea would be balancing between the influences of either dissolved hydrogen sulfide or dissolved carbon dioxide. In open seas the situation would be principally different, in that any hydrogen sulfide present would be oxidized into sulfate.

(4.16) In fact Le Play (1834) described the first *lacustrine* dolomite with the words: "... il semble qu'on ne peut se refuser à admettre que l'ensemble du terrain dolomitique de Badajoz est une altération de la formation lacustre..." (Le Play, 1834, p.357). Only much later Klähn (1928 A,B) and Gevers (1930) described finding lacustrine dolomite again.

(4.17) Writing on limestones (of Paleozoic age) containing dolomite, Fairbridge (1957, p.127) stated: "Worm tracks and tubes (with coarser filling), algal impressions and cavities, etc., have been dolomitized selectively."

(4.18) From their chemical analyses of 25 different samples from calcareous subsoils of the Late Wisconsin drift (a remnant of the Pleistocene Lake Agassiz) in Minnesota Alway & Zetterberg (1935) reached the conclusion, that 32.8 to 78.6 wt. % of the total carbonate had to consist of dolomite. Eardley (1938) had described a double carbonate of the composition $CaCO_3$.2 $MgCO_3$ from the youngest sediments from Great Salt Lake, Utah (and had called it "dolomite"). "The dolomite crystals of the Great Salt Lake clays are undoubtedly primary..": Eardley (1938, p.1353).

(4.19) In addition to the distinct fluctuations in physical chemistry of the water of Florida Bay and the pore water of the sediments, there are marked fluctuations in the aquifer of South-eastern Florida. Measurements made during 20 years on the exact position of the salt-water front of the Biscayne aquifer along the coast of the Miami area, led Kohout (1960) to confirm the hypothesis of Cooper Jr. (1959) on the dynamic balance of fresh water and salt water. Not only "cyclic flow" resulting from seasonal variations in fresh-water recharge, but even horizontal and vertical movement of the groundwater under the influence of tides could be measured.

(4.20) "The soils of this area receive most of their precipitation during very short intervals of the year. Each year these soils become very dry, often to the extent that they show wide and deep cracks. During these periods of drought the salts are brought toward the surface by capillary rise of water. In the process of drying, much of the calcium salt is precipitated at lower levels, while the magnesium salt, owing to its higher solubility, remains in solution": Sherman et al. (1947, pp.42-43).

(4.21) In the fragments of the calcareous algae Philippi (1907) found a distinct overall pattern of replacement: "In Schliff 6 und 7 sind auch die organogenen Hartgebilde, hier überwiegend Kalkalgen, zum großen Teile in Dolomit übergeführt. Besonders bei 7 kann man die Dolomitisierung der Kalkalgen oft an einem Fragment in allen Stadien verfolgen. Zuerst füllt sich das Innere der Hohlräume mit Dolomit, dann wird auch der Kalk der Wandungen in Dolomit übergeführt; kalkige Streifen treten aber auch dann noch an der Grenze von zwei konzentrisch-schaligen Lagen auf. Die Dolomitisierung scheint von außen nach innen fortzuschreiten, gewöhnlich findet man in der Mitte eines

Kalkalgenfragmentes noch den stärksten Kalkgehalt. Ist die Dolomitisierung vollständig, so verschwindet meist auch jede Spur von Struktur": Philippi (1907, p.421).

(4.22) Rex & Murray (1970) had found sepiolite together with dolomite in the core samples from DSPD site 29 (= central Venezuelan Basin, 14° 47.11' N / 69° 19.36' W). Gieskes (1973, p.827) added the observation: "Whenever this authigenic magnesium silicate appears, the montmorillonite component is high and the calcium carbonate low."

(4.23) "Es sind auf Nauru mehrere Höhlen von großer Ausdehnung bekannt, die teilweise einen kleinen See aus brackischem, fast süßem Wasser enthalten; wie beim Wasser der Lagune, äußert sich auch hier Ebbe und Flut in beschränktem Maße. Die ganze Erscheinung möchte ich als ein wohlverstanden den lokalen Verhältnissen angepaßtes Karstphänomen bezeichnen: Großartige Höhlen mit Kalk-, Dolomit- und Phosphat-Stalaktiten, Spalten, Pinnakel, Klüfte, Einstürze von Felsen, Wasserdurchdringungen und Wasseransammlungen, die durch die einwirkende Flut einen Einschlag von Salzwasser erhalten": Elschner (1913, p.38).

V. ORGANIC OR INORGANIC ?

(5.1) "... mais en revenant en Italie, je trouvai que les pierres de montagnes calcaires, qui succèdent à celles de porphyre, entre Bolsano & Trente, avoient cette même particularité, quoiqu'elles soient en bancs horizontaux & que j'y rencontrasse quelques empreintes de coquillages": De Dolomieu (1791, p.5).

(5.2) "Die Versteinerungen kommen hier an den meisten Stellen in solcher Menge vor, daß der Dolomit nur als ein Kitt zwischen denselben zu betrachten ist": Wagner (1831, p.455).

(5.3) "... so kann man dagegen die wässrige Entstehung des Dolomits sogar auf directem Wege, als eine festbegründete THATSACHE erweisen": Wagner (1831, p.462).

(5.4) "This power depends mainly upon the amount of carbon-dioxide dissolved in the water, or liberated on the decay of the organisms composing the rock. Probably the interchange of magnesian for calcium-salts is most readily effected at the moment of solution of the calcium-carbonate of the rock. If this be so, the carbon-dioxide slowly liberated on the decay of plants and animals would help to determine the introduction of magnesium": Skeats (1905, pp.134-135).

(5.5) Earlier Graf Münster (1834) had interpreted the whole of the German Jurassic dolomites as being one gigantic coral reef. But Wagner (1836) could barely find any coral in the same Jurassic dolomite. Wissmann (1841) described finding fossil corals, crinoids and bivalves in the Fassa dolomite of Northern Italy.

(5.6) "Am Aufstieg zum Schlern, wie an der Mendel sind die Schichtenlagen oft so deutlich, daß man auf denselben wie auf Treppen stufenweise emporsteigt": Von Gümbel (1873, p.73).

(5.7) "In the "reef-dolomite" fossil remains are extremely poor and scanty; plant algae are got even more often than Corals, Gasteropods, or Bivalves": Ogilvie (1894, p.4) and: "Corals found abundant "coigns of vantage" and were aided by Echinodermata to form communities of organic life, often prevented from farther growth by new volcanic invasions, but ever and anon settling down afresh. The remains of these form the "Cipit blocks" and "Cipit limestones", which were first observed by Von Richthofen amid Cassian marls on the slopes below Schlern. Mojsisovics recognized similar limestones appearing intermittently over the whole area eastward ... They, and not the mountains of Schlern dolomite, deserve the name of "Coral Reefs" in South Tyrol": Ogilvie (1894, p.7).

(5.8) It will be clear, that when discussing the possible relations between dolomite and coal, an exception must be made to the principle followed up to now in this book, not to discuss dolomite occurrences older than the Quaternary.

(5.9) "Von vornherein ist nur soviel sicher, daß sich der Dolomit bezw. Sphärosiderit aus wässriger Lösung gebildet hat, und daß der Prozeß in einer Zeit stattgefunden oder wenigstens begonnen hat, in der noch kein bedeutender Druck vorhanden war, da die Pflanzenteilchen bis in die zartesten Einzelheiten erhalten sind und keine Spur von Druck aufweisen": Mentzel (1904, p.1170).

(5.10) "Allerdings bilden ja die Wurzeln die Hauptmasse des Torfs. Als unterirdische Pflanzenteile, die nicht mit dem Sauerstoff der Luft in Berührung kamen, ja vielleicht sogar noch funktionsfähig waren als die dolomitischen Lösungen eindrangen, sind sie meist prächtig erhalten": Teichmüller (1955, pp.194-195).

(5.11) "Kohlensauren Kalk dagegen findet sich mit kohlensaurer Magnesia zuweilen in Harnsteinen neben anderen Bestandtheilen": Von Gorup von Besanez (1871, p.441). As early as 1807 Alemanni had analyzed 4 % $MgCO_3$ in a (human) calculus.

(5.12) According to the *Science Citation Index* the first time anyone cited the paper by Mansfield (1980) was six years later. On that occasion Machel & Mountjoy (1986) mentioned it as providing evidence in support of the possible role of organic compounds in catalyzing dolomite formation ("Urease-producing and/or uric acid-fermenting bacteria in carbonaceous sediments may promote dolomitization": Machel & Mountjoy, 1986, p.186; and "Other organic compounds, or ions like Li^+ and Fe^{2+} , are believed to catalyze dolomite formation (e.g., .. Mansfield, 1980 ..)": Machel & Mountjoy, 1986, p.187). In a veterinary journal Osborne et al. (1986) cited Mansfield's (1980) paper in order to demonstrate, that calculi consisting of calcium carbonate were not very seldom, but that dolomite had been found in the form of uroliths on only one rare occasion. After reporting on their finding of minute particles of dolomite, possibly of biogenic origin, Reid & Andersen (1988) referred to Mansfield's (1980) paper as the only known description of dolomite in the form of bladder stones. ("The three bodies found in the cervical nodes in case 1 and the particle in the gallbladder wall in case 4 indicate an endogenous biologic origin, and there are two known examples of recurrent dolomite bladder stones in dogs ...": Reid & Andersen, 1988, p.556.). Machel & Mountjoy (1990) used the observations of Mansfield (1980) to support their view, that growth rates for dolomite may be faster than usually thought. "For example, a dog grew dolomite uroliths up to 8 mm in diameter in less than 8 months at $T = 38\ ^oC$ and $P = 1$ atm (Mansfield 1980)..." (Machel & Mountjoy, 1990, p.1010). The paper by Gault (1993, p.248) stated truthfully "... there is a report of a bladder dolomite stone in a dog (Mansfield, 1980)". Not so the account by Gournay et al. (1999, p.243), because here "the canine" had died: "In a more unusual environment, dolomitic kidney stones were found in the bladder of a deceased canine (Mansfield, 1978)." In addition Mansfield would have suggested the participation of bacteria in the nucleation of dolomite: "Early investigators have noted the presence of bacteria with dolomite ... and others have speculated on mechanisms for the precipitation of dolomite in association with bacteria (e.g. Mansfield, 1978, 1979)" (Gournay et al., 1999, p.243). In the interpretation of Nielsen et al. (1997) the paper by Mansfield (1980) reporting modern dolomite as kidney stones in a Dalmatian dog would prove, that "... bacteria only create physico-chemical conditions for dolomite precipitation (... Mansfield, 1980 ...)" (Nielsen et al., 1997, p.192).

(5.13) As Osborne et al. (1972, p.320) put it: "... ureate uroliths have been associated with hereditary trait of dalmatian dogs to excrete large quantities of uric acid in urine".

(5.14) Ludwig & Theobald (1852, p.106) concluded: "... wir sind aber der Ansicht, daß die meisten an thierischen Resten armen dichten Kalksteine und vielleicht auch viele Dolomite unter Einwirkung ganz niederer Wasserpflanzen (Algen) entstanden seyen."

(5.15) But Murray & Irvine (1890, p.165) noted, that "... when carbonate of ammonia is added to sea-water, the greater proportion of the calcium in solution is after a time thrown down as carbonate of lime; whilst the magnesium salts remain in solution."

(5.16) "... life, except perhaps in its lowest forms, is entirely absent throughout the greater depths, where there is an abundant formation of sulphuretted hydrogen, and, in the deposits on the floor of the Black Sea, chemical precipitations of calcium carbonate and of sulphide of iron take place": Murray (1900, p.678).

