CHAPTER SIX

MAGNESITE & HUNTITE

INTRODUCTION

Numerous authors, among them Berzelius (1820 B, 1821), Soubeiran (1827), Fritzsche (1836), Nörgaard (1851), De Marignac (1855), Beckurts (1881 A), Genth & Penfield (1890), Pfeiffer (1902), Von Knorre (1903), Redlich (1909 B), Leitmeier (1910 B), Wells (1915), Wilson & Yü-Ch'Ih Ch'Iu (1934) and Walter-Lévy (1937), have described unsuccessful attempts to precipitate anhydrous magnesium carbonate from a magnesium bicarbonate solution kept at room temperature and under atmospheric pressure. Instead a hydrated magnesium carbonate (nesquehonite, $MgCO_3.3\ H_2O$ or lansfordite, $MgCO_3.5\ H_2O$) or one of the more complex magnesium hydroxide carbonates precipitated under such conditions.[1]

Magnesite may well form under conditions of room temperature (around 298 K) and atmospheric pressure. This conclusion is based on a number of detailed descriptions of occurrences of magnesite in Recent sediments, sediments that lack any indication of the actions of high temperature and/or high pressure. Such occurrences of modern magnesite have been described for example by Alderman & Von der Borch (1961), Skinner (1963), Von der Borch (1965), Irion (1970), Perthuisot (1971), Gac et al. (1977), and Wells (1977). The obvious discrepancy between finding magnesite of modern age, magnesite that must have formed under conditions of room temperature & atmospheric pressure, and the noted absence of any such syntheses, has led to what might be called "*the magnesite problem*".

No lack of theories on the formation of magnesite under atmospheric conditions exists. The majority of these theories is based on the postulate, that magnesite does not precipitate as magnesite, but as something else to be changed later into true magnesite. In outline seven different theories can be distinguished: 1) the initial precipitate would have been magnesium hydroxide; 2) the initial precipitate would have been $MgCO_3.3\ H_2O$ or $MgCO_3.5\ H_2O$; 3) the initial precipitate would have been magnesium hydroxide carbonate ("hydromagnesite"); 4) the initial precipitate would have been calcium carbonate; 5) the initial precipitate would have been huntite, $CaCO_3.3\ MgCO_3$; 6) leaching of ultrabasic rocks would have initiated magnesite formation; and 7) magnesite did really precipitate as the primary compound.

One of the first to postulate the conversion of magnesium hydroxide carbonate was Daly (1907); in his view the increased pressure and increased temperature during burial would force the crystal water out of the "basic carbonate of magnesium". From his laboratory experiments Gloss (1938) concluded, that a quantity of magnesium hydroxide carbonate kept in a carbon dioxide atmosphere (of less than 1 bar) would be metastable, and that it would gradually change into magnesite[2] (see also D'Ans & Gloss, 1938). Based mainly on field observations, Vitalj (1953) reached a comparable conclusion. In sediment samples from the bottom of Lake Elton (Russia) only very small amounts of magnesite were detected by Vitalj (1953); at the same time relatively large amounts of magnesium hydroxide carbonate were found. As a result Vitalj (1953) postulated a conversion of the primary precipitate magnesium hydroxide carbonate into magnesite. Also on the basis of field observations Graf et al. (1961) advanced the idea, that magnesium hydroxide carbonate had been "*...gradually converted into something akin to magnesite*" (Graf et al., 1961, p.222). Much the same conclusion was formulated by Alderman

& Von der Borch (1963), who found magnesite in the Recent sediments of ephemeral lakes associated with the Coorong Lagoon (Australia). Six different assemblages involving various anhydrous Mg/Ca carbonates were distinguished, among them one involving aragonite and magnesium hydroxide carbonate and another with dolomite plus magnesite. It was suggested by Alderman & Von der Borch (1963), that a carbonate sediment consisting initially of aragonite and magnesium hydroxide carbonate would later change into an assemblage of dolomite and magnesite.

According to Hess (1908) brucite $Mg(OH)_2$ would form "... through the decomposition of magnesian minerals without carbonation" (Hess, 1908, p.20) during the weathering of serpentine, and the thus formed brucite "... may take the CO_2 from carbonated water carrying magnesite and thus precipitate both the newly formed molecule and the magnesite carried in solution, owing to the loss of excess CO_2 in the water" (Hess, 1908, p.20). The gradual conversion of $Mg(OH)_2$ into magnesite, when exposed to moist air, has been postulated by Horn (1969); who added, that this kind of conversion could be expected from a compound such as magnesium hydroxide.[3] There can be no doubt at all, that $Mg(OH)_2$ is a reactive substance, when exposed to CO_2 and H_2O. Only through the exclusion of any carbon dioxide gas pure magnesium hydroxide can be prepared in the laboratory (Fricke et al., 1936). But what forms if carbon dioxide is permitted to come into contact with $Mg(OH)_2$, is magnesium hydroxide carbonate (Le Blanc & Richter, 1923). Similar to the theory proposed by Horn (1969), is the one by Lesko (1972): magnesium hydroxide would re-crystallize into magnesium carbonate trihydrate, which in turn would very slowly dehydrate under low CO_2-pressures into magnesite. These two different conversions would take place without a need for elevated temperatures.[4]

The third group of theories explaining the formation of magnesite in the sedimentary environment, postulates the spontaneous (but gradual) transition of the hydrated magnesium carbonates (nesquehonite and lansfordite) into anhydrous $MgCO_3$. Such a conversion has first been suggested by Doelter (1905), inspired by the laboratory observations on the change of $MgCO_3.5\ H_2O$ into $MgCO_3.3\ H_2O$ (as documented for example by Engel, 1885 A), which in fact takes place at a measurable rate.[5] Leitmeier (1909) drew the same conclusion: gradual dehydration of magnesium carbonate pentahydrate or magnesium carbonate trihydrate would lead to the formation of magnesite.[6] Because according to Rosza (1926) nesquehonite would be labile, it would have to recrystallize into magnesite.[7] Clar (1928) followed Leitmeier's (1909) theory, and added, that the dehydration product of nesquehonite was nothing but a compact, fine-grained magnesite. Siegl (1955) repeated the view on magnesite as the result of a secondary change in an initially hydrated sediment of magnesium carbonate; as did Tewari (1973).

The fourth theory involves the conversion of initially deposited calcium carbonate into magnesium carbonate. Redlich (1909 A) cited the experiments carried out by Klement (1895) in support of his view, that conversion of pre-existing $CaCO_3$ into magnesite would be possible because of a reaction with a concentrated magnesium sulfate brine. The tests of Klement (1895) would have revealed the existence of two different stages in the reaction between $CaCO_3$ and a solution of $MgSO_4$; dolomite would be the first to form, but that compound could react further with the magnesium sulfate solution to give magnesite. In equations:

$$2\,CaCO_3 + MgSO_4 \rightarrow CaMg(CO_3)_2 + CaSO_4 \qquad \text{(eq. 25)}$$

and

$$CaMg(CO_3)_2 + MgSO_4 \rightarrow 2\,MgCO_3 + CaSO_4\,. \qquad \text{(eq. 26)}$$

But when consulting the original paper, it becomes evident, that Klement (1895) had found a minimum temperature of 335 K for the dolomite reaction (at the same time Klement expressed his doubts, whether true dolomite had formed in this particular experiment: more likely a mixture of calcium- and magnesium carbonate had resulted). Klement (1895) stated, that especially magnesium sulfate in solution would readily react with $CaCO_3$ (in the form of aragonite), because in the reaction the insoluble $CaSO_4$ (anhydrite) was formed. No such insoluble reaction product would originate, when using magnesium chloride instead of magnesium sulfate. A different view in this regard has been expressed by Görgey (1912): magnesite would be formed by a reaction between pre-existing calcium carbonate and a solution of magnesium chloride. A third possibility has been advanced by Redlich (1916), who postulated a reaction between solid calcium carbonate and a magnesium bicarbonate solution. But this suggestion was rejected by Leitmeier (1916 B). Nernst's *Löslichkeitsprinzip* (which states, that of two salts sharing a common ion, the most soluble will go into solution and the less soluble will precipitate[8]) predicted, that in such a situation no magnesium carbonate would precipitate, because, as Leitmeier (1916 B) emphasized, magnesium carbonate is the most soluble of the two carbonates. Notwithstanding chemical theory excluding the low-temperature conversion of calcium carbonate into magnesite, and laboratory evidence in support, several authors have followed the example of Redlich (1909 A) and expressed their belief in a secondary conversion of pre-existing calcium carbonate into magnesite. Adherents of the replacement theory (*Verdrängungstheorie*) were for example Clar (1931), Friedrich (1951, 1959, 1963) and Angel & Trojer (1953, 1955).

The fifth theory on magnesite formation is comparable to that postulating a calcium carbonate precursor. In an attempt to explain the formation of magnesite under conditions favoring the nucleation of aragonite, huntite and dolomite, Kinsman (1967) suggested, that possibly huntite had been the original precipitate from which magnesite would have developed. At the same time Kinsman (1967) suggested, that some of the dolomite found in the sabkha at Abu Dhabi had initially been huntite.

The theory that explains magnesite formation in terms of the weathering of ultrabasic rocks, is perhaps the most ancient one of the seven different theories. It can be traced back to Breithaupt (1841), Blum (1843), Von Lasaulx (1875) and Schrauf (1882). On the basis of his field observations Blum (1843) concluded, that the genetic relationship between magnesite and the serpentinite had its origin in the weathering of the serpentinite by carbon dioxide-containing water.[9] Similarly Schrauf (1882) had noted in a weathered olivine-serpentinite in the valley of the Schöninger Bach near Budweis (České Budějovice, Czech Republic), that magnesite had formed in the numerous joints of the serpentinite. Concerning the possible mode of formation Schrauf (1882) left little doubt: magnesite was one of the weathering products (*Auslaugungsproducte*) of the olivine-serpentinite, formed *in situ* by a reaction between rain water and the rock. Redlich (1909 A) postulated two geochemical reaction equations, in which magnesite would form from the magnesium silicates olivine:

$$MgSiO_4 + 2\ CO_2 + H_2O \rightarrow 2\ MgCO_3 + SiO_2 + H_2O\ , \qquad \text{(eq. 27)}$$

or from serpentine:

$$H_4Mg_3Si_2O_9 + 2\ H_2O + 3\ CO_2 \rightarrow 3\ MgCO_3 + 2\ SiO_2 + 4\ H_2O\ . \qquad \text{(eq. 28)}$$

The suggested reactions have been tested by Leitmeier (1916 B) in laboratory experiments. One gram of powdered serpentinite was added to 100 g water, through which carbon dioxide had been bubbling. During 6 months this suspension was continuously shaken (at room temperature). In chemical analyses it was found, that 3.68 % of the weight of the magnesium silicate had been dissolved after that time. But no magnesite formed upon the desiccation of the solution obtained in the experiment: instead magnesium carbonate trihydrate precipitated.

Comparable observations have been made by Lesko (1972): after dissolving powdered serpentinite in carbonated water, and desiccating the bicarbonate solution at 293 K, no magnesite was found. What precipitated were brucite, calcite, nesquehonite, and an unidentified "metastable carbonate". Therefore the conclusion must be drawn, that the theory of Schrauf (1882) still requires completion with an explanation for the low-temperature nucleation of magnesite. In this case too the formation of magnesite under conditions of low-temperature and atmospheric pressure is still largely a mystery, to be solved only by way of reproducible low-temperature syntheses. "Many details are known about the circumstances under which magnesite is formed and thermodynamically stable. However, we do not quite understand why magnesite formation is so difficult and rare in nature, although it is such a simple compound": Möller (1989, p.300).

