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INVESTIGATING MAGNESITE FROM AUSTRIA

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INTRODUCTION

Austria has played a major role in the development of our knowledge of the mineral magnesite. Anhydrous magnesium carbonate has been discovered first in the former Empire of Austria-Hungary, and for many years Austria was the world-wide largest exporter of magnesite. Up to the now theories on the mode of formation of magnesite are dominated by a variety of Austrian publications.

The present paper gives a sketch of the discovery of the mineral magnesite, anhydrous magnesium carbonate, and it reviews much of the existing older literature on magnesite as found in Austria. The rationale for the present account is the discovery of an answer to "the magnesite problem", a scientific problem that has existed for more than two hundred years. For too long no laboratory syntheses of magnesite conducted at temperatures characteristic of the earth's surface were known. Therefore mineralogists have found it hard to accept a possible interpretation of magnesite deposits as having been formed in the sedimentary environment. However, this situation has changed fundamentally, because reproducible low-temperature syntheses of magnesite have become known (Deelman, 1999; Alves dos Anjos et al., 2011 and Hobbs & Xu, 2020).

Certainty about the possible formation of magnesite in the sedimentary environment gives an unexpected new dimension to the ongoing discussions on the formation of Austrian magnesites.

HISTORY

Most likely the first description of anhydrous magnesium carbonate found as a rock in nature was given by Lampadius (1800), who had analyzed a rock sample collected by the Irish mineralogist George Mitchel in Hrubitz, Moravia (formerly Austria-Hungary, now Hrubisçe, Czech Republic). The French version of the paper by Lampadius & Mitchel (1804) contains additional information on the mineral: it had been found in a serpentinite rock together with *Meerschaum* (= sepiolite). The analysis of the new mineral by Lampadius (1800) was confirmed by Klaproth (1807), who had obtained samples of magnesite from Kraubath in Austria.

Lampadius (1800) mentioned, how Werner had included the new mineral in his nomenclature as *reine Talkerde* (as recorded later by Werner, 1804 and by Ludwig, 1804). In this way Lampadius (1800) created the impression, that the definition of magnesium carbonate (*reine Talkerde*) by Werner in 1785 would take historical precedence. However, as Berzelius (1814) pointed out, the mineralogical system of Werner as well as that of Haüy (1801) were based on morphology and did not incorporate any chemical analyses (in contrast to for example the classifications of Cronstedt, 1770; Wallerius, 1772 and Ludwig, 1804). In the absence of an adequate chemical analysis, it cannot be maintained, that *reine Talkerde*

would be the equivalent of magnesite. Actually, Werner (1804) had included *reine Talkerde* into the talc genus of his system together with *Meerschaum* and serpentine.

Brochant (1802) described magnesite as *Terre magnésienne naturelle*. Suckow (1803) gave its name as *kohlenstoffsäure Bittererde* and Ludwig (1804) listed three synonyms for anhydrous magnesium carbonate: *reine Talkerde*, *Talc carbonatum* and *Magnésie native carbonate*. Giobert (1804) reported magnesite from a steatite-like rock near Baldissero; after describing its physical properties, a chemical analysis was performed and it showed the presence of magnesium and carbon dioxide together with a small amount of silica. Giobert (1804) gave the name *magnesia native* to this specific mineral. After finding magnesite near Baldissero, Giobert (1806) also reported on magnesite from the neighbouring town of Castellamonte, Italy. However, this second kind of magnesium carbonate showed a behaviour, which was different from the magnesite from Baldissero: it would dissolve in any kind of acid. Analysis showed it to consist mainly of magnesium and carbon dioxide, but 18 to 20 wt.% silica was present as well.

The name *magnesite* as such probably has been introduced by Delamétherie (1795), but that author used the same name for a variety of magnesium compounds (such as carbonate, sulphate, nitrate and chloride) and not specifically for anhydrous magnesium carbonate found as a mineral. Bronghiart (1807) pointed out, how magnesite resembled chalk and white clay, but that its chemistry was quite different from those two rocks. After dissolving magnesite in concentrated sulphuric acid a solution formed which, upon complete desiccation, gave crystals of magnesium sulphate. Although Bronghiart (1807) was well aware of the magnesite found by Mitchel in Hrubisče, he did not want to consider it to be a new, individual mineralogical species and included for example *Meerschaum* in the same category. By doing so Bronghiart (1807) created confusion over the definition of magnesite, because he included other magnesium containing minerals (such as *magnésite plastique*, which was mentioned as a synonym for *Meerschaum*, and the *magnésite piémontaise* described by Giobert, 1804 from Baldissero, as well as the *magnésite de Vallecas*, Spain).

Ultimately it was Karsten (1808 B, p.95), who restricted the name magnesite to the anhydrous magnesium carbonate found in nature. A sample of magnesite from the type locality of Hrubšitz / Hrubisče was analyzed by Haberle & Bucholz (1809): wet chemical analyses gave its composition as 48 wt.% magnesium oxide plus 52 wt.% carbon dioxide (which equals the molar composition of pure MgCO_3). The chemical analyses of samples of magnesite from the same location by Klaproth (1810) gave the following composition: “*Bittererde 48; Kohlensäure 49; Wasser 3.*”

Stromeyer (1815) analyzed samples of magnesite from the new location of Baumgarten, Silezia (now: Prokolno, Poland) and found these to consist of pure magnesium carbonate, but this kind of magnesite was harder than any other known variety. None of the seven samples analyzed, contained any calcium carbonate, but they were found to contain 1.4 wt.% water. From which Stromeyer (1815) concluded, that some *Talkerdehydrat* (= hydrated magnesium oxide) had to be present. The analyzed percentages of anhydrous magnesium carbonate were invariably around 47 wt.% and carbon dioxide accounted for 50 wt.% of the samples. As Stromeyer (1815) stated, his analyses compared well with those of magnesite from Kraubath (Austria) published earlier by Klaproth (1807) and those by Haberle & Bucholz (1809), who had analyzed the magnesite from Hrubšitz / Hrubisče.