(5.17) The name given originally by Beijerinck (1895) to the microorganism responsible for the process of sulfate reduction was *Sprillum desulfuricans*, because these bacteria resembled in more than one way the *Spirillum tenue* of Cohn (1867). At the same time Beijerinck (1895) suggested a possible resemblance with the *Bacterium hydrosulfureum ponticum* found by Zelinskij (1894) in mud from the Black Sea. (The latter organism had the capacity to reduce sulfate, much like the *Vibrio hydrosulphureus* found by Selinksy & Brussilowsky at the same location, as cited by Omeliansky, 1903.) The bacterium was named *Bacillus desulfuricans* by Saltet (1900), and *Microspira desulfuricans* by Migula (1900). Van Delden (1903) introduced a new species, *Microspora aestuarii*, isolated from the black mud of the tidal flats of the Dutch Waddenzee. The new species was not only adapted to seawater, but also distinguished itself from *Microspira desulfuricans* by a much stronger capacity to reduce sulfate. Holland (1920) and Elion (1924) have proposed to rename the genus into *Vibrio* in accordance with the nomenclature proposed by the Committee of the Society of American Bacteriologists. In 1938 Starkey suggested to rename the genus into *Sporovibrio* (this genus name has been used by for example Brisou, 1955 and Le Gall, 1963). After experiments had shown the capacity of fresh water strains of *Desulfovibrio desulfuricans* to adept to sea water and vice versa, Postgate & Campbell (1966) suggested to describe those strains of *D. desulfuricans* from marine or brackish origin incapable of growing in fresh water, as a sub-species with the name of *Desulfovibrio desulfuricans* subsp. *aestuarii*. Finally the suggestion of Kluyver & Van Niel (1936), to describe the genus as *Desulfovibrio* has been taken up by for example ZoBell (1946), and accepted as such by the Subcommittee on Sulfate-reducing Bacteria of the International Committee on Nomenclature of Bacteria (Postgate, 1967). [sources: Buchanan & Gibbons, 1974, pp.418-420 and Buchanan et al., 1966, p.527.]

(5.18) Beijerinck (1895) had described "malt extract" as a good organic medium for these anaerobe bacteria, but low concentrations K-malate, asparagine, Na-lactate, tartarate or peptone would do as well. Van Delden (1903) found the following combinations of carbon and nitrogen compounds well suited: sodium lactate + asparagine, sodium lactate + ammonium chloride, sodium lactate + glycocol, sodium malate + asparagine, sodium tartarate + asparagine, sodium citrate + asparagine, potassium succinate + asparagine, sodium succinate + asparagine, sodium acetate + asparagine, glucose + asparagine, glucose + ammonium chloride, glucose + peptone. Baars (1930) commented, that Van Delden's (1903) observations were somewhat sketchy, because pure cultures had not been used. For example a medium with glucose + peptone would initiate growth of *Bacillus coli*, which would convert the glucose into lactic acid to be used in turn by the sulfate reducing bacteria. The systematic investigation by Baars (1930) qualified the following hydrogen donors as being well suited for culturing sulfate reducing bacteria: ethyl alcohol, propyl alcohol, butyl alcohol, isobutyl alcohol, glycol, α-propylene glycol, glycerine, 2,3-butylene glycol, erythrite, mannite, glucose, mannose, fructose, formic acid, lactic acid, α-oxybutyric acid, ß-oxybutyric acid, mandelic acid, glyceric acid, racemic acid, fumaric acid, succinic acid, glutaric acid, malic acid, citric acid, α-alanine, asparagine, asparaginic acid.

(5.19) "Der Bacteriengehalt des Schlammes ist stets sehr viel grösser als der gleicher darüber vorhandener Wassermassen ...": Russell (1892, p.203).

(5.20) More recently Puri & Collier (1967) came to the same conclusion regarding the role of actinomycetes in the precipitation of calcium carbonate.

(5.21) After describing how he had found a carbonate precipitate (consisting of a carbonate with both calcium and magnesium) in a sample of black mud after 3½ years standing under anaerobic conditions, and finding a comparable mixed carbonate after 1½ years on top of a peptone-enriched mud sample from the Weissowo Lake, Nadson (1928, p.164) remarked: "Schenkt man gebührende Aufmerksamkeit der Zusammensetzung dieser Ablagerungen und ihrer Entstehung in Reinkulturen des Fäulnisbakteriums *Proteus vulgaris*, so könnten überhaupt diese Erscheinungen bei der Lösung des Problems des Kreislaufs des Magnesiums in Meeren eine wesentliche Rolle spielen."

(5.22) "... mais ceux-ci peuvent être mis dans la classe des pierres puantes, car ils exhalent une odeur très-fétide, lorsqu'ils sont frottés ou fracturés; cette même odeur appartient aux marbres statuaires grecs...": De Dolomieu (1791, p.7).

(5.23) "Welche chemischen Vorgänge die Ausscheidung von Dolomit und Kalk auf der Seine-Bank hervorriefen, läßt sich mit Sicherheit noch nicht angeben. Als sehr wahrscheinlich ist aber wohl anzunehmen, daß Produkte, die bei der Zersetzung von organischer Substanz entstanden, dabei von sehr wesentlicher Bedeutung sind": Philippi (1907, p.425).

(5.24) "Die rezenten oder subrezenten Dolomite treten nur in sehr organismenreichen Meeren auf": Linck (1909 B, p.230).

(5.25) "The sediment is visibly concentrated over areas of heavy plant growth, suggesting not only that carbonate minerals are in actual precipitation from the lake waters but that there is a direct link between plant life and precipitation": Skinner (1963, p.451).

VI. MAGNESITE & HUNTITE

(6.1) The chemical term magnesium hydroxide carbonate will be used here instead of the mineralogical name “hydromagnesite”. In my view the hydrated carbonates $MgCO_3.3\ H_2O$ or $MgCO_3.5\ H_2O$ are more likely candidates for the description “hydromagnesite”.

(6.2) "Bei den tensimetrischen Untersuchungen hat sich jedoch einwandfrei gezeigt, daß ... dieses basische Carbonat in der CO_2-Atmosphäre dann allmählich in den Magnesit übergeht": Gloss (1938, p.7).

(6.3) Horn (1969, p.455) claimed: "... daß sich $Mg(OH)_2$ in Gegenwart von feuchter Luft in $MgCO_3$ umwandelt. Diese Aussage wird durch die Praxis bestätigt." What exactly these confirmations were, was not elucidated by Horn.

(6.4) "Die Bildung von Magnesit ist infolge der CO_2-Empfindlichkeit der aktiven Erdalkalihydroxide durch die stufenweise Umkristallisation der angereicherten, wasserhaltigen Magnesiumverbindungen gegeben:

$$Mg(OH)_2 \rightarrow MgCO_3.3\,H_2O \rightarrow MgCO_3\ .$$

Dieser Vorgang ist sehr langsam, geht jedoch bereits bei sehr geringen CO_2-Partialdrucken im wässrigen Milieu ohne hohe Temperaturen vor sich...": Lesko (1972, p.65).

(6.5) "Wenn die Atmosphärilien oder kohlensäurehaltige Wasser auf Magnesiumsilikate einwirken, bildet sich nicht zunächst das stabile wasserfreie Karbonat, sondern metastabile wasserhaltige Karbonate, wie Lansfordit ... Bei Versuchen durch Verdunsten von Magnesiumbikarbonatlösungen erhält man $MgCO_3.3\ H_2O$, diese gehen dann in stabiles wasserfreies Karbonat über; letzteres bekommt man auch bei Temperatursteigerung": Doelter (1905, p.213).

(6.6) "Keine der beiden Verbindungen, die alle beide in der Natur vorkommen, ist beständig. Am unbeständigsten die an Wasser reichste Verbindung, der Lansfordit, der verhältnismässig rasch in Nesquehonit übergeht. Beide führen durch Abgabe des Wassers zur Bildung von Magnesit": Leitmeier (1909, p.118).

(6.7) "Infolge der grossen Instabilität konnte die Umkristallisierung des Magnesiumcarbonattrihydrat zu Magnesit an keiner Stelle ausbleiben": Rosza (1926, p.227).

(6.8) "Das Nernst sche Prinzip besagt: Wenn die konzentrierte Lösung eines Salzes auf ein festes Salz mit gemeinschaftlichem Ion (in unserem Falle die Kohlensäure) einwirkt, das leichter löslich ist, als das dermalen in Lösung befindliche Salz, so wird sich das schwerer lösliche Salz ausscheiden und leichter lösliches Salz aufgelöst werden. Dieses Gesetz hat Gültigkeit, wenn zwischen den Löslichkeiten der beiden Salze keinen allzugrossen Differenzen bestehen": Leitmeier (1916 B, p.161).

(6.9) "Es ist eine bekannte Thatsache, dass dichte Magnesite, die selbst manchmal noch viel Kieselerde enthalten, häufig in Serpentinen vorkommen; in letzteren sind aber die Hauptbestandtheile von Opal und Magnesit enthalten; könnten daher nicht Kohlensäure haltende Wasser die Zersetzung des Serpentins bewirkt und eine Trennung der Kiesel- und Talkerde herbeigeführt haben? Aus ersterer würde dann Opal hervorgegangen seyn, während letztere sich mit Kohlensäure zu Magnesit verbunden hätte": Blum (1843, p.128).

(6.10) "Wird eine wässrige Auflösung von Bittersalz lange und anhaltend in der Siedehitze mit fein zerpulvertem Kalkspath behandelt, so erfolgt eine langsame und schwache wechselseitige Zersetzung beider Verbindungen, wobei Gips und kohlensaure Bittererde, aber keine Spur von Dolomit, gebildet werden": Karsten (1848, p.567, FOOTNOTE). In order to check this claim, I have boiled 2.5 gr calcium carbonate (p.A., MERCK art.no. 2066) during 30 days in a solution of 0.5 Mol = 121 gr $MgSO_4.7\ H_2O$ (p.A., MERCK art.no. 5886). But what formed in my experiment was the mineral giorgiosite.

(6.11) Waeser (1923/1926) used "$MgCO_3$" in the equation cited here, but only a few sentences later in his patent application he mentioned "$MgCO_3$ or basic magnesium carbonate".

(6.12) Berzelius (1820 B) used the word "carbonate de magnésie" without describing it in chemical symbols such as $MgCO_3$, $MgCO_3.3\ H_2O$ or $Mg(OH)_2.4\ MgCO_3.4\ H_2O$. In this way confusion has been created, that will hamper any serious research. The objectionable practice is encountered especially in the patent literature, but in some scientific papers it is found as well. Such a mere semantic problem should be avoided. At the same time it must be realized, that for example Brongniart (1822) described a water-containing variety of magnesite ("Ainsi une espèce offre la combinaison de la magnésie et de l'eau, elle est nommée *magnésie hydratée*": Brongniart, 1822, p.293). What is now generally known as magnesite, was described by Brongniart (1822) as *magnésie effervescente* ("composée essentiellement de magnésie et d'acide carbonique").

(6.13) Because Steidtmann (1911 A) did not include any reference to a paper by Sorby on this matter (Sorby's name is not included in the footnote references of the two papers by Steidtmann, 1911 A,B), an attempt had to be made to trace any work of Sorby on magnesite. As a first step the titles of the 131 different papers written by H. C. Sorby between 1845 and 1899 [as listed in the CATALOGUE OF SCIENTIFIC PAPERS compiled and published by the Royal Society of London, Vols. V (1871), VIII (1879), XI (1896), and XVIII (1923)] were scanned for the word magnesite. No such title exists. The only title of possible interest found, was "On the magnesian limestone having been formed by the alteration of an ordinary calcareous deposit" (Brit.Assoc.Rept. 1856, pt.2, p.77). After locating the REPORT OF THE MEETING OF THE BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE FOR THE YEAR 1856 (as its official title reads), and finding on page 77 the note by Sorby, it was seen to contain merely some speculations on the possible origin of dolomite crystals within a Permian limestone. Not a word about the formation of magnesite there. But ultimately a second mentioning of the work by Sorby was found. Skeats (1905, p.136) stated: "Dr. Sorby found that magnesite and not dolomite, was formed by the action of magnesium-sulfate upon calcium-carbonate under high pressure." When looking through the paper by Skeats (1905) the reference to the publication by Sorby cannot be found either, but on page 136 Skeats (1905) made reference to a paper by Klement (1895). Perhaps a reference to the work of Sorby could be found there. In Klement's paper reference is made to a paper by Sorby (1879), which was printed in the *Quarterly Journal of the Geological Society of London*, Vol.35, pp.60-.. And indeed on pp.39-95 of the *Proceedings* to Vol.35 of that journal "The Anniversary Address of the President" is printed, in which Sorby (1879, p.73) made the following remark: "The statements made by previous experimenters led me to expect that on keeping a portion of Iceland spar for some time at a high temperature in a solution of chloride of magnesium, I should have obtained a pseudomorph of *dolomite*; but to my surprise I found that the external crust formed by replacement consisted almost entirely of carbonate of magnesia."