SYNTHESES OF MAGNESITE

It is not at all difficult to obtain anhydrous magnesium carbonate in a laboratory experiment, provided only, that a high temperature is used. Most probably it was De Fourcroy (1789), who was the first to establish the occurrence of such a minimum temperature. De Fourcroy (1789) had found in his laboratory experiments, how no anhydrous magnesium carbonate would form, when mixing solutions of magnesium sulfate with solutions of ammonium carbonate. It did form however, upon heating the mixed solution to a temperature of at least 60° Reamur (= 348 K). Karsten (1848) left calcium carbonate powder for a long time in a boiling solution of magnesium sulfate and obtained magnesium carbonate plus gypsum (and not the dolomite he had expected).[10]

De Sénarmont (1849, 1850, 1851 A,B) heated a solution of magnesium sulfate and sodium carbonate in a sealed glass tube to 433 K and obtained magnesite. According to Rose (1851) boiling a solution of magnesium sulfate, to which potassium carbonate had been added, would lead to the precipitation of a compound made up from 4 mol Mg^{2+} and 3 mol CO_3^{2-}. Hunt (1859) reacted a solution of magnesium sulfate with solid calcium carbonate at a temperature of 473 K and found magnesite. Bourgeois (1886 A,B) created small rhombs of anhydrous $MgCO_3$ by way of heating water, that contained magnesium hydroxide carbonate and urea in a closed glass tube to 413 K. According to Leighton (1888) boiling northupite, $Na_2CO_3.MgCO_3.NaCl$, in water gives rise to the precipitation of anhydrous $MgCO_3$. Much the same observation has been made by Winkler (1893), who added, that the northupite disintegrated into NaCl, Na_2CO_3 and anhydrous $MgCO_3$, while NH_3 and water vapor escaped from the boiling solution. The presence of small amounts of NH_3 must have had its origin in the fact, that the triple salt used, had been deposited originally in cooling pipes, through which flowed saturated NaCl brines containing ammonia.

Brill (1905 A) patented an industrial process for the production of an anhydrous, if rather "reactive", type of $MgCO_3$, in which magnesium hydroxide carbonate was heated to temperatures between 423 and 473 K, while at the same time dry CO_2 gas was blown over it. Marc (1911) synthesized the mineral by way of heating a solution of ammonium carbonate and magnesium sulfate to 423 K. Boiling a magnesium bicarbonate solution during at least 40 days also leads to the formation of magnesite (Spangenberg, 1913; Walter-Lévy, 1937). A comparable observation has been made by Marc & Šimek (1913), Manchot & Lorenz (1924) and Menzel et al. (1930), who all synthesized magnesite by way of heating a pure magnesium bicarbonate solution in an autoclave to at least 448 K, thereby reaching pressures of 25 bar and more. The patents of the *Brinkhoff Company* (1920, 1921) claimed magnesite formation from a solution of magnesium salts mixed with ammonium carbonate, heated to at least 373 K and kept under a CO_2 pressure of 10 bar. Hambloch (1922/1923) claimed, that ".. the normal crystalline carbonate" of magnesium would be formed, when heating a solution of magnesium bicarbonate mixed with alkali carbonate or alkali hydrogen carbonate to 373 K. The patent of Crotogino (*Kali-Chemie A.G.*, 1929/1932 A) claimed, that magnesite will be formed, when heating nesquehonite or magnesium hydroxide carbonate in a solution of sodium hydrogen carbonate in closed vessels to temperatures above 373 K. Mixtures of sodium- and potassium hydrogen carbonate could be used too, or even mixtures of these with Na_2CO_3 or K_2CO_3. In a second patent by Crotogino (*Kali-Chemie A.G.*, 1929/1932 B) it was claimed, that ammonium hydrogen carbonate would lead to the same result. Because heating took place in a closed vessel, the pressure would have risen to at least 4 bar. The formation of anhydrous magnesium carbonate under atmospheric pressure at a temperature of 333 K, taking place when leading streams of ammonia gas and carbon dioxide over powdered carnallite ($KCl.MgCl_2.6\ H_2O$) has been described by Kappen (1932/1933).

A French patent of the *Societé Genérale du Magnésium* (1935) claims the conversion of limestone or dolomite into magnesite, upon heating in an autoclave with a magnesium chloride solution to temperatures of at least 473 K (the pressure inside the autoclave would thereby have attained values of about 14 bar). Heating aqueous suspensions of $Mg(OH)_2$ to temperatures between 423 and 453 K in the presence of sufficient amounts of dissolved carbon dioxide, would also lead to the formation of anhydrous magnesium carbonate (*I.G. Farbenindustrie*, 1935/1937). Antonoff (1935/1937) patented a reaction, in which "... a light carbonate of magnesia" formed at a temperature of 313 K from a magnesium bicarbonate solution, to which magnesium oxide had been added. (In this particular patent as well as in a number of other patents no clear distinction is being made between magnesium carbonate in the form of magnesite and magnesium hydroxide carbonate.) Greider & MacArthur (*The Philip Carey Manufacturing Co.*, 1938/1946) patented a process, in which $MgCO_3$ would crystallize from a pure magnesium bicarbonate solution heated to at least 333 K. Lannung & Tovborg Jensen (1949) obtained magnesite, after heating an amount of $MgCO_3.3\ H_2O$ in water during at least 20 hours to 448 K. The hydrothermal experiments by Schloemer (1952) and Schloemer & Nacken (1953) led to the conclusion, that magnesite would not form unless temperatures of 473 K and pressures of at least 250 bar had been reached. Baron (1958) heated a solution of magnesium chloride and sodium carbonate to temperatures of 413 to 423 K under high CO_2 pressures (the CO_2 pressure at 298 K was 5 kg/cm^2; its value after heating the closed vessel to 413 K was not given). Baron & Favre (1958) reported magnesite formation in a magnesium bicarbonate solution heated to 373 K under a pressure of 20 kg/cm^2. Akimoto (*Kurita Industrial Co.*, 1962/1965) obtained magnesite after boiling seawater (and replenishing from time to time the evaporated amounts of water with new seawater) until a salinity of 18.8^o Bé was reached. At that stage a precipitate would have formed, consisting of $CaCO_3$, $Mg(OH)_2$, $MgCO_3$, $CaSO_4.0.5\ H_2O$ and $Na_2SO_4.CaSO_4$. Budan & Effmert (*Wintershall A.G.*, 1964/1965) synthesized magnesite by way of heating a solution of magnesium sulfate and sodium carbonate to 383 K. According to Oh et al. (1973) an equimolal solution of magnesium chloride and sodium carbonate heated in an autoclave to temperatures of 453 to 463 K, gives rise to the formation of magnesite. Dandurand & Schott (1977) described, how they had synthesized magnesite in thermodiffusion experiments at a temperature of 373 K and a CO_2 pressure of 0.6 bar from magnesium hydroxide carbonate. Heating a suspension of magnesium hydroxide carbonate in an aqueous solution of ammonium carbonate during 3 to 7 days to temperatures of 403 to 423 K would, according to Stevula et al. (1979), lead to the precipitation of magnesite.

Magnesite is also known as a by-product from an industrial process, but in that process too high temperatures and elevated pressures are involved. When seawater is used instead of the more usual pure sodium chloride brines as the starting material in the ammonia soda process (Solvay method), various magnesium salts will be precipitated. These include the hydroxide carbonate, the triple salt $Na_2CO_3.MgCO_3.NaCl$, the double salt $Na_2CO_3.MgCO_3$, and also pure

$MgCO_3$ (Hou, 1942). The precipitation of the magnesium carbonate takes place, concomitant with the precipitation of $CaCO_3$, in a stage of the Solvay process known as the ammoniation of the saturated brine. As Hou (1942) described it, the concentrated sea water first acts as a scrubbing medium and then as an absorbing medium for ammonia. After that it reacts with the ammonia and carbon dioxide gas. At this stage in the production process the brine has a temperature of around 313 K (see also Lunge, 1896; Schreib, 1905). This temperature is the result of the introduction of a hot mixture of NH_3 and CO_2 (with a temperature of 341 to 348 K). The gas mixture is coming from the distilling tower, where ammonia is being recovered from the run-off liquor. The brine is nearly saturated with NaCl, containing up to 274 g/dm^3, and after ammoniation it contains 63 to 66 g/dm^3 NH_3 in solution. According to Lafontaine (1925) the system MgO - CO_2 - NH_3 - H_2O would usually precipitate magnesium hydroxide carbonate, or in some instances the ammonium magnesium double carbonate, $MgCO_3.(NH_4)_2CO_3.4\ H_2O$, at temperatures around 303 K. But Waeser (1923/1926) claimed, that at temperatures above 313 K the reaction

$$MgCl_2 + 2\ NH_3 + CO_2 + H_2O = MgCO_3 + 2\ NH_4Cl \qquad \text{(eq. 29)}$$

would become reversible.[11]

Several claims on the low-temperature synthesis of magnesite have become known. One of the very first was published by Berzelius (1820 B). In it Berzelius (1820 B) claimed, that mere contact with water would lead to the decomposition of the double salt $KHCO_3.MgCO_3.4\ H_2O$, thereby giving rise to K_2CO_3 in solution and magnesium carbonate (*carbonate de magnésie*).[12] The reaction between water and $KHCO_3.MgCO_3.4\ H_2O$ at room temperature has also been studied by Fritzsche (1836), but he could only observe the formation of $MgCO_3.3\ H_2O$ (or $MgCO_3.5\ H_2O$ at very low temperatures). Duplication of Berzelius' experiment has been performed by Von Knorre (1903) as well. When leaving $KHCO_3.MgCO_3.4\ H_2O$ in contact with water of 288 K, the solid phase formed was $MgCO_3.3\ H_2O$ and not anhydrous $MgCO_3$. Therefore it is the more surprising to find, that Auerbach (1904) once more claimed the formation of $MgCO_3$ (*festes Magnesiumkarbonat*) upon the spontaneous dissociation of $KHCO_3.MgCO_3.4\ H_2O$ in water at room temperature.

Pfaff (1894) performed a multitude of experiments, aimed at the low-temperature synthesis of dolomite and magnesite. After relating various unsuccessful attempts, Pfaff (1894) described experiments, in which ammonium sulfide and hydrogen sulfide had been used. Such a mixed solution was used to dissolve magnesite, calcium carbonate and magnesium hydroxide carbonate. Especially the last compound was found to dissolve well in the mixed solution of hydrogen sulfide and ammonium sulfide in water (*Schwefelammon*). A solution of calcium carbonate dissolved in *Schwefelammon* was added to one prepared with magnesium hydroxide carbonate, and ammonium carbonate was added. The mixture was slowly evaporated during several days on a water bath. Microscopic examination showed a crystalline and strongly birefringent precipitate, which would not dissolve in dilute acid. A second experiment along the same lines rendered a larger amount of the precipitate, so that quantitative analysis became possible. What had been formed was, according to Pfaff, "... a considerable amount of magnesia with some lime". The next experiment involved hydrogen sulfide only, which was found to dissolve the calcium carbonate even better than the *Schwefelammon*. Magnesite would not dissolve very easily into a solution of hydrogen sulfide, but when using magnesium hydroxide carbonate the dissolved amounts were markedly larger. After preparing "... a rather concentrated" solution of magnesium hydroxide carbonate in hydrogen sulfide, and adding an amount of sodium chloride, Pfaff (1894) desiccated it at a temperature of 323 to 333 K, while bubbling carbon dioxide through the solution. The precipitate did not dissolve entirely after washing it several times with dilute hydrochloric acid. What remained was a crystalline, birefringent precipitate, not to be dissolved by cold, concentrated acid. The claim of Pfaff (1894) to have synthesized magnesite at 323 K is based on an experiment, in which a mixed solution of equal amounts of calcium carbonate in hydrogen sulfide and one with magnesium hydroxide carbonate dissolved in hydrogen sulfide. Once more sodium chloride had been added, and the whole was desiccated on a water bath at 323 K, while leading carbon dioxide through it. Quantitative analysis showed the precipitate to consist of 80.60 % magnesium carbonate and 6.93 % calcium carbonate. Hence Pfaff's statement: "*Das Ergebnis hievon war also wiederum ein kalkhaltiger Magnesit*" (Pfaff, 1894, p.494).