(6.14) My attempts to duplicate experiment 167 of Kazakov et al. (1959) failed. This had much to do with instrumental difficulties, which made it impossible for me at that time to attain the required amount of 490 mg/dm^3 of dissolved carbon dioxide. The amounts of carbon dioxide dissolved in 1 dm^3 of distilled water at room temperature measured by me, were in the order of 20 to 80 mg/dm^3. (Thereby using the same technique as Kazakov et al.,1959, i.e., the method of Fresenius, 1875.) According to Johnston (1916) water in equilibrium with the air contains 44 mg/dm^3 CO_2 dissolved in it (at 298 K). But Kendall (1916) measured as much as 1487 mg/dm^3 of carbon dioxide gas dissolved in water at $pCO_2 = 1$ bar (at a temperature of 298 K).

(6.15) The meaning of "*pierre cornéenne ou cacholong*", mentioned by Giobert (1804), was explained for example by Brochant (1801-1802): "Le *cacholong* est une calcédonie d'un blanc de lait": Vol.1, p.271. But Brochant's description of "*pierre cornéenne*" is not unequivocal, because on p.286 of Vol.1 Brochant gave its meaning as "Silex schistosus Lydius = Lidischer Stein = Probierstein", and on p.428 of Vol.1 as "Hornblende Schiefer = corneus fissilis" as defined by Wallerius (1772).

(6.16) Concerning *Thermaterites magnesius, Br. kürzer Magnesit (Reine Talkerde, W. Magnésie carbonatée, Hy. Magnesite, J.)* Breithaupt (1841, p.324) remarked: "Besteht wesentlich aus kohlens. Magnesia .. Vk. Scheint ein neueres Gebilde zu seyn und fast nur im Serpentin vorzukommen. Zu Baumgarten in Schlesien, Hrubschitz in Mähren, an der Gulsen in Steiermark..".

(6.17) Redlich (1909 A, p.302) spoke of "... stellenweise frisch entstandenen Magnesite". It has been pointed out by Redlich & Großpietsch (1913), that on various occasions Rumpf (1873 B, 1874, 1876) had suggested a sedimentary mode of formation for certain Austrian deposits of magnesite.

(6.18) The etymological curiosity "Montmilch" consists of a combination of the French word for mountain (mont) and the German word for milk (Milch): "Nach der Wortbedeutung versteht man indess unter Mondmilch, Bergmilch, ein weisses, im erdigen Zustande befindliches Fossil, welches mit Wasser gemengt als milchartige Flüssigkeit aus Bergklüften hervorquillt, und dann austrocknet" (Von Holger, 1837 B, p.415). Even though Von Holger (1837 B) wrote "Mond-" instead of "Mont-", from the addition of the German translation *Bergmilch* it becomes clear, that the word "Montmilch" should not be translated by "moonmilk". An additional argument against this practice has been given by Leube (1839), who wrote *Montmilch* with a T and explained, how *Mondmilch* written with a D was a concept from veterinary science ("In der Thierartzneikunde findet diese neuere Bildung, welche fälslich Mondmilch (lac lunae) genannt wird, häufige Verwendung": Leube, 1839, p.39). Emmerling's *Lehrbuch der Mineralogie* (1793) lists *Mondmilch* as one of the various synonyms for *Bergmilch* (other names for the same substance were for example: Bergmehl, Mehlkreide, Mehliger Kalk, Calcareus lactiformis Wern., Stenomarga Agricol., and Terra calcaria pura pulverulenta alba Born.). According to Heller (1966) the misunderstanding concerning the word "moonmilk" originated in 1555, when Gessner in his *Descriptio Montis Fracti sive Montis Pilati* described a *substantia alba & spumosa* from a cave known as "Manloch" (which means man hole, and not moon hole) with the words "*id est lac Lunae".*

(6.19) "Bekanntlich hat man bisher den Magnesit bloß amorphisch angetroffen, und nur in den Bitterspathen ist die kohlensaure Talkerde in Verbindung mit kohlensaurem Kalke krystallinisch gefunden worden": Stromeyer (1827, p.217). Bischof (1847, p.782) repeated Stromeyer's observation: "Es ist characteristisch, daß der Kieselsäurehaltige Magnesit nicht krystallisirt vorkommt...".

(6.20) "Doch sind alle Magnesiahydrocarbonate recht wenig beständig und wandeln sich durch allmähliche Wasserabgabe teils in Carbonate von niederigerem Wassergehalte, teils in das wasserfreie amorphe Carbonat um. Darauf beruht wohl vor allem ihre große Seltenheit": Leitmeier & D'Achiardi (1912, p.261).

(6.21) Hunt (1866) recalled, how Sainte-Claire Deville (1851) had drawn a parallel between dolomite and eitelite, and had even called the latter "soda-dolomite".

(6.22) Beckurts (1881 A) pointed out, that in the chemical industry a different process for the manufacture of magnesia alba had been adopted, capable of producing magnesia alba of a much higher purity. The process patented by Pattison (1841/1842) (see also the account of Stevenson et al., 1863), is based on the marked difference in the solubility of magnesium bicarbonate and that of calcium bicarbonate. The procedure starts out with pieces of dolomite, which have to be roasted and powdered. After mixing with water, carbon dioxide under a pressure of 5 to 6 bar is introduced into the reaction vessel. Part of the magnesium will be dissolved from the dolomite, but not all. As long as solid magnesium carbonate remains, only pure magnesium bicarbonate will be formed without a trace of calcium bicarbonate. The pure magnesium bicarbonate solution thus obtained, can be separated from the remaining solids by way of filtering. Magnesia alba precipitates when boiling the magnesium bicarbonate solution. Filtering and drying leads to the final result.

(6.23) "Quant au hydrocarbonates de composition variable, appelés *magnesia alba*, ... les études précédentes semblent indiques que ce sont de simples mélanges dans lesquels la quantité d'hydrate varie avec la dilution, la proportion des réactifs et la température de la réaction": Joulin (1873, pp.271-272).

(6.24) Brill (1905 B) had not used magnesite from nature in his experiments, but instead $MgCO_3.3\ H_2O$ heated so long in a carbon dioxide atmosphere at 498 K, that a neutral and anhydrous form of magnesium carbonate had formed ("... ein neutrales, wasserfreies $MgCO_3$": Brill, 1905 B, p.283).

(6.25) Trolle Wachtmeister (1828) explained, that a sample from the magnesite deposits at Hoboken (USA) had been sent to him, not only containing magnesite, but also a white powder looking much like *magnesia alba* ("... ein weißes pulverförmiges Mineral..., welches nur sparsam vorkommt und für Talkerdehydrat angesehen wurde": Trolle-Wachtmeister, 1828, p.521). Subsequent chemical analyses showed this powder to be identical with *magnesia alba*.

(6.26) "Kein Anzeichen fand sich in dieser Versuchsreihe, noch in den früheren, für basische Carbonate anderer Zusammensetzung, etwa ($MgO : CO_2 =$) 4 : 3 oder 3 : 2, wie sie doch von der Literatur ernstlich behandelt werden. Mit der Existenz eines Salzes 4 : 3 war am ehesten zu rechnen, da es angeblich als Mineral Hydromagnesit vorkommt und von mehreren Forschern ja noch in den letzten Jahren aufgeführt worden ist": Menzel & Brückner (1930, p.74).

VII. LABORATORY SYNTHESES

(7.1) Although duplication is of crucial importance, it is not often used in present-day geology. One may wonder about the reasons. Perhaps there is truth in the observation made by Broad & Wade (1985, p.215), that "... there is no credit to be gained from replicating someone else's experiment."

(7.2) "Die beschriebenen Versuche zeigen, daß eine Dolomitbildung bei gewöhnlicher Temperatur nicht stattfindet, wenn diejenigen Calcium- und Magnesiumverbindungen, welche man als Bestandtheile des Seewassers, der Boden-, der Quell- und Flusswässer kennt, aufeinander einwirken mit oder ohne Entweichen der freien und der im Bicarbonate locker gebundenen Kohlensäure": Hoppe-Seyler (1875, p.502).

(7.3) 1,4-Dioxane (tetrahydro-1,4-dioxine, or di-ethylene dioxide), $C_4H_8O_2$, is a colorless, inflammable, somewhat oily liquid with a flame-point at room temperature (285 K). On a commercial scale it is being produced since 1930 by the reaction between glycols such as di-ethylene glycol and an acid such as sulphuric acid at a temperature of about 433 K (I.G. Farbenindustrie, 1931/1933). Dioxane and its derivatives are typical man-made synthetics and have not yet been reported in significant amounts from plants or animals (Stumpf, 1956).

(7.4) "Tatsächlich gelang es mir, in dem Bodensatz der Lösung, bei Anwendung der Lembergschen Reaktion, das Vorhandensein von Dolomit, das sich auf optischem Wege nicht konstatieren lässt, nachzuweisen": Cornu (1907, p.597).

(7.5) "Bei kleinen Gehalten an Magnesiumchlorid war die Ausscheidungsgeschwindigkeit nicht verändert ... Bei allmählich gesteigertem Zusatz wurden die Formen mannigfaltiger... Die Krystalle hafteten zum Teil - im Gegensatz zu sonst - fest am Glase und lösten sich auffallend langsam in verdünnter Salzsäure, so daß möglicherweise Dolomit anwesend war": Kohlschütter & Egg (1925, p.477).

(7.6) "Löste man das Karbonat mit Salzsäure weg, so blieb der grösste Teil des dunkeln Saumes zurück. Bei stärkeren Vergrösserungen war zu erkennen, dass der zurückgebliebene Rest zum grössten Teil Ansammlungen lebender Bakterien war": Neher & Rohrer (1958, p.214).

(7.7) "Aus frischen Bohrkernen isolierte Bakterien vermochten bei anschliessenden Modellversuchen in rein anorganischem, stickstofffreiem Substrat die Bildung von Dolomitkristallen einzuleiten. Das Substrat wurde durch Auflösen eines Bohrkernstückes hergestellt, wobei die Lösungsmittel durch Fällungen und Ionenaustausch wieder ausgeschieden wurden. Nicht geimpfte, sowie mit sterilem Dolomit versehene Kontrollschalen zeigten keine Anzeichen einer derartigen Kristallisation. Es darf daher als erwiesen betrachtet werden, dass die in dem genannten Gneis auftretenden Dolomitkristalle unter der Mitwirkung der dort in einer Tiefe von rund 160 m lebend gefundenen Bakterien gebildet worden sind": Neher & Rohrer (1958, pp.214-215).

(7.8) "Bei der anaeroben Kultur in einem flüssigen Substrat, das durch Auflösung eines Bohrkernstückes von Biotitgneis erhalten wurde, konnte die Bildung von Dolomitkristallen festgestellt werden" and "Mit Bakterien konnten auf diese Weise Kristalle gezüchtet werden von mehr als 1 mm Grösse, die dann röntgenographisch durch Einkristallaufnahmen nach Präzessionsmethode von Buerger als reiner Dolomit identifiziert wurden": Neher & Rohrer (1959, p.624).

(7.9) Non-accessible to me, that is. Copies of this book, and most other Russian publications, were not available in the scientific libraries of The Netherlands. Of course it might have been possible to write to Russian libraries, but reading and writing in the Cyrillic alphabet is beyond my abilities.

(7.10) Concerning earlier experimental work by Usdowski (1967) Carpenter (1980, p.114) made the following remark: "Usdowski (1967) has presented a temperature-dependent constant, expressed as calcium-magnesium concentration ratios, for calcite-dolomite equilibrium in dilute and in NaCl-saturated solutions for the temperature range 50 - 180°C [= 323 to 453 K]. However, the experimental work on which this equation is based is insufficiently documented to permit other investigators to attempt repeating the experiments or to assess the validity of the work."

(7.11) "Eine Solution von kohlensauer Kalkerde in kohlensäurehaltigem Wasser und eine solche Solution von kohlensaurer Magnesia mischte ich in verschiedenen Verhältnisse mit einander und überliess alle diese Mischungen der Verdunstung bei gewöhnlicher Temperatur": Scheerer (1866, p.11).

(7.12) Although Scheerer (1866) did not mention it, he might have been inspired by the observations published by Moitessier (1863) on the low-temperature formation of dolomite crystals in a bottle with bicarbonate water from the source at Lamalou (located north of Narbonne, in the south-western part of the Languedoc, France) after standing for 6 to 7 months. The short note contained in the *Extraits des Procès-Verbaux* of the *Mémoires de l'Académie des Sciences et Lettres de Montpellier, Section des Sciences* (Vol.5, 1861-1863, p.446) reads: "À la suite d'un travail sur les eaux bicarbonatées du Vallon de Lamalou, M. Moitessier avait conservé, dans plusieurs bouteilles bouchées, des eaux de diverses sources. L'une d'elles, examinée après six à sept mois, renfermait des cristaux assez volumineux déposés au fond du vase. Ces cristaux sont transparents et incolorés; bien d'acolés les uns aux autres, ils laissent nettement apercevoir des faces de rhomboèdres qui atteignent dans quelques-uns 2 à 3 millimetres de côté. L'analyse chimique leur assigne la formule de la dolomie $MgOCO^2.CaOCO^2$.

	Expérience	Calcul
MgO	21.58	22.16
CaO	30.41	30.27

Cette substance, dont le poids était de 1 gr, 5 , s'était produite dans trois litres d'eau de la grande source de Lamalou l'Ancien; d'autres bouteilles receuillies à la même époque et placées dans les conditions en apparance identique, n'ont pas donné lieu au même phénomène. M. Moitessier attribute la formation de ces cristaux au dégagement très-lent de l'acide carbonique à travers quelques fissures du bouchon. L'analyse a démontré, en effet, qu'une portion considérable de ce gaz avait disparu dans le liquide où s'était déposée la dolomie, tandis que l'eau contenue dans les autres vases n'avait éprouvé aucune altération."

(7.13) "Die Lösungen der Dolomite verhalten sich nämlich beim Verdunsten, wie nachstehende Versuche lehren, wesentlich anders als man erwarten sollte. Sie verhalten sich einfach wie Gemenge der beiden Carbonate und setzen zu keiner Periode ihrer Verdunstung Bitterspath ab": Von Gorup-Besanez (1872, p.239).

(7.14) "Meine Versuche mit Mischungen wässriger Lösungen welche Calcium- und Magnesiumbicarbonat im Aequivalentverhältniss erhielten, stehen mit den Versuchen von Gorup-Besanez in vollster Uebereinstimmung und ich habe mich überhaupt durch eine Reihe von Versuchen, deren Einzelheiten hier anzuführen nutzlos wäre, überzeugt, dass weder Lösungen, welche beide Bicarbonate in irgend welchem Verhältniss enthalten, noch Lösungen, welche Magnesiumbicarbonat enthalten und im geschlossenen oder offenen Gefäß mehrere Monate in Berührung mit überschüssigem Calciumcarbonat stehen, auch nur Spuren von Dolomit geben": Hoppe-Seyler (1875, p.500).

(7.15) The calcium carbonate used in my experiments was, in this case as well as in all other experiments (unless stated otherwise), "Calciumcarbonat gefällt reinst, Art.2064 (Öab.9 , Ph.Belg. V, Port.IV , 2 Ed.)" of the MERCK Company (Darmstadt, Germany). The producer gave its composition as at minimum 99 % $CaCO_3$ and at maximum 0,3 % water soluble components. Analysis was given as:

chloride	0.03 %
sulphate	0.02
phosphate	0.02
heavy metals (as Pb)	0.001
iron	0.002
zinc	0.02
magnesium	0.05
barium, strontium (as Ba)	0.05
arsenic	0.0005
loss upon desiccation at 378 K	1

(7.16) The magnesium compound used in all instances was magnesium hydroxide carbonate (MERCK art.no. 5828). Because this compound is somewhat ill defined, the $MgCO_3$ content of the particular lot used, had to be measured. The titration (see p.45 in: "*Komplexometrische Bestimmungsmethoden mit Titriplex*" published by the MERCK Company) showed, that out of a random sample of 50 mg magnesium hydroxide carbonate 36 mg consisted of magnesium carbonate. In other words 72 % of this magnesium compound consisted of $MgCO_3$. Gasometric determination, performed with the "*Karbonatbombe*" described by Müller & Gastner(1971), showed, that 71 % of this magnesium hydroxide carbonate consisted of $MgCO_3$.

The chemical analysis of article number 5827 ("Magnesiumhydroxidcarbonat zur Analyse") of the MERCK Co. as given by its manufacturer, is as follows:

percentage (Mg)	min. 24 %
water soluble components	max. 0.5
in HCl insoluble components	0.01
chloride	0.005
sulfate	0.003
total nitrogen	0.001
heavy metals (as Pb)	0.001
copper	0.0005
iron	0.001
zinc	0.001
calcium	0.01
barium, strontium (as Ba)	0.001
sodium	0.1
potassium	0.002

(7.17) The ammonium sulfide (*Schwefelammon*) used by Pfaff (1894), once was a widely used laboratory ingredient, as for example Ostwald (1919) has documented. The compound forms, when bubbling H_2S gas through an ammonia solution. With an excess of H_2S predominantly NH_4HS will be formed; after adding an equal amount of ammonia, mainly $(NH_4)_2S$ will be present in the solution. Solutions of ammonium sulfide, open to the air will obtain rather quickly a yellow color, which is due to sulfur precipitation because of hydrolytic formation of H_2S, followed by the oxidation of H_2S to sulfur by oxygen from the air. Ammonium sulfide solutions were used in quantitative analysis, more in particular in the precipitation of metal ions. In addition it was used in organic chemistry, because it has a distinct reducing power.

Pfaff (1894) explained his choice for the use of hydrogen sulfide and ammonium sulfide, by pointing out, that H_2S invariably had been found in chemical analyses of sea water and that these two compounds originated upon the decomposition of protein-containing organic material. Such decomposition processes were known to lead to the reduction of the calcium sulfate and the magnesium sulfate present in seawater. Ammonia would also be set free in the process of decay. At the same time large quantities of carbon dioxide would be freed, and this CO_2 would associate itself with calcium and magnesium to give mixed Mg/Ca carbonates.

It is perhaps not too far fetched to suppose, that Pfaff (1894) had found his inspiration for the somewhat unusual choice of H_2S in one of the reactions of the Le Blanc soda process. The Chance-Claus reaction is used in that process to recover $CaCO_3$ from the so-called tank waste, according to

$$CaS + CO_2 + H_2O \rightarrow CaCO_3 + H_2S \;;$$

a reaction, that takes place in two steps:

$$CaS + H_2S \rightarrow Ca(HS)_2$$

$$Ca(HS)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2\,H_2S \;.$$

Perhaps Pfaff speculated, that a comparable reaction would take place, when using magnesium instead of calcium:

$$Mg(HS)_2 + CO_2 + H_2O \rightarrow MgCO_3 + 2\,H_2S \;.$$

It must be realized, that the Le Blanc soda process had been in use for a considerable time prior to 1894, when Pfaff made his claim. The process for the industrial production of sodium carbonate had been patented by Le Blanc in 1791 (see also the historical survey published in Hou, 1942).

(7.18) Murray & Irvine (1895) performed much the same experiment as that described by Pfaff (1894), but perhaps due to the excess carbon dioxide the initially formed sulfides dissolved into a bicarbonate solution: "Hydrosulphuric acid was passed into water holding carbonates of calcium and magnesium in suspension, and resulted in a yellowish solution of the sulphides of calcium and magnesium, carbonic acid being expelled. The sulphides in turn were decomposed by excess of carbonic acid, with the evolution of hydrosulphuric acid, bicarbonates being formed, the reaction apparently depending on which acid is in excess": Murray & Irvine (1895, p.497).

(7.19) "Da etwas mehr Material genommen worden war, wurde davon eine qualitative Analyse ausgeführt, die neben einer beträchtlichen Menge Magnesia etwas Kalk ergab": Pfaff (1894, p.490).

(7.20) "Es geht aus diesem Versuch hervor, daß zur Entstehung des Magnesits und Dolomits die Mitwirkung einer wasserentziehende Substanz, wie das Kochsalz es ist, nothwendig ist, vorausgesetzt, daß bei gewöhnlicher Temperatur gearbeitet wird": Pfaff (1894, p.496).

(7.21) The successful synthesis was described by Pfaff (1903, p.659) as follows: "Lässt man nun Kohlensäure durch Erhitzen auf längere Zeit in Wasser einwirken und überlässt die Lösung bei Gegenwart von $MgSO_4.7\ H_2O$, $MgCl_2$, $CaCl_2$ und NaCl erhaltenen $CaSO_4$ der langsamen Verdunstung bei 20 - 25^o (C) [= 293 to 298 K], so findet sich nach oftmaliger Widerhohlung ein in Wasser und verdünnter Chlorwasserstoffsäure in der Kälte unlöslicher Rückstand."

(7.22) Like in so many other instances in the older literature it is not clear, whether the percentages given are weight per cent or mol per cent. Unless stated otherwise, it will be assumed, that in these cases weight percentages were meant.

(7.23) "Sehr eingehend hat sich mit der Dolomitsynthese auch F.W. Pfaff beschäftigt; allein seine Untersuchungen, so interessant sie an und für sich sind, entfernen sich doch allzusehr von der Basis die die Nachahmung natürlicher Verhältnisse verlangt...": Leitmeier (1915, p.535).

(7.24) "Man löst 1 Molekül (2,4 gr) $MgCl_2$ und 1 Molekül $MgSO_4$ in 50 ccm Wasser und vermischt diese Lösung mit einer anderen, welche 1½ Moleküle Ammoniumsesquicarbonat in ca. 150 ccm Wasser enthält. Die Mischung bleibt klar. Hierauf setzt man eine Lösung von 1 Molekül $CaCl_2$ in ca. 100 ccm Wasser zu und schüttelt um": Linck (1909 B, p.235).

(7.25) "Daraus geht zunächst hervor, dass ein wasserfreies Mischsalz von Calcium- und Magnesiumcarbonat existiert, das aber nicht mit dem Dolomit zu identifizieren ist, für dessen Bildung jedoch im Meere alle Bedingungen gegeben sind": Linck (1909 B, p.237).

(7.26) "... paralischen Mooren, die also von Zeit zu Zeit vom Meerwasser überflutet werden...": Linck (1937, p.280).

(7.27) It was Geh. Hofrat Prof.o. Dr. Dr.h.c. Gottlob Linck, in 1909, who exclaimed (perhaps somewhat prematurely): "Ich glaube mit gutem Gewissen behaupten zu können: das Problem der Dolomitbildung ist prinzipiell gelöst !" (Z. Deut. geol. Gesellschaft, Bd.61, p.240).

(7.28) "Es ist möglich, daß sich hier Dolomit gebildet hat": Leitmeier (1910 A, p.56) and "Das Vorkommen von Dolomit konnte schon in weit reichlicherer Menge konstatiert werden, auch waren hier die für den Dolomit so sehr charakteristischen Hahnenkammformen entwickelt. Durch die Lemberg'sche Reaktion lassen sie sich deutlich von den Calcit- und Aragonitbildungen trennen": Leitmeier (1910 A, p.57).

(7.29) "Dolomit hatte sich auch in ganz kleinen feinen Partien ausgeschieden. Auch wurden einige ganz feinen Nädelchen gefunden, die deutlich schief auslöschten und dem Aussehen nach Gipsnädelchen gewesen sein dürften": Leitmeier (1910 A, p.58).

(7.30) "Dolomit bildet sich bei Einwirkung von ziemlich reichlichen Mengen von dissoziierten Magnesiumsalzen auf Calcit, so wie man es für die Dolomitbildung in der Natur z.T. annehmen kann. Diese Bildung geht allmählich vor sich und braucht ziemliche Zeit": Leitmeier (1910 A, p.62).