Steidtmann (1911 A, p.366) stated: "... Sorby found that a crystal of calcite placed in a concentrated solution of magnesium chloride became slowly encrusted with magnesium carbonate." But after Sorby's own publication on this matter had finally been located, it turned out, that Sorby (1879) had described an experiment conducted "... at a high temperature".[13]

In his dissertation Gloss (1938) described, how he had created magnesite in an experiment at 338 K. A small quantity of magnesium carbonate trihydrate "under carbon dioxide gas" was sealed in a glass tube and heated to 338 K during 4 weeks. After that time magnesite was found. When conducting the same test at 328 K, it took as long as 4 months to obtain magnesite. In these two experiments not only an elevated temperature was involved, but an increased pressure as well. In a quite different experiment Gloss (1938) had found magnesite to have been formed at 307 K and even at a pressure of less than 1 bar. The observation was made in an experiment intended to measure the changes in CO_2-pressure of a quantity of magnesium carbonate trihydrate gradually converting into magnesium hydroxide carbonate. The instrument used to follow the changes in carbon dioxide pressure, was a tensimeter according to Bremer-Frowein (see also Van 't Hoff et al., 1895). One glass bulb of the instrument contained water, and the other contained a small amount of wet magnesium carbonate trihydrate. The experiments showed, how the $MgCO_3.3\ H_2O$ would loose about one fifth of its original carbon dioxide content after one year, and thereby change into magnesium hydroxide carbonate. When continuing the test, the magnesium hydroxide carbonate would start to take up carbon dioxide and gradually change into magnesite. As an example of this spontaneous and gradual change into magnesite Gloss (1938) mentioned his experiment III: after 300 days a quantity of 3 g $MgCO_3.3\ H_2O$ had reached a maximum CO_2-pressure of 902 mm Hg, and after that the CO_2-pressure started to decline. After 22 months the contents of the tensimeter were analyzed: no more trihydrate remained, instead magnesium hydroxide carbonate and a number of idiomorphic magnesite rhombs were seen under the microscope (see also D'Ans & Gloss, 1938).

Kazakov et al. (1959) claimed to have precipitated magnesite from a pure magnesium bicarbonate solution with 0.240 kg/m^3 MgO and 0.490 kg/m^3 CO_2 at a temperature of 333 K (but only in one instance: their experiment 167). Comparable tests at 298 K did not yield any magnesite (instead nesquehonite or magnesium hydroxide carbonate formed). Therefore the synthesis by Kazakov et al. (1959) can not be considered to be a real *low* temperature synthesis.[14, 15]

High-temperature syntheses of magnesite should not be taken into account, when considering the mode of formation of magnesite in the sedimentary environment; syntheses conducted at temperatures well above 298 K are being considered as unrealistic on the basis of Playfair's *Principle of Actualism*. Equally unrealistic are those experiments, in which elevated pressures were involved. As a consequence the claim of Schloemer (1952) can be left out of consideration, because pressures of more than 10 bar and temperatures above 473 K were used in that instance. Baron & Favre (1958) synthesized magnesite in hydrothermal experiments, in which a magnesium bicarbonate solution was subjected to temperatures of at least 373 K and carbon dioxide pressures of 19 to 47 bar. Baron & Wyart (1958) described how they had created magnesite in tests, in which temperatures of 413 to 423 K had been used and pressures up to

4.69 bar must have been reached. Baron (1960) produced magnesite from a solution of magnesium chloride and sodium carbonate in water heated to a temperature of 423 K and under a carbon dioxide pressure of 12.9 bar. Johannes (1970) synthesized magnesite at a temperature of 473 K in solutions under 1000 bar pressure. Sayles & Fyfe (1973) produced magnesite from an aqueous suspension of magnesium hydroxide carbonate at 399 K. Sandengen et al. (2008) were able to synthesize magnesite from magnesium hydroxide carbonate (in the presence of monoethylene glycol) at 423 K under atmospheric pressure. Magnesite synthesis at 393 K in a reaction between sodium carbonate and magnesium chloride solutions under a carbon dioxide pressure of 3 bar has been described by Hänchen et al. (2008). All of these experiments will be left out of consideration here.[16]

OCCURRENCES OF RECENT MAGNESITE

The investigation of Recent occurrences of the mineral magnesite might well be fruitful, in that possibly one or more factors might be traced, that could be instrumental in the low-temperature nucleation of magnesite. Ultimate evidence that a particular sample of magnesite is of Holocene age can of course only be obtained from isotope datings, but geological field observations supply in many instances adequate (if circumstantial) evidence.

One of the earliest mentionings of modern magnesite must have been that by Brochant (1801-1802, vol.2, p.500), who recalled, how the English mineralogist Mitchel had been the first to describe pure, crystalline and anhydrous magnesium carbonate from Hrubschitz, the present-day Hrubšice (near Ivančice in the Czech Republic). Giobert (1804) described the deposits at Baudissero (near Castellamonte, north of Turin, Italy). The virtually pure magnesium carbonate (it contained only a small amount of silica) had originated from a "*pierre cornéene ou cacholong*". The magnesite found at Castellamonte, Italy is associated with serpentinite (Haberle & Bucholz, 1809). The relationship between modern magnesite and serpentinite has been stressed by Breithaupt (1841).[17] Blum (1843) emphasized the observation, that magnesite formed from such a serpentinite always contained considerable amounts of silica. Redlich (1909 A), in his description of magnesite formed upon the weathering of peridotite or Mg-rich gabbro into serpentinite in the Kraubat region (Austria), clearly postulated an authigenic origin.[18] Magnesite of Recent age has been found by Vakhrameeva (1956), Polyakov (1959), Sedelnikov et al. (1968) and Andriyasova et al. (1973) in the evaporite deposits of the Kara Bogaz Gol. The Kara Bogaz salt deposits not only contain modern magnesite and dolomite, but also glauberite, bloedite, carnallite, kainite and picromerite. Sedelnikov et al. (1968) described calcite, aragonite, brucite and hydrated forms of magnesium carbonate from this location. The salt deposits of Lake Balkhash contain anhydrous magnesium carbonate according to Beremzhanov (1970). In hydromorphic soils of the Zeravshan Valley (Uzbekistan) Recent magnesite has been found by Kugochkov (1960).

Holocene magnesite has been found in caves too. Pobeguin (1960) described magnesite, occurring in the fine-grained powder known as *Montmilch*[19] in a cave near Saint-Cézaire (Département Alpes-Maritimes, France). Infrared spectroscopy not only established the presence of magnesite, but of carbonates such as aragonite, calcite, dolomite, and huntite as well. Debye-Scherrer photographs confirmed the presence of magnesite. Because the host rock of the Saint-Cézaire cave consists of a Jurassic dolomite, devoid originally of any magnesite or huntite, the magnesite had to be of authigenic origin. At the same time the conclusion was reached, that this magnesite must have formed under conditions of low-temperature and at atmospheric pressure. Modern magnesite has been found in the Zbrašov caves near Teplice nad Bečvou (Czech Republic) by Paděra & Povondra (1964). The magnesite occurred there in the form of white, tuberous aggregates together with huntite. Identification took place with differential thermal analysis as well as X-ray diffraction. Modern magnesite from caves on the island of Kauai (Hawaii) has been reported by Léveillé et al. (2000 A). Because the unweathered basalt of Kauai, nor the overlying soils, contain any magnesite, it had be of an authigenic origin. The speleothems containing magnesite showed microstromatolitic textures, most likely deposited as microbial mats (Léveillé et al., 2000 A, B).

Magnesite of Quaternary origin occurring in an ephemeral lake close to the Coorong Lagoon (southeast South Australia), was first described by Alderman & Von der Borch (1961). In papers by Skinner (1963), Von der Borch (1965) and Langmuir (1965) more details on this occurrence of modern magnesite were given. The magnesite was found in playa-lake carbonate deposits some 1.6 km south of Salt Creek. The pH of the water in the winter season is alkaline; pH = 10 has been measured (Alderman & Von der Borch, 1961). Near the surface of these deposits the magnesite is intermixed with about an equal quantity of dolomite, but at a depth of 15 cm there is approximately 4 times as much dolomite as magnesite. No magnesite at all is present at a depth of 25 cm; pure dolomite makes up the entire sediment there. At approximately 50 cm depth, the carbonate sediment changes into black, sulfide-bearing sand. Plant growth gradually reclaims the salt marsh into dry land. The grass-like *Ruppia maritima* Linn. thrives during the wet winter season, much as numerous algae. High salinities reached during the dry summer months, but especially the phases of complete desiccation, are responsible for the disappearance each year of almost all vegetation. By way of a possible explanation for the occurrence of magnesite at this site, Von der Borch (1965) pointed out, that the pH of "Magnesite Lake" is notably higher than that of all other ephemeral lakes "... due to the presence of significant aquatic plant life" (Von der Borch, 1965, p.797).

Additional information on the occurrence of magnesite in "Magnesite Lake" has been supplied by Langmuir (1965), who had corresponded with Von der Borch on the matter. The initial composition of the water in Salt Creek would have been close to that of normal sea water, but Von der Borch pointed out, that it possessed an unusually high carbonate-bicarbonate ratio due to ground-water seepage. Subsequent desiccation during the summer led to the precipitation of aragonite. This precipitation of aragonite continued until the Ca^{2+} concentration had been reduced to about 10 % of its original value. At this point of concentration of the brine magnesium hydroxide carbonate started to precipitate. The pH value measured at that moment was approximately 8.9 to 9.0 . Von der Borch had analyzed the brine at this stage of desiccation for sodium, chloride and sulfate ions, and had found values like those of normal seawater concentrated to the same degree. In his book on sedimentary carbonate minerals Lippmann (1973, p.85) stated, that the magnesite of "Magnesite Lake" must have formed due to the "... influx of ground water unusually high in alkali carbonate".

Magnesite, in a dolomitic sediment of 11,300 ± 250 years old (C^{14} measurement), has been found by Graf et al. (1961) some 30 cm below the surface of the Great Salt Lake Desert, Utah (USA). The unconsolidated sediment consists mainly of mixtures of calcite, aragonite, dolomite and quartz, but locally some layers of pure aragonite are present. In five of the 23 short cores, notably the five cores taken near the shore of former Lake Bonneville, magnesite was found in association with aragonite. According to Graf et al. (1961) the magnesite had to be authigenous, since it certainly was not of detrital origin. The magnesite showed in X-ray diffraction an enlarged unit cell: a_o and c_o values were expanded relative to the corresponding values for a synthetic magnesite, prepared at a temperature of 673 K. Such an expanded unit cell could be explained by the substitution of for example 8 mol % $CaCO_3$, but subsequent spectrographic analyses of the magnesite showed no such high amounts to be present (only 0.2 % $CaCO_3$ was found). The explanation given was the following: "We suppose that these expanded-cell materials result from an intimate association of water with the solid ... and that they form at temperatures and solution compositions close to those at which basic carbonates and well-defined carbonate hydrates become stable" (Graf et al., 1961, p.222).

The same dolomite-magnesite deposits underneath the Great Salt Lake Desert have been studied by Bissell & Chilingar (1962), who added observations on the prominent rhythmic character of the dark and light laminations. The dark layers are significantly higher in silicate plus SiO_2, and contain about twice as much magnesium ions as the light layers. The light-coloured laminations contain more clay minerals than carbonates: some 10 % in the form of kaolinite and the other 90 % is either illite or montmorillonite. In the dark coloured layers carbonates such as dolomite, aragonite, and magnesite are predominant. As Graf et al. (1961) pointed out, these carbonate layers are essentially devoid of fossils: no plant spores or brine shrimp eggs could be found, only some finely comminuted plant debris. In the interpretation of Bissell & Chilingar (1962) the laminated sediment of the Great Salt Lake Desert represents many intervals of aridity and desiccation, alternating with times of lacustrine sedimentation during the waning stages (the last few thousands of years) of Pleistocene Lake Bonneville.

Details on the Tuz Gölü salt lake, Turkey have been given in Chapter 4, and it suffices to refer to that description. The deposits of the Tuz Gölü contain, according to Irion (1970), magnesite of Holocene age. Modern magnesite has been described by Schmid (1987) from the Salda Lake, Turkey, some 150 km northwest of Antalia. From his study Schmid (1987, p.23) was able to conclude: *”The new formation of magnesite from this mud occurs, in the Salda Lake, at the mud-air-water interfaces, ie. on the shores where the lake level, as a result of climatic conditions, periodically changes.”* Perthuisot (1971) has found modern magnesite in the sediments of sabkha El Melah de Zarzis. Much like the situation that exists in the Tuz Gölü, pronounced fluctuations in water chemistry exist in the case of sabkha El Melah in Tunisia.