(7.31) In this case I have used a different quality of calcium carbonate: it was "Calciumcarbonat gefällt zur Analyse", MERCK article number 2066. According to the manufacturer it contained at least 99 % $CaCO_3$ (as measured in titration), and less than 0.005 % substances insoluble in HCl. The following maximum percentages of possible contamination's were given by the manufacturer:

chloride	0.005 %
sulfate	0.01
total nitrogen	0.001
barium	0.005
lead	0.0005
iron	0.001
potassium	0.01
copper	0.0005
magnesium	0.05
sodium	0.2
strontium	0.1 .

(7.32) Ricour (1960) stated, that the carbonate formed in Lalou's experiment could not have been dolomite. Ricour mentioned as evidence, that Messrs. Lévy, Nicolas and Pierrot, who had X-rayed Lalou's samples at the B.R.G.M. (Bureau des Recherches Géologiques et Minéralogiques at Orléans, France), had not detected any superstructure lines in the diffractograms. As a consequence the carbonates formed in Lalou's (1957) experiment could only have been magnesium calcite, as Ricour (1960) argued.

(7.33) This carbonate sand had been collected by me, while scuba diving at a depth of about 10 m in the Mediterranean Sea near Bandol (W. of Toulon, France). Microscopic examination showed grains 1 to 2 mm in diameter, consisting of fragments of gastropods, lamellibranchiata, spines and plates of echinoids, and fragments of calcareous algae. X-Ray diffraction showed this sediment to be composed of calcite, some magnesium calcite (with its main diffraction peak at 30.0 nm), aragonite, alpha-quartz, montmorillonite (140 nm) and halloysite (100 nm).

(7.34) The original recipe for artificial sea water as given by Lyman & Fleming (1940) is as follows: 23.477 g NaCl , 4.981 g $MgCl_2.6\ H_2O$, 3.917 g Na_2SO_4 , 1.102 g $CaCl_2.2\ H_2O$, 0.664 g KCl , 0.192 g $NaHCO_3$, 0.096 g KBr , 0.026 g H_3BO_3, 0.24 g $SrCl_2$ and 0.003 g NaF are added to water to make 1 dm^3 . In the present experiment, as well as in all others where this artificial seawater was used, the small amounts of KBr, H_3BO_3, $SrCl_2$ and NaF were left out.

(7.35) Three different reactions are possible, when using $Ca(NO_3)_2.4\ H_2O$, $MgSO_4.7\ H_2O$ and Na_2CO_3 . When adding calcium nitrate to a solution of magnesium sulfate, the precipitate will be calcium sulfate (gypsum, bassanite or anhydrite depending on the temperature of the solution). Adding magnesium sulfate to a solution of sodium carbonate leads to the precipitation of magnesium hydroxide carbonate. And when mixing calcium nitrate solution with sodium carbonate, the precipitate will be calcium carbonate. Nevertheless the instructions of Siegel (1961) are quite clear.

(7.36) It will be remembered, that Baron (1958) synthesized dolomite at a temperature of 423 K; Medlin (1959) synthesized it at temperatures from 473 to 523 K; Daughtry et al. (1962) performed successful synthesis at 483 K; Usdowski (1964) obtained dolomite in tests conducted at 453 K; Bubb & Perry (1968) at 473 K; Sureau (1974) created dolomite at a temperature of 423 K; Katz & Metthews (1977) synthesized it at temperatures between 525 and 568 K; and Sibley et al. (1987) obtained dolomite at a temperature of 491 K.

(7.37) In the original text the following description gives all the details: "Aus einer 2 m $(Ca,Mg)Cl_2$-Lösung wurde durch Fällung mit Na_2CO_3-Lösung ein feinkörniger, sphärolitischer Niederschlag erhalten. Die röntgenographische Prüfung ergab Dolomit" (Budzinski, 1961, p.31).

(7.38) Duplication of the experiments of Oppenheimer and Master was made possible through the generous help of Donald F. McNeill, at that time assistant to Prof. R. N. Ginsburg, University of Miami (Fisher Island Station), who kindly sent samples of algal mats, mangrove peat and pore water from mangrove peat deposits from the Miami area. His help is acknowledged with sincere gratitude.

(7.39) The peptone used, is described by its manufacturer as "peptone from meat, peptic digest": FLUKA art.70174 .

(7.40) At this place the experiments with living algae by Gebelein & Hoffmann (1971, 1973) should be mentioned once more. Gebelein & Hoffmann have tried to synthesize dolomite at room temperature with the aid of cultures of *Schizotrix calcicola*. Although magnesium was concentrated from the surrounding sea water medium 3- to 4-fold by these blue-green algae, only magnesium calcites with at maximum 20 mol % $MgCO_3$ resulted (possibly influenced by the addition of ammonium carbonate to the cultures). In their 200 different experiments Gebelein & Hoffmann did not obtain any trace of dolomite ("None of the experiments thus far have resulted in the formation of dolomite": Gebelein & Hoffmann, 1971, p.325). Therefore the conclusion was reached, that dolomite formation must be a "secondary process" not amenable to laboratory experimentation ("Dolomite formation under these conditions may occur over a time-span too long for experimentation": Gebelein & Hoffmann, 1971, p.325).

(7.41) Exactly how difficult it is to compare the laboratory observations made by Oppenheimer & Master (1963, 1965) to the situation in a particular outdoor environment, has been shown by Friedman & Foner (1982). The latter two authors set out to verify the presence, and measure the effects, of diurnal fluctuations in pH and Eh in two of the sea marginal pools of the Red Sea. However neither in the Sun Pool (Gulf of Eilat) nor in the sea-marginal pool at Ras Muhammed (on the southern tip of the Sinai Penninsula) any clear fluctuations in pH could be measured (due to technical difficulties no Eh measurements could be made in the field). Even after removing parts of the algal mats together with supernatant sea water from the pools and keeping these in glass beakers in the laboratory, no clear diurnal variations in pH could be observed. Attempts to create diurnal fluctuations in pH by way of exposing the beakers to alternating phases of artificial light and periods of complete darkness, met with no success. But the artificially introduced phases of light and dark were quite effective in changing the Eh from about - 380 mV to - 280 mV. Because Friedman & Foner (1982) had noted, that the algal mats emitted considerable amounts of hydrogen sulfide, in the field as well as in the laboratory, they concluded, that this production of H_2S must have blocked the effects on the pH of CO_2 production and CO_2 removal. The fluctuations in Eh, correlated with the alternating phases of dark and light, would find their origin in the production of oxygen/carbon dioxide during the photosynthesis of the algae.

(7.42) In his paper Liebermann (1967) spoke consistently of the solubility of magnesium carbonate, and cited in support the data obtained in experiments by Wattenberg & Timmermann (1937). It turns out from the *Kieler Meeresforschungen*, Bd.2 (1937), pp.81-94, that not the solubility of magnesite had been measured but instead that of magnesium carbonate trihydrate. The reason was that Wattenberg & Timmermann (1937, p.82) had the impression, that no equilibrium reactions involving magnesite had become known: "Für das wasserfreie Magnesiumkarbonat, also die Form, die in der Natur als Magnesit vorkommt, sind dagegen die Gleichgewichtsbedingungen mit einer wäßrigen Lösung noch unbekannt, und es fragt sich, ob sie überhaupt realisierbar sind."

(7.43) It is of some significance to note here, that Britton (1926) has pointed out, that in order to get a precipitate of $MgCO_3.3\ H_2O$ instead of one of magnesium hydroxide carbonate "... a precipitant must be used which will supply the necessary carbonate ions without introducing the concentration of hydroxyl ions that causes the precipitation of magnesium hydroxide" (Britton, 1926, p.146). Because Britton had established at an earlier time, that magnesium hydroxide carbonate will start precipitating at the same pH at which $Mg(OH)_2$ starts precipitating, he concluded: "As magnesium hydroxide is precipitated at pH = 10.5 , it is obvious that sodium bicarbonate (pH = 8.7), even although added in large excess, cannot produce the corresponding concentration of hydrogen ions, and therefore cannot precipitate basic magnesium carbonate. It can, however, supply the carbonate ions that, provided that the magnesium salt solution is sufficiently concentrated, will cause magnesium carbonate to separate. Boussingault (1825) found that sodium sesquicarbonate, $Na_2CO_3.2\ NaHCO_3$, also could be used for this purpose. The data of Auerbach & Pick (1911) show that the pH of such a mixture is approximately 9.9 , which is just a little below the value required for the precipitation of the hydroxide" (Britton, 1926, p.146).

(7.44) It is perhaps good to remember the suggestion by Bäckström (1921) concerning the active role of urea. Although his explanation concerned the use of urea in the high-temperature experiments by Bunsen (1847) and Bourgeois (1886 A), and postulated the hydrolysis of urea into ammonium carbonate to take place at the high temperatures used (around 413 K), Bäckström (1921) stressed the importance of the thus formed *carbonate* groups. At the same time the suggestion was made, that ammonium ions played an active role in the precipitation of carbonates such as $CaCO_3$, $MgCO_3$, $SrCO_3$, $BaCO_3$, $CdCO_3$ and $PbCO_3$ in the experiments of Bourgeois (1886 A). But that role could not be played by the ammonium ions of NH_4Cl, because experiments using this compound had failed. According to Bäckström (1921) hydrolysis of NH_4Cl caused slightly acidic conditions detrimental to any attempts to precipitate carbonates.

(7.45) The thermal dissociation of magnesium hydroxide carbonate will set in at a temperature of about 973 K (Kerr & Kulp, 1948; Rowland & Beck, 1952). According to Kallauner (1913) dolomite starts its thermal decomposition at about 773 K; Mitchell (1923 A) measured dolomite decomposition to start at about the same temperature, and Hedvall (1925) gave 853 K as the temperature, at which dolomite starts its thermal decomposition.

(7.46) The information contained in this section has been kindly supplied by Dr.H.J. McCunn in the form of two comprehensive letters to me (one dated 19 March 1974 and one dated 11 March 1975). It had been McCunn's (1972) paper, that had aroused my interest in his work. In April 1976 an abstract entitled "Origin of Dolomite - Model Based on Cyclic Interaction of Continental Soda-Rich Waters with Concentrated Sea Water" by Dr. McCunn appeared in the Bull. Am. Assoc. Petrol. Geol. (Vol.60, p.696). By the end of 1976 I received a copy of a typescript of his planned paper "Origin of dolomite: A depositional model based on the decomposition of hydrated sulphates and magnesium chloride by bicarbonate salts derived from plant decay" (64 pages). This typescript carries a stamp with the text "Editorial Dept. AAPG : Received Oct. 20 1975"; but as far as I am aware, it has never been published [at least the CHEMICAL ABSTRACTS Vols. 76(1972) - 131(1999), do not list it, nor does the Science Finder list it for the years 1999 – 2002.]. Although strictly speaking the letters and the typescript are not true publications, it was felt, that these communications had to be included here. If only to show my gratitude for the kind co-operation.

(7.47) Authors such as for example Mazé (1903) and Söhngen (1906) have shown, how bacterial decomposition of plant leaves leads in general to large amounts of carbon dioxide and methane.

(7.48) The ascorbic acid used in my experiments was L(+)-ascorbic acid of "pro Analysi" quality (MERCK art.no. 127).

(7.49) For example Von Gorup-Besanez (1851), Scheerer (1866), Hoppe-Seyler (1875) and Pfaff (1894) all had tried to produce dolomite under conditions of room temperature and atmospheric pressure.

(7.50) Various authors have mentioned the 1967 paper by Liebermann, not always in converging ways. To give some examples: Taylor & Illing (1969, p.103) cited Liebermann's experiment as providing evidence on the low-temperature formation of magnesium calcite ("Meanwhile, evidence for the precipitation of magnesian calcite at low temperatures in the laboratory was also forthcoming (... Liebermann, 1967)". Von Brand et al. (1969) have mentioned Liebermann's (1967) claim on the low-temperature synthesis of dolomite, but added that the salinity used was perhaps somewhat "exaggerated". ["It is well known that synthesis of crystalline dolomite in the laboratory has been achieved in the past only at high temperatures and pressures, but more recently synthesis succeeded also at quite low temperatures under conditions exaggerating, but at least approximating those prevailing in high-salinity sea water (Liebermann, 1967)": Von Brand et al., 1969, p.303.] Davies et al. (1977, p.207) stated: "... Liebermann (1967) showed experimentally that dolomitic carbonates precipitate around pH 8.1.." and: "... almost all workers have explained the origin of dolomite by variations in the cationic ratio Mg^{2+}/Ca^{2+} (... Liebermann, 1967)" (p.208). Ohde & Kitano (1978, p.115) recalled: "Many studies have been carried out to know the factors controlling the formation of sedimentary dolomites (... Liebermann, 1967...)". Ricketts (1980, p.963) stated, that "A variety of experimental techniques has been used which have met with varying degrees of success; these include precipitation from modified sea water solutions (... Liebermann, 1967)." Morrow (1982 A, p.9) remarked: "Liebermann (1967) also synthesized dolomite from artificial solutions more saline than sea water and with a Mg/Ca ratio approximately that of sea water but with relatively high pH and CO_3^{2-} concentration." Oomori et al. (1983, p.147) wrote: "Syntheses of Mg bearing carbonates were performed by ... Liebermann (1967)". Morrow & Ricketts (1986, p.408) noted: "Prior to 1980 three possible kinetic factors had been identified: ... 2) the carbonate ion concentration (Liebermann, 1967...)". Oomori & Kitano (1987, p.59) made the somewhat disparaging remark: "Syntheses of magnesian calcite and protodolomite from aqueous solutions at low temperatures and pressures have also been attempted by ... Liebermann (1967)". Oomori et al. (1987, p.327) repeated: "Synthetic studies of Mg-bearing carbonates at low temperature were also carried out by ... Liebermann (1967)". Sun (1994, p. 398) stressed the possible role of the Mg/Ca ratio with the words: "A second effect of an ice-free global climate is salinity and Mg/Ca ratio, which are the two overriding controls on dolomitization (Liebermann, 1967; Folk & Land, 1975 ...)". In their account Brady et al. (1996, p.727) claimed: "To achieve discernable reaction in the laboratory, high temperatures (200 - 300 °C) ... and/or extreme supersaturation (e.g., Liebermann, 1967 ...) are required". But in general these authors thought it sufficient to mention Liebermann's claim on the low-temperature synthesis of dolomite in one way or another, but would not go so far as to duplicate the experiments [e.g., "We have not attempted to reproduce the experiments of Liebermann (1967), Mirsal and Zankl (1985), or Kocurko (1986), who have reported forming ordered dolomite at low temperatures": Sibley et al., 1994, p.630.]

VIII. MECHANISM OF DOLOMITE FORMATION

(8.1) "Il y a donc toujours un retard; ces dissolutions ne commencent à déposer des cristaux de sel modifié que lorsque leur température a été abaissée d'un certain nombre de degrées au-dessous de la température qui limite ou détermine leur point de saturation": Loewel (1850, p.92).

(8.2) "La sursaturation d'un sel cesse par le contact d'un de ses isomorphes à l'état cristallisé, pourvu cependent que la solution soit dans un certain état de concentration dont la grandeur peut varier d'un isomorphe à l'autre": Lecoq de Boisbaudran (1866, p.95).

(8.3) "On constate, en effet, que les solutions fortement sujettes à la sursaturation, lorsqu'elles cristallisent spontanément, ne fournissent pas, le plus souvent, l'espèce chimique employée à preparer la solution, mais des cristaux de forme différente, de solubilité plus grande et contenant souvent une quantité différente d'eau de cristallisation": De Coppet (1875, p.281). The reverse of this observation, i.e., that a solution of for example sodium sulfate hydrate (Glauber's salt) may well crystallize into several forms including the anhydrous Na_2SO_4 , had been published earlier by Ziz (1815).

(8.4) "Aus Flüssigkeiten, die sich erheblich unterkühlen lassen, scheidet sich spontan in der Regel nicht eine Art von Krystallen, sondern gewöhnlich mehrere polymorphe Arten ab": Tammann (1898, pp.441-442).

(8.5) "Die spontane Kristallisation unterkühlter Flüssigkeiten ist ein Vorgang, der in einzelnen Punkte der Flüssigkeit eintritt und in hohen Maße dem Zufall unterworfen ist. Diese beiden Eigentümlichkeiten der spontanen Kristallisation weisen auf eine atomistische Struktur der Flüssigkeiten hin": Othmer (1915, p.209).

(8.6) Tammann (1903) described his method for counting the number of nucleï as follows: the compound used should first be melted (in most cases organic compounds with melting points only slightly above room temperature were chosen). Rapid cooling to the desired degree of undercooling is the next step, followed by keeping the undercooled liquid at this temperature for a certain period of time. It is during this phase of the experiment, that the nucleï are being formed. The third step made it possible to actually count the number of nucleï formed: the undercooled liquid should be cooled quickly to a markedly lower temperature in order to speed up subsequent growth of the now formed nucleï. As a result a clearly recognizable number of crystal aggregates would form, ready to be counted. Tammann (1898) had tested some 150 different organic compounds, but his student Othmer (1915) restricted his tests to compounds such as piperonal (heliotropine or 3,4-methylenedioxidebenzaldehyde), allylthiourea, phenol, salol (phenylsalicylate), stearic acid, lauric acid, naphtalene, bromonitrobenzene, palmitic acid, myristic acid, glycerylmyristate and tripalmitin.

(8.7) Kornfeld (1916) introduced the useful concept of *Ueberschreitungserscheinungen* (= overstepping phenomena) to delineate crystallization from undercooled melts or from supersaturated solutions. Haber (1922) declared, that precipitation from supersaturated solutions in general, whether leading to crystalline or amorphous substances, would be the result of Ueberschreitungsvorgänge (= overstepping processes).

(8.8) Such concentration fluctuations possess both an amplitude and a frequency, as has been pointed out by Von Smulochowski (1916, p.560): "In der Theorie der Konzentrationsschwankungen handelt es sich um zweierlei Probleme, einerseits um die wahrscheinliche Größe der momentanen Abweichung der Konzentration in einem gewissen Volumelement vom durchschnittlichen Zustand, andererseits um die zeitliche Veränderlichkeit jener Abweichungen oder, wie man kurz sagen kann, um die *Schwankungsgröße* und die *Schwankungsgeschwindigkeit*."

(8.9) Einstein (1910, pp.1282-1283) formulated that conclusion in the following manner: "Wegen der Unregelmässigkeit der Wärmebewegung wird die Dichte ρ in einem Punkte der Flüssigkeit von ρ_o im allgemeinen verschieden sein", and similarly on p.1285: "Nachdem wir aus dem Boltzmann'schen Prinzip das statistische Gesetz ermittelt haben, nachdem welchem die Dichte einer einheitlichen Substanz ... mit dem Orte variiert...".

(8.10) "Nun kann ein Gebilde offenbar mehrere stabile Gleichgewichtszustände besitzen, welche verschiedene Minima der Energie entsprechen, und die durch relative Maxima getrennt sind": Ostwald (1893, p.516), "Jede dieser Lagen ist die eines stabilen Gleichgewichts, und die zunehmende Stabilität entspricht der abnehmenden Energie. Um einen kurzen Namen für solche Gebilde zu haben, welche zwar stabil sind, für welche aber andere Zustände grösserer Stabilität möglich bleiben, will ich sie metastabile Gebilde und ihre Zustände metastabile Zustände nennen. Jeder metastabile Zustand eines Gebildes ist durch eine bestimmte endliche Energiemenge charakterisiert, welche ihm zugeführt werden muss, damit es in eine Lage grösserer Stabilität übergehen kann": Ostwald (1893, p.517).

(8.11) "Ich habe a.a.O. vorgeschlagen, solche Zustände metastabil zu nennen ... Hier möchte ich diesen Namen ausdrücklich auf solche Zustände beschränkt wissen, wie sie eben als unmittelbar auf die Überschreitung der Schmelztemperatur folgend geschildert sind, d.h. solche Zustände, in denen keine andere Ursache, als die Berührung mit der anderen Phase, die Umwandlung bewirkt": Ostwald (1897, p.302). Generally it is assumed, that Ostwald (1893, 1897) was the first to define metastability. Although perhaps Ostwald did indeed use the word "metastable" for the first time, others had been quite aware of the phenomenon as such. To mention only one example: in the *Leçons sur l'affinité* of Sainte-Claire Deville (1867, p.81) the following "Résumé des expériences de M. Gernez" can be found: "Une solution sursaturée, comme un liquide surfondu, est dans un état d'équilibre peu stable que l'on peut détruire dans des circonstances si singulières en apparance, si capricieuses, que leur explication a donné lieu aux hypothèses les plus diverses." And in more detail: "Comme pour les corps surfondus, une parcelle infiniment petite de la matière dissoute ou d'une substance isomorphe suffit pour produire la solidification qui est accompagnée d'un dégagement de chaleur souvent considérable" (Sainte-Claire Deville, 1867, p.81). In addition Lecoq de Boisbaudran (1866), Baumhauer (1872) and Thomson (1879) had described the capacity of isomorphous salts to initiate crystallization from supersaturated solutions. On p.773 of Volume II of his *Lehrbuch der allgemeinen Chemie* Ostwald (1902) revealed, that the actual inspiration for distinguishing two different kinds of supersaturated solutions came from the observations made by Loewel (1850).

(8.12) "Solche Erscheinungen treten auch beim Schmelzen, beim Verdichten von Dämpfen, ja sogar bei homogenen chemischen Reaktionen überaus häufig auf, und ich möchte die Gesamtheit der bisherigen Erfahrungen über den Gegenstand in den allgemeinen Satz zusammenfassen, dass beim Verlassen irgend eines Zustandes und dem Übergang in einen stabileren nicht der unter den vorhandenen Verhältnissen stabilste aufgesucht wird, sondern der nächstliegende.": Ostwald (1897, pp.306-307).

(8.13) "Während unter idealen Bedingungen die Metastabilitätsgrenze für die metastabile Form bei höherer Temperatur liegt, als diejenige für die stabile Form, kann durch geeignete kritische Stellen die Grenze für letztere über diejenige für die unbeständigere Modification verschoben werden, und somit die stabile Form zuerst krystallisiren. Die krystallisation der verschiedenen Modificationen wird also durch kritische Stellen verschiedenartiger Beschaffenheit ausgelöst": Schaum & Schoenbeck (1902, p.659).

(8.14) In various laboratory experiments on the crystallization of CdI_2 , Cohen & Moesveld (1920) noted, how the nucleation rate of each of the two modifications from supersaturated solutions was influenced by the presence of other compounds in the solution. In addition Cohen & Moesveld (1920) observed, that the presence of nucleï of the stable modification was not able to exert its influence, when crystallization took place from highly supersaturated solutions. ("Dieser Versuch, zeigt dass auch die stabile Modifikation Keimwirkung fast nicht ausübt, wenn man sie einer stark übersättigten Lösung zusetzt": Cohen & Moesveld, 1920, p.494). Later Cohen & Van Hengel (1932) pointed out, how the calorimeter measurements of Berthelot (1875) must have been influenced by the presence of several modifications of $BaCO_3$.

(8.15) "Da bei geringen Unterkühlungen die Anzahl von Kristallisationszentren gewöhnlich sehr gering ist, so hat es, wenn man kleine Flüssigkeitsmengen untersucht, häufig den Anschein, als ob sich bis zu einer gewissen Temperatur unterhalb des Schmelzpunktes keine Kristallisationszentren bilden. Diese scheinbare Temperaturgrenze hat W. Ostwald als Grenze der Metastabilität bezeichnet": Tammann (1903, p.149).

(8.16) As Gibbs(1876/1878; reprinted pp.58-59) explained: "... if the system is in a state in which its entropy is greater than in any other state of the same energy, it is evidently in equilibrium, as any change of state must involve either a decrease of entropy or an increase of energy, which are alike impossible for an isolated system", and "We may add that this is a case of *stable* equilibrium, as no infinitely small cause (whether relating to a variation of the initial state or to the action of any external bodies) can produce a finite change of state, as this would involve a finite decrease of entropy or increase of energy" (Gibbs, 1876/1878; reprinted p.59).