Modern magnesite has been found by Kinsman (1967) in the carbonate sediments of the coastal plain along the Persian Gulf at Abu Dhabi. These supra-tidal flats are situated some 90 to 150 cm above mean sea level, and are flooded only a few times a year, when strong on-shore winds coincide with spring tide. During most of the year the surface of the supra-tidal flat is dry. Air temperatures at Abu Dhabi range from 288 to 320 K, with an annual average of 301 K. Rainfall is less than 3.73 cm per year, and high evaporation rates exist. As a consequence the pore water of the supra-tidal flats is concentrated to brine about 6 times as saline as normal seawater. The Mg/Ca ratio of this pore water was measured as 5.3 to 5.5 ; its pH ranged from 6.5 to 7.5 , and its temperature was about 307 K, with extremes from 298 to 312 K. Precipitation of gypsum, starting when the pore water was 3 to 4 times as concentrated in dissolved salts as normal sea water, further increases the Mg/Ca ratio. At the beginning of the precipitation of aragonite, when the brine is still more concentrated, the Mg/Ca ratio reaches its maximum of about 10 to 30. Magnesite was found only in the upper 10 - 20 cm of the Abu Dhabi sabkha (Kinsman, 1969). The presence of magnesite in the Recent sediments of the sabkha at Abu Dhabi has been confirmed by Bush (1973). The magnesite there was found exclusively in the supra-tidal areas.

Cole & Lancucki (1975) found Recent magnesite on top of a weathered basalt at Deer Park (near Melbourne), Australia. The only information given was, that this magnesite occurs together with huntite in a soil profile some 2.5 m thick, at the basis of which there was a discontinuous layer of magnesite nodules. Wells (1977) reported on magnesite in the form of nodules, found in a calcrete crust near Gosses Bluff (Northern Territory, Australia). The calcrete consists of grains of quartz and feldspar, with fragments of sandstone, in a matrix of fine-grained calcite. The magnesite is microcrystalline (under the light microscope, that is), and it contains little or no admixtures. Fractures and vugs in the magnesite nodules are frequently lined by microcrystalline calcite. Magnesite near vugs and cavities is often coloured by iron. Not only this characteristic was explained by Wells (1977) to be indicative of the process of weathering, but weathering of magnesium-containing limestones and dolomites in the neighborhood was thought to have been responsible for the rich supply of magnesium in solution. The magnesite must have originated in much the same way as the calcrete, which formed in a sandy soil on top of an impact breccia. "Presumably the magnesium-rich solutions were concentrated in topographically low areas underlain by the more consolidated breccia, and magnesite was formed during drier phases of the climate. The later and more widespread calcrete was probably a response to a change in the chemistry of groundwater, and to probably wetter conditions, although its precipitation would still require dry climatic phases": Wells (1977, p.66).

Modern magnesite has been found by Gac et al. (1977) at the beaches of Lake Yao, a saline lake in northern Chad. Magnesite was found there in a definite sequential paragenesis, which included (going from the lake up the beach) calcite, aragonite, magnesium calcite, dolomite, huntite, magnesite, sodium carbonates (nahcolite, thermonatrite, trona), sodium sulfates (burkeite, thenardite), halite and sylvite. The high concentrations of sodium and potassium in the accompanying brines cause high pH values: pH = 10 was measured by Gac et al. (1977) in several instances. In two caves of the Transvaal region (South Africa) Martini & Kavalieris (1978) found modern magnesite. Rouse & Sherif (1980) have found magnesite in Holocene sediments of the coastal sabkha of the western Gulf of Sirte, Libya. Wasson et al.(1984) supplied a wealth of information on the modern magnesite present in Lake Didwana (Rajasthan, Northern India). Here magnesite precipitated from brine consisting mainly of sodium chloride, sodium sulfate, sodium carbonate and sodium hydrogen carbonate. Apart from various clay minerals (montmorillonite, illite, kaolinite), and dolomite, considerable amounts of northupite $MgCO_3.Na_2CO_3.NaCl$ are present at this particular location. In the interpretation of Wasson et al. (1984) the magnesite deposits must have originated under distinctly fluctuating conditions.

Magnesite of modern age has been found by Bourrouilh-Le Jan et al. (1985) in the carbonate sediment at the bottom of the lagoon of the (semi-) atoll Clipperton. Some 2850 years before present the lagoon started to become filled with rain water instead of seawater. At present the upper 14 to 15 m of the water column has a salinity of only 14 ‰, while the underlying water mass up to the maximum depth of 34 m is truly marine (with a salinity of 33 to 34 ‰). An abundance of land crabs (*Geocarcinus planatus* Stimpson) inhabits the island, but no other land animals (dragonflies and numerous birds do occur). A wealth of water plants inhabits the lagoon (Phanerogames such as *Potamogeton pectinatus*, *Ruppia maritima* L., *Zostera marina*, *Najas* sp.), leading to large quantities of decomposed and dissolved organic matter in the upper 14 m of the lagoon. The seawater below is virtually free of organic matter in suspension, but it contains numerous bacteria such as *Thiobacillus* sp. and marine yeasts. This is not the only difference: the sea water layer is depleted in oxygen, virtually anaerobe, and contains high concentrations of dissolved hydrogen sulfide (± 75 ml/dm^3). At the same time there is a considerable contrast in pH: the upper layer of brackish water has a pH of about 9, but the underlying layer of sea water is slightly acidic with pH = ± 6.5. In the interpretation of Bourrouilh-Le Jan et al. (1985) the marked contrast between the normal marine conditions, under which the carbonates making up the atoll were originally deposited, and the euxinic conditions prevailing now in the lower part of the stratified lagoon water, must be thought to be responsible for considerable changes in carbonate mineralogy. Apart from the observed dissolution of the aragonite fraction, neoformation of magnesite, kutnahorite (a double carbonate with Ca, Mg, and Mn) and phosphates (fluorapatite and hydroxylapatite) takes place on Clipperton.

Magnesite in Holocene sediments of lakes in the Kiskunság National Park (central Hungary) has been described by Tóth & Molnár (1987), Molnár (1991) and Molnár & Botz (1996). These shallow lakes in the Danube-Tisza interfluve go through a pronounced annual cycle of desiccation (air temperatures around 303 K are common in summer) and flooding. As a consequence strongly fluctuating Mg/Ca ratio's have been measured (for example from 64 to 2 during the season 1976/1977) and salinity changes in the same annual rhythm (from 52 to 10 ‰ during 1976/1977).

In the Playa Pito and especially in the Playa Gualla, salt playas S.E. of Zaragoza (Spain) considerable amounts of Holocene magnesite have been found by Pueyo Mur & Inglès Urpinell (1987). The magnesite is associated here with calcite, dolomite, gypsum, halite, thenardite, and bloedite. Throughout each year the brines of the Cl^- - SO_4^{2-} - Na^+ - (Mg^{2+}) type are subject to large-scale seasonal fluctuations. "Crystallization from the surficial waters of the lakes develops as a response to their seasonal evolution": Pueyo Mur & Inglès Urpinell (1987, p.119). In addition the deposits are affected by organisms such as algae, small crustaceans and coleoptera. In the Gallocanta ephemeral lake (SE of Zaragoza) Holocene magnesite has been found by Pérez et al. (2002). Here the modern magnesite was found together with halite, gypsum, anhydrite, dolomite, aragonite, calcite, quartz and some authigenic caly minerals. Much like Playa Pito, Playa Gualla, the Gallocanta Lake is a distinctly seasonal lake, if not a playa. Water depth of the Gallocanta Lake is never more than 2 m; during most summers the whole playa will become dry.

Modern magnesite from lakes in the Western Plains District of Victoria (some 150 km west of Melbourne, Australia) has been described by De Deckker & Last (1988). This magnesite had to be of an authigenic origin, since no magnesite at all occurs in the rocks (lava flows) and soils surrounding the shallow lakes. Extensive deposits of Recent magnesite have been reported by Renaut (1990) and Renaut & Long(1989) from the sediments of a number of saline lakes of British Colombia (Canada). In recently weathered serpentinites of Oman magnesite has been found by Stanger & Neal (1994). In salt lakes of Xizang (China) modern magnesite was found by Zheng & Yang (1983). According to the compilation by Hill & Forti (1997) magnesite has become known from various caves, including for example the Beremend Crystal cave, Hungary; the Blue Lagoon cave, South Africa, and caves in Venezuela.

Small amounts of recent magnesite were found by Léveillé et al. (2000) in microbial mats adhering the walls of a cave in basalt on the island of Kauai, Hawaii. These microbial mats are found exclusively in the photic zone of the cave. The bulk of the distinctively laminated mats consists of aragonite, calcite and kerolite (a magnesium-rich silicate). Around the microbial mats thin coatings of magnesite, magnesium hydroxide carbonate, gypsum, and monohydrocalcite. “Desiccated and mineralized microbialites contain few preserved cells, and instead are dominated by mineralized material, which is typically laminated on a micrometer scale”: Léveillé et al. (2000, p.351).

After having studied all of these occurrences of modern magnesite, attention should be focused again on the question asked at the beginning of this section. What can be concluded from the field observations made in various parts of the world? Is there really a common factor to be found?

AMORPHOUS MAGNESIUM CARBONATE

There is a somewhat unusual question, which must be asked at this point. Could it be, that the attempts to investigate the low-temperature nucleation of magnesite are in vain at the very outset? Is it not possible, that magnesite does not really precipitate as magnesite, but that the initial precipitate is for example an amorphous form of $MgCO_3$?

The question is not at all unusual at close inspection, because as early as 1827 Soubeiran had described an amorphous form of magnesium carbonate, formed in the laboratory after adding a solution of sodium carbonate to one containing magnesium sulfate. It has been stated by Stromeyer (1827), that up to that time only amorphous magnesium carbonate had become known (and only when magnesium carbonate was associated with calcium carbonate a crystalline form could be found).[20] Authors such as for example Fritzsche (1836), Favre (1844), and Jacquelain (1851) have confirmed the observations of Soubeiran (1827) and Stromeyer (1827). In 1836 Berzelius distinguished between a crystalline form of magnesium carbonate found in nature, with rhombic crystals resembling those of calcite, and a second kind of magnesite without any recognizable crystallites ("... *eine weisse Masse, mit erdigem Bruch*": Berzelius, 1836, p.308). Of the three different types of magnesium carbonate distinguished by Breithaupt (1841), two were crystalline and one was amorphous.

As early as 1809 Haberle & Bucholz related, how the magnesite ("*wasserfreie kohlensaure Talkerde*") of Hrubschitz was found on a weathered serpentinite. At this location the magnesite was associated with magnesium hydroxide carbonate ("*erdigem Talke*"), *Meerschaum*, chalcedony and opal. Both Schrauf (1882) and Leitmeier (1916 A) observed, that especially upon the weathering of magnesium silicates (as occurring in serpentinites and olivinites) this amorphous magnesium carbonate would be formed. At low temperatures carbonic acid would be a stronger acid than silicic acid, and consequently magnesium silicate would be changed into magnesium carbonate. Schrauf (1882) thought, that especially humic substances from the soil would aid in the weathering process of magnesium silicates, but Leitmeier (1916 A) emphasized the role played by carbon dioxide in solution.