(8.17) "We started, indeed with the assumption that we might neglect the part of the energy, etc., depending upon the surfaces separating heterogeneous masses. Now, in many cases, and for many purposes, as, in general, when the masses are large, such an assumption is quite legitimate, but in the case of these masses which are formed within or among substances of different nature or state, and which at their first formation must be infinitely small, the same assumption is evidently entirely inadmissable, as the surfaces must be regarded as inifintely large in proportion to the masses. We shall see hereafter what modifications are necessary in our formulæ in order to include the parts of the energy, etc., which are due to the surfaces..." Gibbs (1876/1878; reprinted p.75).

(8.18) "Nun sind aber die sich bildenden ersten Teilchen der stabileren Phase außerordentlich klein, infolgedessen wird, wie Gibbs bemerkt, die Energie der Oberflächenbildung pro Masseneinheit einen der Entropiedifferenz gegenüber nicht zu vernachlässigen Wert besitzen. Der Wert dieser Oberflächenenergie ist aber auch, wenn die Entropiedifferenz bekannt ist, nicht bestimmbar, und infolgedessen ist das Gibbssche Stabilitätsmaß: Entropiedifferenz plus Energie der Oberflächenbildung, dividiert durch die absolute Temperatur, in praxi nicht verwendbar": Tammann(1903, p.156).

(8.19): "Nach ihr dürften dauernd übersättigten Lösungen (oder dauernd überkaltete Schmelzen), überhaupt nicht möglich sein, da niemals die Möglichkeit eines günstigen Zusammentreffens der erforderlichen Molekeln ausgeschlossen werden kann": Ostwald (1902 A, p.753).

(8.20): "Man kann eine Lösung nun durch sehr geringe Änderungen der Temperatur und Konzentration aus Umständen, unter denen sie sehr bald freiwillig krystallisiert, in solche bringen, unter denen die freiwillige Kristallisation in absehbarer Zeit überhaupt nicht stattfindet, während die aus den genannten Grössen abzuleitende Wahrscheinlichkeit der Zusammenstösse sich nur um einen kleinen Bruchteil geändert hat": Ostwald (1902, p.753).

(8.21): "Il ne faut pas perdre de vue que la sursaturation est *relative*. Une solution saline peut être, à la fois, sursaturée par rapport à une des formes du sel, et non saturée par rapport à une autre de ces formes": De Coppet (1907, p.469).

(8.22): "Un seul et même liquide surfondu ou sursaturée peut, *à la même température*, et quelquefois *au même instant*, donner naissance, par cristallisation spontanée, à deux phases cristallines distinctes": De Coppet (1907, p.469).

(8.23) "Man hat in Verkennung des Gesetzes der großen Zahlen geglaubt, ein Unterkühlungsgebiet annehmen zu dürfen, in dem die spontane Kristallisation überhaupt nicht vor sich ginge. Diesen fundamentalen Irrtum, der seine Wurzeln in einer Nichtachtung der Atomistik hatte, habe ich im ersten Teil meiner Arbeit durch Versuche direkt widerlegen können": Othmer (1915, p.209).

(8.24) "Diese merkwürdige Erscheinung ist auf eine eigentümliche Abhängigkeit der Kernzahle von der Dauer der Unterkühlung zurückzuführen. Bedingung für das Auftreten instabiler Formen ist, daß die Kernzahl der instabileren Form bei der betreffenden Unterkühlung erheblich größer ist als die der stabileren Form, und daß die Kernzahl der stabileren Form bei ihrer Entstehung aus der instabileren sehr gering ist. Wenn neben diesen Bedingungen auch noch die lineare Kristallisationsgeschwindigkeit der instabileren Form viel größer ist als die der stabileren, so sind die Bedingungen für das ausschließliche Enstehen der instabileren Form besonders günstig": Othmer (1915, pp.237-238).

(8.25) Writing on the possible application of thermodynamics to irreversible chemical reactions, Nernst (1921, p.754) stated: "Nur über eine, vielleicht bedeutungsvolle Regel verfügen wir, die bereits 1861 von Jul. Thomsen (vgl. dazu Bjerrum, Ber. deutsch. chem. Ges., **42**, 4975 [1909]) aufgestellt wurde; hiernach haben Reaktionen, die mit kleiner Wärmetönung verlaufen, im allgemeinen eine höhere Reaktionsgeschwindigkeit, so daß die entwickelte Wärme also ein Minimum wird; diese Regel erklärt, daß Verbindungen sich um so leichter bilden (in der Regel, keineswegs immer!), je instabiler sie sind, wofür die organische Chemie viele Beispiele liefert. Doch sind diese Verhältnisse noch wenig geklärt und es ist nicht statthaft, wie neuerdings geschehen, hier von einem "Stufengesetz" sprechen zu wollen." [Reading Bjerrum's (1909) obituary for Hans Peter Jürgen Julius Thomsen reveals, how Thomsen's statement of the *principe du travail maximum* appeared in print in 1852, that is to say 17 years prior to Berthelot's(1869) paper. Although the 1852 paper by Thomsen appeared in the Danish language, two papers enlarging on the same subject in the German language were printed in 1853 and 1854 in *Poggendorff's Annalen*.] It must be stressed, that Ostwald (1902 A, p.781) reached a comparable conclusion regarding the relation between stability and solubility: "Die Löslichkeit verschiedener fester Stoffe, die mit demselben Lösungsmittel übereinstimmende Lösungen ergeben können, folgt der umgekehrten Reihenfolge ihrer Beständigkeit; die beständigste Form giebt also die verdünnteste Lösung, und die unbeständigste die konzentrierteste." On p.744 of Volume II, Part II of his textbook on general inorganic chemistry Ostwald (1902 A) attributed this observation to Lecoq de Boisbaudran (1866).

(8.26) "Die Thermodynamik gibt die Begründung durch die Schwankungen der freien Energie": Haber (1922, p.1722).

(8.27) "Schwankungen der freien Energie von ausreichender Größe und Dauer bedingen, daß einzelne kleinste, geordnete Aggregate dem Rückzerfall in ungeordnete Moleküle entgehen und sich zu größeren Keimen auswachsen": Haber (1922, p.1723).

(8.28) "Die Kapillarkräfte sind die alleinige Ursache für die Metastabilität": Volmer & Weber (1926, p.277).

(8.29) "Der enorm starke Abfall der *e*-Potenz mit steigender Übersättigung ist die Ursache für die Beobachtung einer scheinbaren metastabilen Grenze": Volmer & Weber (1926, p.285). And "Die heutige Auffassung geht - bekräftigt durch Versuche von Tammann, Othmer, Frl. Kornfeld und anderen - dahin, die sogenannte metastabile Grenze anzusehen als vorgetäuscht durch einen schnellen Abfall der Keimbildungshäufigkeit mit abnehmender Übersättigung": Volmer (1929, p.556).

(8.30) "Befindet sich eine übersättigte Lösung in der Nähe der metastabilen Grenze, so scheidet sie leicht freiwillig Kristalle ab, wenn sie wechselnden Einflüssen, wie Verschiedenheiten des Druckes, der Temperatur, örtlicher Verdunstung u. dgl. ausgsetzt ist. Denn da jede Überschreitung der Grenze, wenn sie auch an einem noch so kleinen Orte stattfindet, alsbald an dieser Stelle Kristallisation hervorrufen kann, welche sich dann durch die ganze Masse fortsetzt...": Volmer (1939, p.7).

(8.31) Writing on the stability of metastable solutions, Volmer (1939, pp.7-8) stated: "... so ist für die Beständigkeit einer solchen Lösung nicht der Mittelwert der Zustandsgrössen, wie ihn unsere gewöhnlichen Messinstrumente angeben, entscheidend, sondern sie reagiert auf die vorhandenen minimalsten Abweichungen, welche im Sinne der Annäherung an die Grenze liegen". And added: "Ihre Beständigkeit ist daher von dem Betrage abhängig, welche diese Abweichungen annehmen können." Volmer (1939, p.8).

(8.32) "Nur die Anlagerung des ersten Bausteines ... erfordert eine Schwankung der freien Energie. Gegenüber allen folgenden Bausteinen der Reihe ist die Gleichgewichtsumgebung übersättigt": Stranski & Kaischew (1935, p.397); and "Alle Versuche, die Kristallkeimbildung und das Kristallwachstum theoretisch zu erfassen, führen zu Ausdrücken, deren wesentliche Faktoren Exponentialfunktionen von Energieschwellen (den bei den spontanen Vorgängen der Keimbildung aufzubringenden Arbeiten) darstellen": Stranski (1950, p.289).

(8.33) "Das Entstehen und Weiterwachsen von Kristallen zeigt ausgeprägter und reichhaltiger die Merkmale der Autokatalyse, als es bei Flüssigkeitströpfchen der Fall ist. Der ersten und größten Energieschwelle beim Bilden des dreidimensionalen Keims folgen die kleineren bei der Bildung einzelner Netzebenen und -reihen, wobei der Kristall einmal mit einer glatten und das zweite Mal mit einer gestuften Oberfläche seine eigene Wachstumsreaktion beschleunigt": Stranski (1950, p.291).

(8.34) In order to explain the Second Law of thermodynamics in a simple way Clausius (1865) made the assumption, that changes in the system were taking place in a *cyclic process*, so that the system would return to its initial state again. In this definition of the Second Law dQ is an inifinitesimal amount of the heat absorbed, and T is Kelvin temperature. In the case of *reversible* processes the definition would be given by:

$$\int \frac{dQ}{T} = 0$$

And in the case of *irreversible* processes the equation would change into:

$$\int \frac{dQ}{T} < 0$$

The definition of the entropy concept, was introduced by Clausius (1865) by way of the equation:

$$\int \frac{dQ}{T} = S - S_o$$

in which S was described initially as the *Verwandlungsinhalt* of a system, but immediately renamed into *entropy*.

In his 1854 paper Clausius had used an equation, in which the differential dQ was negative. That definition resulted from a model in which the amount of heat taken up by the system was negative, because the heat was thought to have been withdrawn from "a neighbouring heat reservoir". As a consequence the definition of entropy would have to be changed into

$$\int \frac{dQ}{T} \geq 0$$

, when using a negative differential dQ. But in his 1865 paper Clausius liked to consider an amount of heat absorbed by a system as positive, and an amount of heat given off as negative. In 1904 Planck pointed out, that according to Gibbs entropy was by definition the negative logarithm of probability, whereas Boltzmann had defined entropy as the positive value of the very same logarithm ("Während nämlich Boltzmann die Entropie durch den Logarithmus der Wahrscheinlichkeit definiert, is die Entropie nach der ersten Definition von Gibbs der negativ genommene mittlere Logarithmus der Wahrscheinlichkeit. Bei irreveriblen Prozessen nimmt also bei Gibbs der mittlere Logarithmus der Wahrscheinlichkeit ab, während bei Boltzmann der Logarithmus der Wahrscheinlichkeit zunimmt": Planck, 1904, p.116). This ambiguity of the two different definitions still lingers in the form of uncertainty regarding the question, whether entropy is "being produced" or is "being lowered" in irreversible reactions.

(8.35) "Clausius, instead of enlarging his theory enough to include the processes he chose to call "uncompensated" (irreversible) contended himself with describing them in physical terms ... With this decree, thermodynamics turned its back on the real world. Henceforth, relinquishing steam engines, it would treat mainly a "universe" - an infinite space filled with some gas, the constitutive relation of which was specified only for the case when it was at rest with uniform density and temperature. Hence grew the thermodynamicist's notorious disregard for constitutive relations altogether, their illusion that thermodynamics can do without them and deal only in extremely general principles": Truesdell (1980, pp.338-339).

(8.36) "Die Berechnung der freien Energie lässt sich der Regel nach nur bei solchen Veränderungen ausführen, die im Sinne der thermodynamischen Betrachtungen volkommen reversibel sind": Helmholtz (1882, p.23).