An amorphous, anhydrous form of magnesium carbonate has been prepared by Engel (1885 A) by way of heating $KHCO_3.MgCO_3.4\ H_2O$ to a temperature of at least 343 K. But not only this double salt would give rise to amorphous $MgCO_3$. Engel (1899) described, how heating magnesium ammonium carbonate to temperatures exceeding 403 K would give the same result. If the heating had not reached 403 K, the magnesium carbonate would still be in a hydrated form. Heating magnesium ammonium carbonate to temperatures considerably above 403 K, caused a loss of CO_2 from the magnesium carbonate and its subsequent decomposition. Comparable observations have been made by Menzel et al. (1930) and Storch & Fragen (1931). That the thus created form of magnesium carbonate is X-ray amorphous, has first been noted by Menzel et al. (1930). The amorphous form of magnesium carbonate also forms upon boiling magnesium hydroxide carbonate in an aqueous solution of an ammonium salt such as ammonium chloride or ammonium nitrate (Bourgeois, 1886 A). An amorphous magnesium carbonate formed at room temperature has been claimed by Neuberg & Rewald, 1908). In their experiment magnesium hydroxide carbonate was shaken in methyl alcohol until a gel-like suspension formed, followed by the bubbling through of carbon dioxide. Cesàro (1910) claimed to have observed the formation of amorphous magnesium carbonate, after adding a droplet of water to a small quantity of $MgCO_3.5\ H_2O$ on a microscope slide. Most of what formed (at room temperature) was $MgCO_3.3\ H_2O$, but part of it appeared to be amorphous. Leitmeier (1909) found, that colloïdal magnesite had precipitated from a pure magnesium bicarbonate solution upon gradual desiccation at temperatures between 273 and 279 K. At the same time nesquehonite and lansfordite would have been formed. A slightly different observation was published a few years later by Leitmeier (1916 A): exposure of $MgCO_3.3\ H_2O$ to the air would lead to the spontaneous formation of small amounts of amorphous magnesium carbonate (at room temperature). Contradicting Leitmeier's claim, are statements by Centnerszwer & Bružs (1925) and Menzel et al. (1930), that a minimum temperature of 593 K is required to change nesquehonite in a stream of CO_2 gas into an amorphous form of $MgCO_3$.

Once formed, the amorphous form of magnesium carbonate is not very stable; it reacts readily with water vapor and turns into nesquehonite (Engel, 1899; Menzel et al., 1930). But here too Leitmeier (1910 B) advanced a different view: nesquehonite would gradually change into amorphous $MgCO_3$. This conversion of nesquehonite into an amorphous magnesium carbonate would, according to Leitmeier (1910 B), explain the scarcity of the magnesium carbonate trihydrate in nature. The amorphous form of magnesium carbonate has been found for example by D'Achiardi (1913) and Grill (1923) in natural deposits.

For a long time Redlich (1909 A) included an amorphous form of $MgCO_3$ in his classification system, but in 1934 Redlich concluded, that the investigation of Clar (1928) had revealed most of the so-called amorphous varieties to consist of very fine grained, crystalline forms of magnesium carbonate. In this respect it is useful to note the remark made by Walter-Lévy (1937), that almost all of the magnesium carbonates are so very fine grained, that under the microscope these compounds seem to be amorphous. But even years after Walter-Lévy (1937) made her remark, *amorphous* forms of magnesium carbonate have been described. For example Shcherbina (1950), Atoda (1957), and Halla & Van Tassel (1964) have described such amorphous forms of $MgCO_3$. The X-ray amorphous magnesium carbonate analyzed by Halla & Van Tassel (1964) was a so-called gel magnesite, found near Kraubath, Steiermark (Austria).

HYDRATED MAGNESIUM CARBONATES

The fact, that from a magnesium bicarbonate solution kept at room temperature, magnesium carbonate will precipitate in its trihydrated form (in most instances) and not in its anhydrous form, has been established by Berzelius (1820 B). Subsequent investigators could only confirm this observation. Even when heating a magnesium bicarbonate solution, the precipitate will be $MgCO_3.3\ H_2O$ (Fritzsche, 1836; Beckurts, 1881 B; Pfaff, 1894; Monhaupt, 1904). But as soon as the temperature rises above 358 K , magnesium hydroxide carbonate will precipitate as well (Davis, 1906).

The discovery of $MgCO_3.3\ H_2O$ in the Nesquehoning coal mine near Lansford, Schuylkill County, Pennsylvania (USA) by F. Keeley and its description by Genth & Penfield (1890), marked the introduction of the mineral nesquehonite. One year later Friedel (1891) described a sample of nesquehonite from the collections of the *École des Mines* (Paris). Because this particular sample had not been collected by Friedel himself, he could not give details except, that it came from an adit in a coal mine at La Mure (Dept. Isère, France). Leitmeier (1916 A) mentioned nesquehonite as filling small voids in the weathered serpentinites of the Kraubath region (Austria). Artini (1921) had visited the caves at Val Laterna (Italy), and had found crusts on the partly serpentinized peridotite rock there, consisting of very small, water-clear crystallites (some of these measured 3 mm) in fibrous aggregates. Chemical analyses showed the specimen to contain MgO, CO_2 and H_2O. In subsequent quantitative analyses its composition of $MgCO_3.3\ H_2O$ was established. Not only because the nesquehonite would readily change into magnesium hydroxide carbonate (as for example Davies & Bubela, 1973 have claimed), but also because of the constantly humid atmosphere in the cave, this nesquehonite had to be a Recent formation, formed under conditions of normal temperature and atmospheric pressure. Fenoglio (1930) found nesquehonite, together with brucite, brugnatellite, artinite and magnesium hydroxide carbonate on a weathered serpentinite of Mount Fubina, east of Viu (Val di Lanzo, Italy). The nesquehonite occurred there as a white powder directly on the serpentinite; at times crystallites could be discerned, often in radial-fibrous aggregates. Fenoglio (1935) described nesquehonite as an encrustation on a serpentinite in a mine at Cogne (Val d'Aosta, Italy). Nesquehonite occurring as a coating in abandoned mine shafts of the Mitterberg near Kraubath (Austria) has been described by Meixner (1950). Brousse & Guerin (1966) reported nesquehonite as white coatings on joints in the breccia of the "Roc Blanc" of the Cujols-bas hill near Fontanges (France). Marschner (1969) found nesquehonite as crusts in the air scrubbers of air-conditioning equipment. Carbonate had been deposited on the walls of the scrubber compartment, on the reflecting panels and in the nozzles of the water spray, because the water used was high in magnesium bicarbonate. The carbonate crust (monohydrocalcite and nesquehonite) reached a maximum thickness of 2 mm. Temperature in these air scrubbers was in general from 283 to 287 K. Nuryagdyev & Sedelnikov (1966) found nesquehonite in the sediments of the Kara Bogaz Gol salt sea (Russia). Fischbeck & Müller (1971) and Fischbeck (1976) have described nesquehonite from the Eibengrotte, a cave in the Fränkische Alb (near Bamberg, Germany), where the host rock is a Jurassic dolomite. Nesquehonite lining the walls of a gold mine at Baleisk, Siberia has been described by Pisarskii & Konev (1971). Suzuki & Ito (1974) found the mineral nesquehonite on the surface of a weathered serpentinite at Yoshikawa, Aichi Prefecture (Japan). Nesquehonite from caves in the Transvaal region (South Africa) was described by Martini & Kavalieris (1978). Nesquehonite, occurring as an efflorescence on Holocene lava flows of ultrabasic composition, has been described by Kovyazin (1978). Much like the deposits of nesquehonite described by Meixner (1950) from a mine shaft, Kirchner & Simonsberger (1982) found the mineral on the wall of a mine near Salzburg, Austria.

In laboratory experiments $MgCO_3.3\ H_2O$ has been synthesized, and from these experiments data on the stability of nesquehonite can be gathered. Genth & Penfield (1890) remarked, that it was easy to synthesize $MgCO_3.3\ H_2O$: magnesium carbonate had to be dissolved in CO_2-rich water, and the thus obtained solution could be left standing until crystals were seen to form. Much the same procedure had earlier been described by Klaproth (1810), Berzelius (1836) and De Marignac (1855). Kazakov et al. (1957) added that magnesium bicarbonate solutions deposited $MgCO_3.3\ H_2O$ in dependence of the concentration of the dissolved carbon dioxide. At concentrations of dissolved CO_2 from 2 to 19 g/dm^3 nesquehonite formed (at a temperature of 293 K), but at lower concentrations (from 0.27 to 2.0 g/dm^3) artinite would be formed.

The addition of sodium carbonate to sea water (at 293 K) leads to the precipitation magnesium carbonate trihydrate, as Lucas (1948) noted, after an initial precipitate of aragonite. Lucas (1949) added carbonated forms of amines such as di-methyl amine, di-ethyl amine and tetra-methyl ammonium to sea water (at room temperature) until pH = 8.5 was reached, and obtained "... in some instances" $MgCO_3.3\ H_2O$. By way of a reaction between natural sea water and ammonia plus carbon dioxide (stemming from the gradual decomposition of ammonium carbonate) Towe & Malone (1970) obtained in one of their experiments nesquehonite at a temperature of 296 to 298 K. After desiccating the water from Lake Balkhash at 303 K Beremzhanov & Pokrovskaya (1964) noted, that among other salts nesquehonite had been precipitated. Adding a solution of magnesium chloride or magnesium nitrate to a solution of sodium carbonate in water (at room temperature) will also lead to the formation of $MgCO_3.3\ H_2O$ as Sainte-Claire Deville (1851), Nörgaard (1851), and Von Knorre (1903) described. Tewari (1973) obtained precipitates of nesquehonite at a temperature of 303 K by adding ammonium carbonate or sodium carbonate plus potassium carbonate to a 10 % solution of magnesium chloride. According to Cesàro (1910) the reaction between sodium hydrogen carbonate and a solution of magnesium chloride will give rise to $MgCO_3.3\ H_2O$ at room temperature, but at temperatures below 273 K the pentahydrate will be precipitated along with the trihydrate. When leaving $KHCO_3.MgCO_3.4\ H_2O$ in contact with water (at room temperature) decomposition takes place, followed by the precipitation of the trihydrate of $MgCO_3$ (Berzelius, 1820 B; Fritzsche, 1836; Von Knorre, 1903).

A second kind of hydrated magnesium carbonate has been found in laboratory experiments conducted at temperatures below 289 K: the pentahydrate. Engel (1885 B) noted how the precipitation of $MgCO_3.5\ H_2O$ took place at temperatures between 289 and 295 K. According to Leitmeier (1909) the maximum temperature for the formation of the pentahydrate would be 279 K. Cesàro (1910) analyzed $MgCO_3.5\ H_2O$ that had been formed at 283 K under a CO_2 pressure of 5 to 6 bar. A slightly different temperature was indicated by Gjaldbæck (1921): 279.3 K, but Terada (1928) measured 286.7 K as the maximum temperature. Haehnel (1924 A) confirmed the temperature range indicated by Engel (1885 B). Ming & Franklin (1985) obtained nesquehonite instead of lansfordite from a solution at a temperature of 277 K. The explanation given by Menzel et al. (1930) for the observed variation in the measured maximum temperatures for pentahydrate formation was, that this variation must have been caused by differences in the composition of the solutions used by different investigators, in CO_2 pressures, et cetera. Menzel et al. (1930) described $MgCO_3.5\ H_2O$ as metastable, and noted that it would quickly change into nesquehonite even at room temperature. Fenoglio (1933) prepared the pentahydrate by way of adding a saturated $NaHCO_3$ solution to a 20 % magnesium chloride solution, while keeping both at a temperature between 278 and 283 K.

Magnesium carbonate pentahydrate has been discovered by D.M. Stackhouse & F.J. Keeley in a coal mine near Lansford, Pennsylvania (USA); the mineral lansfordite was described by Genth (1888) and Genth & Penfield (1890) from this location. Poitevin (1924) described an occurrence of lansfordite from the hydromagnesite deposits of Atlin, Canada. The mineral has been found by Fenoglio (1933) in a magnetite mine near Cogne (Val d'Aosta, Italy); it occurred there together with nesquehonite, artinite, brucite and magnesium hydroxide carbonate. The mine at Cogne is excavated in a serpentinite; in the adit, where the lansfordite was found, a virtually constant temperature of 277 K exists.

Magnesium carbonate monohydrate, $MgCO_3.H_2O$, has been prepared by Davis (1906) by way of boiling nesquehonite in xylol (boiling point = 410 K: see also Menzel & Brückner, 1930). This method of preparing the monohydrate has been confirmed by Menzel et al. (1930). The latter authors obtained magnesium carbonate monohydrate after desiccating $MgCO_3.3\ H_2O$ in a closed container above P_2O_5 at room temperature. Their X-ray analyses furthermore revealed the formation of $MgCO_3$ monohydrate, when heating nesquehonite in air to temperatures between 373 and 423 K. Magnesium carbonate monohydrate has not yet been found in nature, in contrast to the pentahydrate, trihydrate and dihydrate of magnesium carbonate.

Barringtonite, $MgCO_3.2\ H_2O$, has been discovered by Nashar (1965) on the surface of an olivine basalt under a waterfall in Sempill Creek (Barrington Tops, New South Wales), Australia. The (new) mineral occurred there as nodular encrustations on a part of the basalt's surface, which was continuously wet with (river) water. Temperature at the site was around 278 K. "Barringtonite is formed as the result of this cold meteoric water percolating through olivine basalt and leaching magnesium from it": Nashar (1965, p.370). Nesquehonite was found associated with barringtonite at this location. It has been claimed by Engel (1885 C), that (amorphous) $MgCO_3.2\ H_2O$ had formed in a highly concentrated magnesium chloride solution reacting with alkali carbonate, but the dihydrate would quickly change into magnesium hydroxide carbonate.

In their experiments Ming & Franklin (1985) observed, that $MgCO_3.5\ H_2O$ is unstable when exposed to the atmosphere at temperatures of more than 285 K. In that case lansfordite would dehydrate into nesquehonite, $MgCO_3.3\ H_2O$. The dehydration of lansfordite into nesquehonite started within a few minutes after exposure to the air at room temperature. Observations in a stereo scanning electron microscope with a stage cooled by liquid nitrogen on the change in the exterior of the crystallites showed that from 285 K upwards dehydration of lansfordite takes place at a measurable rate (Ming & Franklin, 1985). When making a comparison between the pentahydrate and the trihydrate of magnesium carbonate, it would be logical to conclude, that the trihydrate must be able to dehydrate even further. As Davies & Bubela (1973) pointed out, magnesium carbonate trihydrate synthesized in the laboratory changes rather quickly to magnesium hydroxide carbonate, when heated to a temperature of 325 K. Perhaps this dehydration of nesquehonite to magnesium hydroxide carbonate could be followed in nature by further dehydration to magnesite. At least Tewari (1973) suggested, that nesquehonite would be the "precursor" of magnesite.

DEHYDRATION BARRIER

After having noted, that $MgCO_3.3\ H_2O$ will precipitate in most cases from a magnesium bicarbonate solution at room temperature, one might be inclined to conclude, that anhydrous carbonate will develop merely by way of some process of dehydration. Such a secondary process of dehydration would explain at the same time the relative scarcity of the hydrous forms of magnesium carbonate, as has been pointed out by Leitmeier & D'Achiardi (1912).[21] The idea that dehydration would lead to the formation of magnesite, seems to be supported by laboratory observations: magnesite can indeed be produced from nesquehonite or lansfordite. But then the conditions required to bring about this change are not exactly in the low-temperature & atmospheric pressure range.

Heating $MgCO_3.3\ H_2O$ in water does not give rise to the formation of any anhydrous form of $MgCO_3$: magnesium hydroxide carbonate forms instead (Soubeiran, 1827; Davis, 1906; Menzel & Brückner, 1930). Similarly no anhydrous $MgCO_3$ precipitates from a boiling magnesium bicarbonate solution: there too magnesium hydroxide carbonate will be formed (Fritzsche, 1836; Rose, 1837; Rinne, 1907). Magnesium hydroxide carbonate also results from heating a quantity of $MgCO_3.5\ H_2O$ in water (Fritzsche, 1836; Haehnel, 1924 A).

It has been claimed by Engel (1881 A), that magnesium carbonate ("kohlensaure Magnesia") plus $KHCO_3$ or K_2CO_3 would form upon heating $KHCO_3.MgCO_3.4\ H_2O$, whether dry or in water. Four years later Engel (1885 C) stated that a "reactive kind of anhydrous magnesium carbonate" would have formed after heating $KHCO_3.MgCO_3.4\ H_2O$ to temperatures of 423 to 473 K. The thus created magnesium carbonate was not stable at all: within 2 to 3 hours it would be hydrated to $MgCO_3.3\ H_2O$ or $MgCO_3.5\ H_2O$. The formation of anhydrous $MgCO_3$ upon the decomposition of $KHCO_3.MgCO_3.4\ H_2O$ has been confirmed by Walter-Lévy (1937); but she found, that magnesite formed only when heating the double salt in water in closed glass tubes to temperatures of at least 373 K.

It will be difficult to dehydrate $MgCO_3.3\ H_2O$ or $MgCO_3.5\ H_2O$ merely by heating, because, as Engel (1885 D) has pointed out, these carbonates will start decomposing and will give off carbon dioxide gas. But Brill (1905 B) claimed, that decomposition does not set in unless temperatures of 513 K or more are reached. Various attempts to dehydrate $MgCO_3.3\ H_2O$ below that temperature have become known. For example Davis (1906) heated the trihydrate to 393 K and obtained magnesium carbonate monohydrate. Manchot & Lorenz (1924) found, that carbon dioxide would be given off by nesquehonite heated to temperatures above 473 K. One way to prevent the decomposition of $MgCO_3.3\ H_2O$ while being heated to high temperature, would be to heat it in a closed glass tube. In fact Walter-Lévy (1937) performed this very test, but she had to observe, how only magnesium hydroxide carbonate would form when heating the sample to 373 K. Another possibility to prevent the decomposition of nesquehonite, might be found in the use of carbon dioxide overpressure. In his patent Brill (1905 A) claimed to have created magnesite after heating nesquehonite to 493 K in a stream of carbon dioxide gas. A comparable observation has been made by Centnerszwer & Bružs (1925) and Menzel et al. (1930); the latter authors used X-ray diffraction for the identification of the reaction products and confirmed, that magnesite had been formed after heating $MgCO_3.3\ H_2O$ in a CO_2-stream to 493 K during a few hours and then to 593 K for several days. Brill (1905 B) obtained anhydrous magnesium carbonate after heating nesquehonite in a stream of carbon dioxide gas to 498 K. Davis (1906) could not detect any change in $MgCO_3.H_2O$ heated during one and a half hours in alcohol at a temperature of 351 K. Lannung & Tovborg Jensen (1949) found, that dehydration of nesquehonite into anhydrous $MgCO_3$ will take place at a temperature of 448 K. Curiously enough the presence of water vapor was found to be a requirement for the conversion. A markedly higher temperature for the change of nesquehonite into magnesite has been measured by Konstant & Vaivads (1963): a minimum temperature of 653 K would be required. The formation of a new compound, $MgO.2\ MgCO_3$, has been claimed by Hladky (1975) to take place, when heating nesquehonite to 743 K.

Menzel et al. (1930) made several attempts to dehydrate $MgCO_3.3\ H_2O$ at room temperature. When placed over concentrated H_2SO_4 the trihydrate was seen to quickly loose one molecule of crystal water, along with some carbon dioxide, but after that the dehydration process slowed down considerably. After approximately two years the trihydrate had changed into a magnesium carbonate hydrate with 1.5 molecules of crystal water. X-Ray diffraction gave the impression, that a magnesium hydroxide carbonate had been formed. In a second experiment the trihydrate was dehydrated over P_2O_5: after 6 months reaction time chemical analysis showed, that $MgCO_3$. 1.73 H_2O had been formed. But in X-ray diffraction a compound resembling $MgCO_3.H_2O$ was detected. From a comparable experiment involving the desiccation of nesquehonite over P_2O_5 during one year, Lannung & Tovborg Jensen (1949) concluded, that an X-ray amorphous compound with a chemical composition of $MgCO_3$. 1.43 H_2O had been formed.

The suggestion of Leitmeier (1909), repeated by Leitmeier in 1953, that nesquehonite as well as lansfordite would change by way of mere dehydration into magnesite, has been taken up by various authors. It has even been supplied with physico-chemical considerations on the dehydration process. For example Lippmann (1960) stressed the observation, that both magnesium and calcium cations in solution possess a strongly bonded layer of water dipoles. These adhering water molecules should be removed before incorporation of the magnesium cations into a crystal of anhydrous carbonate can take place. To this end the total hydration energy must be overcome. In the case of calcium cations 1791 kiloJoule/mol and in the case of magnesium 2097 kiloJoule/mol (data from Eley & Evans, 1938) must be supplied. These amounts are so high, that effective barriers against the nucleation of the anhydrous carbonates would result, in the case of magnesium as well as in the case of calcium. Because of the marked difference in cation size between calcium and magnesium, there will be a clear difference in cation-dipole interaction. From theoretical considerations on the hydration energies Lippmann (1973, p.82) concluded, that "... calcite should crystallize about 10^{10} times faster than magnesite at 25 ^oC (= 298 K)." If during the nucleation of any magnesium carbonate nucleï of magnesite formed at any time, their surfaces would be instantaneously "poisoned" by firmly adsorbed water molecules. The existence of such a "dehydration barrier" would explain the fact that no form of anhydrous $MgCO_3$ will precipitate from bicarbonate solutions at room temperature. In addition it would explain the reluctance of the low-temperature formation of dolomite.

It must be remarked here, that the theory of a "dehydration barrier" neglects the fact, that there is no real need to dehydrate nesquehonite or lansfordite or magnesium cations in solution to obtain magnesium carbonate in its anhydrous state. All too often the fact is overlooked, that the mixed crystals known as magnesium calcites contain *anhydrous* magnesium carbonate. Similarly the double carbonate eitelite[22] , $Na_2CO_3.MgCO_3$, contains water-free $MgCO_3$, much like northupite, $Na_2CO_3.MgCO_3.NaCl$.

MAGNESIA ALBA AND HYDROMAGNESITE

Slévogt (1709) related, how *magnesia alba* had been the name for a white powder used in Roman times in Italy as a harmless purgative. Hoffmann (1748) recommended *magnesia alba* as a "*cur maximè in malo hypochondria*". Chemical analyses of the "*pulveris Comitis de Palma*", as Slévogt (1709) had described it, were performed by Lancisi (1718), Black (1755), and Bergman (1775). The powder could be prepared from solutions of Epsom salt (= magnesium sulfate). In pharmaceutical practice the method of preparation as given by for example Fritzsche (1836), is still being followed: magnesium sulfate is dissolved in boiling water; a boiling solution of sodium carbonate should be added and the mixture should be kept at 368 K for at least 10 minutes while stirring. The precipitate is filtered off, and the sodium sulfate in solution should be washed out.[23] Analyses of the thus produced precipitate by Berzelius (1820 B, 1821), Nörgaard (1851), Kraut (1880), Beckurts (1881 A,B), Kolthoff (1914), Menzel et al. (1930), Walter-Lévy (1932) and Bowers (1935) have shown *magnesia alba* to consist of magnesium hydroxide carbonate.

There has been considerable debate around the question of the exact composition of magnesium hydroxide carbonate. Berzelius (1836) analyzed *magnesia alba* as consisting of 44.75 parts MgO , 35.77 parts carbon dioxide and 19.48 parts water; the *magnesia alba* used had been precipitated from a boiling solution of magnesium chloride or magnesium sulfate, to which potassium carbonate had been added. In other words the composition found by Berzelius (1836) was $4\ MgO.3\ CO_2.4\ H_2O$. Fritzsche (1836) obtained a slightly different magnesium hydroxide carbonate after boiling $MgCO_3.3\ H_2O$ in a solution of ammonium carbonate; its composition was given as $5\ MgO.4\ CO_2.5\ H_2O$. Favre (1844) used the same procedure as Fritzsche (1836), but reported to have obtained a magnesium hydroxide carbonate with a composition identical to that found by Berzelius (1820 B). Jacquelain (1851) added sodium carbonate or potassium carbonate to solutions of water-soluble magnesium salts kept at different temperatures and so obtained two magnesium hydroxide carbonates: $5\ MgO.4\ CO_2.10\ H_2O$ and $6\ MgO.5\ CO_2.14\ H_2O$. A comparable experiment has been performed by Rose (1851); who obtained a variety of magnesium hydroxide carbonates with compositions of $5\ MgO.4\ CO_2$ with 5, 6, 7, 8, 9, 10, or 11 water molecules; with a composition of $4\ MgO.3\ CO_2$ with 5 or 7 water molecules, and a magnesium hydroxide carbonate with a composition of $3\ MgO.2\ CO_2.3\ H_2O$. On the basis of these observations it cannot be surprising, that Joulin (1873) suggested, that all magnesium hydroxide carbonates are but mixtures of $MgCO_3$ and $Mg(OH)_2$.[24] But many chemists would not agree with that view: for example Engel (1885 B) rejected the idea. In his own tests, consisting of adding a concentrated, cold solution of magnesium chloride to a similar solution of an alkali carbonate, Engel (1885 B) had obtained a well-defined magnesium hydroxide carbonate with a composition of $5\ MgO.4\ CO_2.11\ H_2O$.