(8.37) "Irreversibel erscheint uns ein Vorgang, wenn der betreffenden Zustand eine im Verhältnis zur Beobachtungsdauer lange Wiederkehrzeit besitzt; und Reversibel erscheint uns ein Vorgang, wenn der betreffende Zustand im Verhältnis zur Beobachtungszeit kurze Wiederkehrzeit besitzt": Von Smoluchowski (1915, p.365). This definition contrasts markedly with the more rigid view expressed for example by Planck (1913, p.82): "Ein Prozess, der auf keine Weise vollständig rückgängig gemacht werden kann, heisst "irreversibel", alle anderen Prozesse "reversibel"."

(8.38) Fürth, who edited Volume 207 of *Ostwald's Klassiker der exakten Wissenschaften* (1923), in which Von Smoluchowski's *Abhandlungen über die Brownsche Bewegung* were reprinted, enthusiastically remarked (p.145): "Diese Auffassung des zweiten Hauptsatzes von Smoluchowski räumt endgültig mit dem Clausiusschen Satz vom Wärmetod auf, nach welchem, infolge des ständigen Wachsens der Entropie im ganzen Weltall, schließlich ein absolutes Gleichgewicht eintreten müßte. Nach Smoluchowski kann es sich höchstens um einen statistischen Gleichgewichtszustand handeln, in dem sich die "Welt" befindet, gegen den aber immer ieder Schwankungen, und zwar beliebig große Schwankungen eintreten müssen; nur ist deren Wiederkehrzeit so enorm groß, daß uns darüber jede Vorstellung abgeht." What Fürth had not realized apparently, was that earlier Boltzmann (1897) had made serious objections against Clausius pessimistic interpretation of the Second Law (the notoriously depressing dictum "*Die Energie der Welt ist constant. Die Entropie der Welt strebt einem Maximum zu*": Clausius, 1865, p.400), because planet earth cannot be considered to be a "closed system" as required in equilibrium considerations. Boltzmann (1897) had particularly stressed the fact, that the earth was constantly receiving a tremendous input of solar energy. And it had been Clausius (1865) himself, who had noted, that when considering the energy and entropy of the universe, the transmission of heat radiation and other forms of radiation had to be taken into account. At the same time Boltzmann had expressed his conviction, that the solar system as a whole might well be far from equilibrium and therefore subject to large-scale fluctuations.

(8.39) "In jeder beliebigen Umgebung eines willkürlich vorgeschriebenen Anfangszustandes gibt es Zustände, die durch adiabatische Zustandsänderungen nicht beliebig approximiert werden können": Carathéodory (1909, p.363).

(8.40) "Ein jeder Vorgang in der Natur, der ein System von Körpern aus einem gewissen Anfangszustand in einen gewissen Endzustand bringt, besitzt entweder die Eigenschaft, daß er sich auf irgendeine Weise vollständig rückgängig machen läßt, oder er besitzt die Eigenschaft, daß er sich auf keinerlei Weise vollständig rückgängig machen läßt. Die eine Eigenschaft schließt die andere aus. Im ersten Falle heißt der Vorgang reversibel, im zweiten Falle irreversibel.": Planck (1926, p.463).

(8.41) "Jeder in der Natur stattfindende Prozeß verläuft in dem Sinne, daß die Summe von Entropien aller an dem Prozeß beteiligten Körper vergrößert wird. Im Grenzfall, für einen reversibln Prozeß, bleibt diese Summe ungeändert. Oder kürzer ausgedrückt: Die Entropie ist ein Maß für die Wahrscheinlichkeit.": Planck (1926, p. 463).

(8.42) Bockris (1949) used the concept "primary hydration" (chemical hydration) to describe the situation, where the cation and its attached water molecules move together as one entity through the solution. In that situation the water molecules adhering the cation, have lost their own mobility with respect to the cation. The concept "secondary hydration" (physical hydration) was applied to those interactions between cations and water dipoles, in which electrostatic forces play a role, but whereby these bonding forces are not strong enough to lead to primary hydration. Bockris & Saluja (1972) suggested to use the term "coordination number" to replace the concept of primary (chemical) hydration, and to use the term "hydration number" to describe all those water molecules, that are influenced in their dynamical behaviour by the presence of the cations.

(8.43) The name "dolomite reaction series" given by Alderman & Von der Borch (1963) has now been shown to be misleading, in that it implies a chemical reaction on the basis of the hypothetical "Haidinger reaction". As demonstrated in chapter 1, there is no reason at all to believe that for example a magnesium calcite will take up more and more Mg^{2+} (under conditions of room temperature and atmospheric pressure), and gradually change into dolomite, huntite or magnesite. The actual mechanism consists of course of the dissolution of this magnesium calcite and the nucleation of dolomite under the influence of fluctuations. Temperature during the fluctuations will determine whether dolomite or other carbonates such as huntite or magnesite will nucleate. Continued growth of the respective nucleï depends in particular on the amplitude (and to a lesser extent on the frequency) of the fluctuations in pH.

(8.44) "Le mot *stabilité* ne présente pas en chimie une signification absolue: la stabilité est relative aux conditions dans lesquelles on place le composé, sur lequel raisonne. Cependent la signification qu'on attache le plus souvent à cette expression concerne la résistence de corps à l'action d'une température progressivement croissante": Berthelot (1879, Vol.II, p.11).

(8.45) "Ein ... nicht-erreichtes Gleichgewicht scheint bei den Lösungen der genannten Erdalkalicarbonaten mit Luft als Gasphase vorzuliegen": Halla (1960, p.270).

(8.46) "... mais en revenant en Italie, je trouvai que les pierres de montagnes calcaires, qui succèdent à celles de porphyre, entre Bolsano & Trente, avoient cette même particularité, quoiqu'elles soient en bancs horizontaux & que j'y rencontrasse quelques empreintes de coquillages": De Dolomieu (1791, p.5).

(8.47) "The sediment is visibly concentrated over areas of heavy plant growth, suggesting not only that carbonate minerals are in actual precipitation from the lake waters but that there is a direct link between plant life and precipitation": Skinner (1963, p.451).

(8.48) "Es ist die allgemein bekannte Tatsache, daß die allein stabile Modifikation des kohlensauren Kalks der Calcit ist": Leitmeier (1910 A, p.73).

(8.49) In his paper *On the structure and Origin of Coral Reefs and Islands* Murray (1880) attributed the differences in rates of dissolution between different fossils to differences in thickness of the calcium carbonate shells: "Analysis shows that carbonic acid is most abundant in sea water, and especially so in deep water. Pteropod and Heteropod shells are very much larger than the Foraminifera, yet are very much thinner; and hence, for the quantity of lime contained in them, they represent a much greater surface to the action of the sea water. This seems to be the reason why all large and thin shells are first removed from the deposits with increasing depth, and the the fact that some shells are composed of arragonite and some of calcite, as has been suggested." (Murray, 1880, p.510)

(8.50) In this respect Nernst (1921) followed the example of Rüdorff (1873), who had studied mixed crystals of NH_4Cl and NH_4NO_3 and had concluded, that these mixed crystals were truly one phase and did not consist of an array of thin layers.

(8.51) "Offenbar hängt dieses Abwechseln der einzelnen Schichten innig zusammen mit der durch Adsorption bedingten Entstehungsweise der Mischkrystalle und scheint dem Umstande zu entsprechen, dass das Wachstum eines Krystalles nicht stetig sondern sprungsweise ... vor sich geht": Sommerfeldt (1902, pp.60-61).

(8.52) In the original definition of Sommerfeldt (1902, pp.61-62): "... eine Zonarstruktur kann bei denselben nur durch Veränderungen, welche das Lösungsmittel in seiner procentischer Zusammensetzung erleidet, veranlasst werden, oder durch beträchtlichen Schwankungen der äusseren Variabelen (Druck und Temperatur)." And: "Bei den isomorphen Mischkrystallen schreitet das Wachstum in Schichten von stets gleichbleibender procentischer Zusammensetzung fort, solange die thermodynamischen unabhängigen Variabelen (Concentration der flüssige Phase, Druck, Temperatur) als annäherend constant betrachtet werden dürfen": Sommerfeldt (1902, p.62).

(8.53) Liesegang (1911) drew a parallel between "the ripening" of the silver chloride or silver bromide of photographic emulsions and the rhythmic precipitation created by him, by way of adding droplets of calcium chloride solution and droplets of silver nitrate solution onto a layer of gelatin on a glass plate. In photographic terms this "ripening" is in fact the increase of the grain size of the silver chloride (or -bromide). In the explanation given by Ostwald, the larger grains would become enlarged at the expense of the smaller ones. According to Kolthoff (1936, p.376) "Ostwald ripening" should, by definition, always be accompanied by pronounced changes of the external surface. But in his own experiments on the changes taking place in freshly precipitated lead sulfate, barium sulfate, and silver chloride, Kolthoff (1936) could not observe the phenomenon to be taking place. Instead a process of recrystallization was noted in a film of saturated solution surrounding the primary particles. Irregularities on the surface of the crystallites would supply the ions. This process would be taking place at such a rate, that the lattice ions hardly had an opportunity to enter the bulk of the solution and so lead to "Ostwald ripening". All factors which would decrease the solubility of the precipitate, were noted to inhibit the speed of perfection (= recrystallization). The speed of this "process of perfection" (as Kolthoff called it) is not determined by the (overall) solubility of the precipitate, but instead by solubility in the film of solution surrounding the particle. At the same time Kolthoff (1936) was able to explain the process of agglomeration taking place: in many instances the crystallites became cemented by bridges up to such a degree, that a mosaic of crystalline material will result. This cementing process is *irreversible*. Ostwald Ripening is usually considered to be the final stage of a first order phase transition, in which coarsening takes place (e.g., Wagner, 1961; Marqusee & Ross, 1983; Voorhees, 1985; Beenakker & Ross, 1985).

(8.54) "Die Gleichgewichtseinstellung zwischen Schicht und Kristall erfolgt dagegen nicht durch direkten ungeordneten Molekülübergang, sondern nur durch Aufbau oder Abbau von Netzebenen": Volmer (1922, p.271). Only later Volmer, Stranski & Kaischew revealed the important role played by fluctuations in free energy in starting each new layer during two-dimensional nucleation.

(8.55) Compare the following effusions: "Augenscheinlich ist es die thermodynamische Form, die das Zutrauen erweckt, daß hier der Vorgang vollständig erfaßt sei": Kossel (1934, p.461), and "Unverkennbar ist das Bestreben der Neuzeit, allmählich die erste, rein thermodynamische Auffassung, auf Kosten der zweiten, der molekularen, zu entwickeln ...": Van ’t Hoff (1898, p.4).

(8.56) "Der Gegensatz zwischen der thermodynamischen und der kinetischen Methode beruht bekanntlich darauf, daß die erstere mit Begriffen (wie Dichte, Druck, Temperatur usw.) operiert, welche der makroskopischen Beobachtung enstammen und durch Annahme räumlicher und zeitlicher Homogenität idealisiert werden, während letztere dieselben durch statistische Begriffe ersetzt, welche die Anwendung von Wahrscheinlichkeitsbetrachtungen erfordern": Von Smoluchowski (1904, p.205).

(8.57) In the years after 1986 M. J. Kocurko published only one paper (Kocurko, M. J. & Kocurko, D. J., 1992: Fossil Octocorallia of the Red Bluff Formation, Lower Oligocene, Mississipi. *Journal of Paleontology*, Vol.66, pp.594-602), but nothing more on dolomite formation. That is to say as far as I know at present, on the basis of the compilation of the *Chemical Abstracts / Science Finder* 1987-2002. Several attempts to contact Mr. Kocurko in 1999 met with no success.

(8.58) Roman Smoluchowski is the son of Marian von Smoluchowski. Roman was born on 31 August 1910 in Zakopane (then Austria-Hungary, but now part of Poland). After an education at the universities of Warsaw (Poland) and Groningen (The Netherlands), Roman Smoluchowski emigrated to the United States in 1935 and became a U.S. citizen in 1946. His education was in physics; his main interests were in solid state research, metallurgy, and astronomy. (source: Marquis *Who's Who*, 41st ed., 1980-1981; Vol.2, pp.1923-3745; Chicago, Ill.)