From experiments on the thermal decomposition of magnesite Brill (1905 B) had concluded, that numerous magnesium hydroxide carbonates would exist. Each of the different stages in the step-wise decay of magnesite had to be considered as a "well-defined chemical species", because, as Brill (1905 B) put it, each of these phases possessed its own characteristic vapor pressure. Davis (1906) expressed his doubt concerning the nature of the "magnesium carbonate" used by Brill (1905 B), the more because Anderson (1905) had measured the decomposition of magnesite not to start until a temperature of 678 K had been reached.[25] Centnerszwer & Bružs (1925) confirmed the step-wise character of the thermal decomposition of magnesite, but in their analyses no magnesium hydroxide carbonate could be found: mixed crystals between MgO and $MgCO_3$ formed.

Davis (1906) agreed with Joulin (1873): all of the different magnesium hydroxide carbonates were in fact mere mixtures of $Mg(OH)_2$, $MgCO_3.3\ H_2O$ and $MgCO_3.H_2O$. Much like Joulin's concept, the idea advanced by Davis (1906) certainly had the appeal of simplicity; exactly what was needed to bring about some order in the disarray of numerous different magnesium hydroxide carbonates. As a consequence the concept of a mixture instead of a relatively large number of well-defined chemical species started to attract more and more adherents.

The problem of the bewildering multitude of different magnesium hydroxide carbonates was solved relatively quickly after the introduction of X-ray diffraction. The first of these structural analyses of the magnesium hydroxide carbonates was carried out by Levi (1924). After preparing eight different magnesium hydroxide carbonates in laboratory tests, and subjecting these to X-ray diffraction in a Debye-Scherrer camera, Levi (1924) found that although there were some minor differences, all of his samples made in the laboratory were identical to the mineral hydromagnesite. The differences were explained to have been the result of small variations in the film used or in the set-up as well as considerable changes in grain size and in orientation of the powder samples. The X-ray pattern obtained from a sample of the mineral artinite was different from that of hydromagnesite.

In 1899 Brugnatelli had found an unknown magnesium carbonate different from nesquehonite, lansfordite and the known magnesium hydroxide carbonates. In 1906 Brugnatelli was able to describe this mineral in more detail. Artinite had been found in asbestos (chrysotile) deposits at Val Brutto, near the town of Franscia, in the Veltlin region of Italy. Lincio (1930) found the same mineral in encrustations occurring in small cavities of the Monte Ramazzo near Borzoli, Italy. Ferrari & Ghiron (1931) recognized the mineral artinite in a sample of hydromagnesite from Hoboken, New Jersey (USA). Later two more naturally occurring magnesium hydroxide carbonates were found, exhibiting a X-ray diffraction pattern different from that of hydromagnesite. The first one was giorgiosite, analyzed with X-ray diffraction by Caillère (1943). The mineral giorgiosite had been discovered by Lacroix (1905) in rock samples, that had been collected on the Greek island of Thira (= Santorini) by Fouqué. Its name had been derived from the collecting site: the volcano Mount Giorgio. There, in a salt crust formed by fumarolic exhalations in a lava deposit near the village of Aphroësse, Fouqué had collected the material, that was later found to contain the new mineral. The chemical composition of giorgiosite was given by Lacroix (1905) as $Mg(OH)_2.4\ MgCO_3.4\ H_2O$.

Chemical analyses had been sufficient for Lacroix (1905) to recognize the new magnesium compound, different from the well-known *magnesia alba*, but Caillère (1943) was able to use X-ray diffraction, as well as differential thermal analysis, on the samples originally collected by Fouqué (1879). Especially the Debye-Scherrer photographs made by Caillère (1943), provided evidence that the mineral giorgiosite was different from hydromagnesite. X-Ray diffraction data on giorgiosite have also been published by Raade (1970) and Friedel (1975). The latter author had been able to prepare this magnesium compound in laboratory experiments, carried out at temperatures of 335.0 and 335.8 K by way of reacting aqueous solutions of 1 mol $MgCl_2$ or $MgSO_4$ with a solution containing 1 mol $Na_2CO_3.NaHCO_3$. Friedel (1975) had to experience, that it was quite difficult to obtain giorgiosite in this manner: in 215 different experiments giorgiosite formed in only 10 instances (in 178 other tests magnesium hydroxide carbonate formed, and 27 times nesquehonite was obtained).

The mineral dypingite was found by Raade (1970) as a coating on weathered serpentinite samples from the Snarum magnesite deposit, southern Norway. Chemical analysis gave its composition as $Mg_5(CO_3)_4(OH)_2.5\ H_2O$; X-ray diffraction revealed it to be different from hydromagnesite, artinite, and giorgiosite. The mineral had to be of Recent origin, because, as Raade (1970) pointed out, it formed as a weathering product on serpentine rock fragments in a dump (i.e., after being mined). "It is probably deposited from cold, leaching solutions during wintertime": Raade (1970, p.1464).

The names "*Talkerdehydrat*" introduced by Trolle Wachtmeister (1827, 1828),[26] much as the actual "*Hydromagnesit*" of Von Kobell (1835), the "*hydrocarbonate de magnésie*" used for example by Engel (1885 C) and the "*hydrogiobertite*" (literally "hydromagnesite") introduced by Scacchi (1885) should be avoided, because those names are misleading. Even when using these only for a well defined mineral species, the names give the false impression, that the mineral meant would be some hydrated form of magnesite. In this respect the minerals nesquehonite, $MgCO_3.3\ H_2O$, and lansfordite, $MgCO_3.5\ H_2O$, are much more likely candidates for a term like "hydromagnesite". Even though there is more than one magnesium hydroxide carbonate, this term or its synonym basic magnesium carbonate is to be preferred over the word "hydromagnesite".

Menzel & Brückner (1930) expressed their doubts concerning the very existence of the compound hydromagnesite, because in their experiments no hydromagnesite at all had been formed.[27] Even attempts to duplicate the syntheses of hydromagnesite described by Le Blanc & Richter (1923) were to no avail: Menzel & Brückner (1930) obtained in all the duplication experiments only the magnesium hydroxide carbonate with MgO : CO_2 = 5 : 4, and not with MgO : CO_2 = 4 : 3 as in hydromagnesite. The magnesium hydroxide carbonates obtained in their own experiments had a composition of 5 MgO.4 CO_2.5 H_2O or of 5 MgO.4 CO_2.6 H_2O. In his reaction Levi (1930) objected, that the composition of a mineral found in nature such as hydromagnesite was prone to variation. In general the composition of hydromagnesite would be 4 $MgCO_3$.$Mg(OH)_2$.3 H_2O (= 4 MgO.3 CO_2.4 H_2O). Levi (1930) added, that he had been able to distinguish hydromagnesite in an unequivocal manner in X-ray diffraction. Two different magnesium hydroxide carbonates were recognized by Walter-Lévy (1937): 5 MgO.4 CO_2.5 H_2O and 4 MgO.3 CO_2.3 H_2O . The first would form upon boiling $MgCO_3$.3 H_2O in water (Walter-Lévy, 1932). The second formed when boiling K_2CO_3.$MgCO_3$.4 H_2O in water (Walter-Lévy, 1935).

In order to delineate the conditions, under which magnesium hydroxide carbonate forms, in contrast to those under which magnesium carbonate trihydrate forms, several observations must be taken into account. It was noted for example by Bineau (1857) as well as Von Knorre (1903), that when adding small amounts of a solution of an alkali carbonate (or alkali hydrogen carbonate) to a magnesium sulfate solution, not the expected magnesium hydroxide carbonate but instead $MgCO_3$.3 H_2O precipitates. When adding NH_4OH to a pure magnesium bicarbonate solution, magnesium hydroxide carbonate will be formed instead of magnesium carbonate trihydrate according to Lafontaine (1925).

The suggestion of Kline (1929), that at very low pCO_2 values the precipitation of $Mg(OH)_2$ would be inevitable, has been rejected by Menzel & Brückner (1930). In the view of the latter two authors the experiments of Auerbach (1904), Le Blanc & Richter (1923), as well as their own experiments, had shown, that no low-temperature transition of $MgCO_3$.3 H_2O into $Mg(OH)_2$ takes place and that instead magnesium hydroxide carbonate will be formed in virtually all instances.

The amount of water in magnesium hydroxide carbonate varies to a considerable degree. Menzel & Brückner (1930) measured from 6.3 to 15 mol H_2O (calculated for 5 mol MgO making up the magnesium hydroxide carbonate molecule). Magnesium hydroxide carbonates precipitated from a boiling solution usually contain less crystal water than one precipitated from a solution at room temperature. Nevertheless all of these differently hydrated magnesium hydroxide carbonates showed in X-ray (Debye) photographs identical patterns. From this fact Menzel & Brückner (1930) drew the conclusion, that considerable amounts of water would be associated with the hydroxide carbonate in ways other than purely as crystal water. This "... *andersartig gebundenes Wasser*" possibly would be adsorbed.

In theory at least it would be possible, that after magnesium hydroxide carbonate precipitated from a magnesium bicarbonate solution, it would gradually change into anhydrous magnesium carbonate. Vitalj (1953) suggested, that the magnesite of modern age found in Lake Elton (Russia) had been formed by way of some secondary conversion from magnesium hydroxide carbonate, which would have been the primary precipitate. In this regard it must be realized, that changes in magnesium hydroxide carbonate do take place after precipitation. Authors such as De Fourcroy (1789), Soubeiran (1827), Fritzsche (1836), Favre (1844), Jacquelain (1851), and Rose (1851) all have described, how freshly precipitated magnesium hydroxide carbonate gradually changed into $MgCO_3$.3 H_2O, when remaining in contact with the mother liquor. Davis (1906) has explained this phenomenon by pointing out, that the magnesium hydroxide carbonate reacts with atmospheric carbon dioxide being absorbed by the solution.

B. HUNTITE

INTRODUCTION

Faust (1953) found a new kind of carbonate in the hydrothermal dolomite-magnesite deposits of the Current Creek Formation in White Pine County and Nye County, Nevada (USA). The mineral resembled magnesite, but in the flame-test it showed the presence of calcium. In subsequent chemical analyses huntite was found to consist of $CaCO_3$.3 $MgCO_3$. The host rock of the Currant Creek Formation is a bedded tuff of Tertiary age, and the magnesite in it is closely associated with faults. Faust (1953) concluded, that initially the tuffs had been weathered to give calcite and montmorillonite, and that later magnesia-rich hydrothermal solutions had been introduced into the host rock. From the reaction with the calcite present in the tuffs dolomite resulted; magnesite and deweylite formed at the same time. It was mainly in the carbonate deposits filling vugs in part of the replaced tuff, that Faust (1953) had found the new mineral huntite. X-Ray diffraction showed, that huntite is not a solid solution of magnesite in dolomite, but that it possesses its own characteristic structure with an orthorhombic unit cell. Graf & Bradley (1962) were able to determine its space group as R 3 2 . Structure refinement of huntite has been performed by Dollase & Reeder (1986); their study essentially confirmed the measurements of Graf & Bradley (1962).

High-temperature syntheses of huntite have become known. For example Biedl & Preisinger (1962) synthesized huntite in hydrothermal tests, in which MgO, SiO_2, and "... small amounts of calcium" reacted at 373 K under 3.2 bar CO_2 pressure. Only one claim on the low-temperature formation of huntite in a laboratory experiment has been published. Davies et al. (1977) described how the mineral formed in an experiment, whereby nesquehonite reacted with carbonate sediments in a hypersaline brine, aided by the presence of an abundant microbial population. The reaction time was ten months; temperature prevailing during the test was between 293 and 303 K. In the explanation of Davies et al. (1977) the high CO_2 concentration (caused by the intense microbial activity) would have been responsible for the formation of huntite (and that of dolomite, magnesium hydroxide carbonate, calcite and monohydrocalcite as well).

Longo & Voight (1989) reported the formation of huntite when grinding calcite and magnesium hydroxide carbonate in a ball mill during 1 hour at a temperature of 373 K.

RECENT DEPOSITS OF HUNTITE

In 1953 Koblencz & Nemecz described huntite as occurring in the Dorag mine (Hungary). Apart from descriptions of chemical analyses, DTA curves and X-ray data, no details on the locality as such or the possible mode of formation can be found in the paper by Koblencz & Nemecz (1953). The presence of huntite in the *Montmilch* deposits in the La Clamouse cave near Saint-Guilhem le Désert, Hérault (France) has been documented by Baron et al. (1957). Although various analytical methods were used to describe the mineral collected at this site, information on the cave itself, chemistry of water in it and the like, were not given by

Baron et al. (1957) nor in their subsequent publication (Baron et al., 1959).

Skinner (1958) has described huntite occurring as a weathering product of Precambrian dolomites near Tea Tree Gully, South Australia. Huntite from the weathered mantle of a serpentinized dolomite in the Kurgashinkan lead-zinc deposits (Almalyk region, Uzbekistan) has been described by Golovanov (1959). At this location huntite was found in association with dolomite, magnesium hydroxide carbonate and opal. The mineral huntite has been found by Carpenter (1961) at Crestmore, California (USA). It occurred there together with magnesium calcite, aragonite, and dolomite as an incrustation on a brecciated calcite-monticellite rock. At Gabbs (Nevada, USA) huntite occurs in a mineralized dolomite formation, and it has been described by Vitaliano & Beck (1963). The hydrothermal conversion of dolomite into magnesite and brucite was followed by weathering and the formation of huntite.

Huntite, in association with dolomite, magnesite, and gypsum, has been found by Kinsman (1967) in the Recent carbonate sediments of the Trucial Coast (Abu Dhabi, Persian Gulf). The only mineral found together with the huntite was halite. Huntite of Recent age has been described from the Tuz Gölü, a seasonal salt lake in Central Anatolia (Turkey) by Irion & Müller (1968). Details of this particular occurrence have been published by Irion (1970). The ephemeral mud flats around Lake Acigöl contain modern huntite (Müller et al., 1972; Mutlu et al. 1999).

In a quarry of an Ordovician dunite near Rockville, Montgomery County (Maryland, USA) huntite occurs associated with brucite (Larrabee, 1969). The dunite itself is serpentinized and cut by gabbro dikes. Thin veins of calcite and dolomite were found throughout the quarry. The mineral huntite occurs here together with chrysotile, clinochrysotile, tremolite, talc, chlorite, calcite, dolomite, aragonite, deweylite, magnesite, hyalite and magnesium hydroxide carbonate. In the Carlsbad Caverns of New Mexico (USA) huntite has been found in *Montmilch* deposits by Thrailkill (1971). Because such *Montmilch* deposits usually are powdery or pasty, Thrailkill (1971) concluded, that these deposits must have formed in the driest parts of the cave. Other carbonates found in the Carlsbad Caverns are calcite, aragonite, dolomite and magnesium hydroxide carbonate. Thrailkill (1971) attributed the formation of these carbonates to deposition by vadose seepage water. That the huntite of the Carlsbad Caverns must have had a low-temperature origin could be concluded from temperature measurements: the caves have a virtually constant temperature of 288 K. This particular occurrence of huntite in the Carlsbad Caverns has been confirmed by Hill (1973) and Gonzales & Lohmann (1988). Polyak & Güven (2000 A, B) not only found dolomite in the Carslbad Cavern as well as in the neighbouring Spider Cave and Hell Below Cave (New Mexico, USA). The presence of huntite of Holocene age in the El Melah sabkha near Zarzis (Tunesia) has been documented by Perthuisot (1971, 1974) and Pertuisot et al. (1990). Huntite, accompanied by aragonite, in nodules from a clayey soil near Katherine (Northern Territory, Australia) has been described by Veen & Arndt (1973). White nodules, about 1 to 5 cm in diameter, were found there at the basis of a plateau basalt. Maleev (1974) found huntite in a small karst cave in a fluorite mine of the Rhodope Mountains, Bulgaria. Because the huntite, together with calcite, aragonite, dolomite and magnesite, had been deposited here on the most protruding parts of the ceiling, Maleev (1974) concluded, that the carbonate must have precipitated from solutions sickering into the cave from overlying formations. These bicarbonate solutions would be enriched in magnesium, because the overlying rocks are dolomitized marbles. In addition any aragonite being precipitated would increase the magnesium content of the solution, since aragonite does not incorporate magnesium in its lattice. No genetic relationship could be found between the formation of huntite and that of the fluorite deposits.

Considerable quantities of huntite, in association with magnesite, dolomite, aragonite and calcite, were found by Wetzenstein (1974) in limnic deposits of Plio-Pleistocene age in northern Greece. The (former) lakes in which the carbonate minerals had accumulated, are situated in an intramontane basin formed by ultramafic igneous rocks, mainly serpentinites. With some emphasis Wetzenstein (1974) pointed out the association between huntite and organic matter such as bitumen, brown coal, coal anthracite and graphite. Cole & Lancucki (1975) described huntite, associated with magnesite, occurring in weathered basalt at Deer Park, near Melbourne, Australia. On top of the basalt there is a soil profile about 2.5 m thick; at its basis a discontinuous layer of magnesite nodules with huntite was found. Not only there the mineral huntite was present: it was found as well in a fossil soil developed on an underlying basalt flow.

The presence of huntite in the *Montmilch* deposits of the La Clamouse cave (Baron et al., 1957, 1959) has been confirmed by Fischbeck (1976). Huntite has been found by Strunz (1976) in weathered serpentine from a quarry near Haidberg (Bavaria, Germany). In caves of the Transvaal region of South Africa Martini & Kavalieris (1978) identified in X-ray diffraction modern huntite. In the Wolkberg, the Bob's and Apocalypse Caves of the Transvaal province huntite occurs in a microcrystalline form in *Montmilch* deposits and as a loose powder on the soil of the caves. Modern huntite has been found by Gac et al. (1977) in Lake Yao, a saline lake in the northern part of Chad. A number of springs feed the lake, but the arid climate of the region leads to such high evaporation rates, that salts accumulate on its beaches. X-Ray diffraction established the presence of huntite. In a weathered serpentinite at Hrubšice (Czech Republic) Němec (1981) found huntite together with magnesite. At this particular location the mineral huntite must have originated under conditions of low-temperature and atmospheric pressure: it occurred as a coating in fissures of the weathered serpentinite immediately below the soil profile. Where the soil profile is only thin and the serpentinite is relatively fresh, no huntite originated; instead dolomite and calcite formed. Modern huntite has been described by Renaut (1990) from Clinton Lake, a saline lake in British Colombia (Canada); huntite was found there together with aragonite, Mg-calcite, dolomite, magnesite, gypsum, thenardite and hexahydrite. According to Perthuisot et al. (1990) the formation of huntite in the sediments of Sabkha el Melah would have been caused by bacterial activity. Stanger & Neal (1994) found huntite on weathered serpentinite in Oman; this huntite was found in the form of nodules some 1 to 10 cm in diameter. The nodules were so soft, that within a few years after disclosure almost all of these new occurrences in Oman will have been washed away by the rain. The ease and rapidity of the weathering of huntite might well explain the rarity of the mineral in surface exposures (Stanger & Neal, 1994). In the Castañar Cave near Cáceres (Spain) modern deposits of huntite have been reported by Alonso-Zarza et al. (2005) and Alonso-Zarza & Martín-Pérez (2008).[28]

A number of occurrences of huntite is mentioned in the *Chemical Abstracts* (now Science Finder) in such a way, that additional information is required (e.g., Danilova, 1959; Levshov et al., 1964; Paděra & Povondra, 1964; Ivanov & Palgueva, 1976; Ivanov, 1982; and Popov & Sadykov, 1986). But there are more occurrences of huntite, which await further research. For example in the Oberen Süsswassermolasse near Dächingen (Germany) huntite is known to occur (Wetzenstein, 1974). At a depth of 40 to 60 cm in a soil profile developed on a gypsum deposit near Oglat Meteba (S.W. of Gabès, Tunesia) Kemp (1985) found huntite. At present only the fact that huntite occurs there together with quartz, bloedite, aragonite, vaterite and thenardite, has been established. Huntite has been found on the Isla de Margarita (Venezuela), and it might well be of limnic-sedimentary origin (Wetzenstein, 1989; pers.comm.). Huntite as a weathering product of ultramafic rocks in the Ingessana Hills chromite deposits (Sudan) still awaits further investigation (Wetzenstein, 1989; pers.comm.).

Oomori, Kaneshima, Taira & Kitano (1983) claimed the formation of huntite in one of their experiments. Essentially these experiments consist of adding a 0.4 mol sodium carbonate solution drop by drop to seawater brine. The seawater used came from a coral reef at Okinawa, and had been concentrated to 1/8 of its original volume by boiling. Because I did not have any of the seawater from the coral reef near Okinawa at my disposal, recourse had to be taken to the use of the seawater from the North Sea. Through slow boiling the "... seawater concentrated to 1/8 of its volume" was obtained. Oomori et al. (1983, p.147) had saturated their stock solution of sea water brine with calcium bicarbonate ("Powdered limestone was suspended in the filtered brine solutions. Carbon dioxide was bubbled through the suspensions, which were filtered again."). Instead of limestone I have used reagent grade calcium carbonate.

The formation of huntite took place according to Oomori et al. (1983) at 306 K through the addition of 60 ml of the 0.4 M sodium carbonate solution to 380 ml of the "seawater concentrated to 1/8 of its volume" saturated previously with calcium bicarbonate. But it is not clear, how long the experiment had taken. It must have been between 0 and 7 days, but I was not able to find a more exact indication. Upon boiling down several batches of natural sea water from 1 dm^3 to 125 cm^3 , a white precipitate formed (which turned out to be bassanite, $CaSO_4$. 0.5 H_2O upon X-ray diffraction). Once 380 cm^3 of concentrated brine had been obtained, excess calcium carbonate was added (2.0 g $CaCO_3$ powder, p.A. quality MERCK art.no. 2066) and CO_2 was bubbled through during 48 hours. The remaining calcite powder was filtered off, washed on the filter, and dried. In the 380 cm^3 brine about 0.5 g $CaCO_3$ had been dissolved. The clear brine was decanted into a 500 cm^3 glass beaker. During the experiment the brine was stirred slowly, and heated to a constant temperature of 306 K. Because room temperature was markedly lower (about 288 K), evaporation of the solution was so high, that several times distilled water had to be added to restore the original volume. The actual experiment took place during 6 days, during which every 30 minutes a small amount (some 0.18 cm^3) of a concentrated sodium carbonate solution (containing 6,8 gr Na_2CO_3.10 H_2O, D.A.B., MERCK art.no.6384 in 60 cm^3 distilled water) was added automatically to the brine. After 6 days the precipitate was filtered off, washed on the filter with some 2.5 dm^3 water and dried. The fine-grained powder (some 1.6 g) was found to consist entirely of magnesium hydroxide carbonate upon X-ray diffraction; no huntite at all was found.

The precipitation of huntite at room temperature and atmospheric pressure has been noted by Zaitseva et al. (2006). In these laboratory experiments cultures of cyanobacteria (also known as Cyanophyta or blue-green algae) of mainly, but not exclusively, the *Microcoleus chthonoplastes* species were added to the solution used by Ohde & Kitano (1978)[29] in their syntheses of magnesium calcites. After 10 months of continuously shaking the samples, Zaitseva et al. (2006) found huntite, magnesite and aragonite.