Walmstedt (1822) described, how he had analyzed a rock sample from the collection owned by Berzelius. The crystals resembled in a way those of calcite (*Kalkspath*), but exact measurements with a goniometer gave slightly different values for the interplanar angles. Density of magnesite was measured as 3.063 kg/m^3 . Chemical analysis showed the rock to consist of 84 wt.% magnesium carbonate (*kohlensaure Talkerde*), 10 wt.% iron carbonate, 3 wt.% manganese carbonate plus traces of silica and water. Walmstedt (1822) stressed the

fact, that according to Mitscherlich (1820, 1821 A, B), the three aforementioned carbonate minerals are isomorphous and therefore able to form mixed crystals of intermediate compositions. Brooke (1823, p.382) also used crystallographic measurements to underline his conclusion, that he had found a carbonate different from “*bitter spar*, or *magnesian carbonate of lime*” (i.e., dolomite). After dissolving a sample of that very carbonate from Tirol in dilute sulphuric acid, a precipitate of magnesium sulphate was obtained, which tasted very strongly of iron. Except for a small amount of talc, no insoluble residue remained. Therefore Brooke (1823, p.383) described this mineral sample to be “a carbonate of magnesia and iron”. In an additional analysis Brooke (1823) found the sample to contain 90 % magnesium carbonate plus 10 % iron carbonate. Mitscherlich (1827) analyzed a sample of magnesite from the Pfitschtal, Austria (now: Val di Vizze, Italy) and, found it to consist of 82.91 wt % MgCO_3 , 15.59 wt.% FeCO_3 and 1.19 wt.% MnCO_3 .

Stromeyer (1827 A, B, C) analyzed a mineral he called *Magnesitspath*, which was in fact a well-crystallized form of anhydrous magnesium carbonate. The analyses showed the mineral to consist of virtually pure MgCO_3 without a trace of calcium carbonate, but with small amounts of iron (II) carbonate and manganese carbonate. According to Stromeyer (1827 A, B, C) magnesium carbonate had been found up to that moment only in an amorphous form. The crystalline form of MgCO_3 had been described before, but it had been given the name of *Bitterspath*. The name *Bitterspath* later became restricted to the mineral dolomite. Mohs (1820) gave in his definition of *Brachytypes Kalkhaloid* the following synonyms: *Braunspath*, *Rautenspath* (after Werner); *chaux carbonatée ferrière perlée*, *chaux magnésifère* (after Haüy) and even included dolomite. Because Mohs was not really sure about the distinction between the new mineral and dolomite, he had sent samples to Stromeyer at the University of Göttingen. Ultimately Stromeyer (1827 A, B, C) could only confirm, that the newly defined *Brachytypes Kalkhaloid* of Mohs did not contain any calcium carbonate. On the other hand, the samples analyzed by Stromeyer were found to contain 8 to 17 wt.% FeCO_3 .

MAGNESITE IN AUSTRIA

In publications on the origin of Austrian magnesite the concept of “metasomatism” is often invoked to explain the mode of formation of magnesite. Therefore it is necessary to trace the origin of this concept and to clearly define it.

Presumably the first time the concept of metasomatism was used, is recorded in the textbook on mineralogy by Naumann (1828). The concept was introduced in the following manner: some changes in mineralogy would originate upon mere contact with water, heat, light or air; those were the reactions typical of the process of weathering. There were, however, other changes affecting minerals, taking place in a somewhat mysterious way, and leading to what might be considered as a kind of inorganic decomposition. After this change in mineralogy, the outer form of the crystal might well be preserved. In other words the minerals had undergone a kind of metamorphosis, renamed for the occasion into “metasomatosis”. In his later publication Naumann (1850) wrote more clearly about the relations between pseudomorphosis and the newly defined process: all pseudomorphs were the result of “metasomatosis”. In one of the few subsequent papers dealing with the definition of metasomatism, Goldschmidt (1922) restricted the rather wide-ranging definition of Naumann (1828) to “changes in the overall mineralogy of a rock under the influence of an external supply of material”. In translation Goldschmidt’s definition reads: “Metasomatism is the conversion of a rock, during which material is introduced into that rock, followed by

bonding or enrichment of the newly introduced material by way of certain chemical reactions, in which both original and newly formed minerals take part.” The materials introduced could be gases, solutions or liquid melts. In the absence of any metasomatic processes, each metamorphic rock would reflect the exact chemical composition of the rock before metamorphism took place. As a good example of metasomatism Goldschmidt (1922) mentioned the conversion of limestone into dolomite, but the conversions typical of metasomatism would not be restricted to carbonate rocks. Other examples could be found among the metamorphic silicates, especially when associated with ore deposits.

According to Lindgren (1933) rocks will be affected in two different ways by water (or rather: aqueous solutions). In the first place rain water would be able to soak into the porous or fissured rocks and start descending through it. Ascending hot solutions would affect the rocks even more; such hot solutions were known to emanate from plutonic intrusions or resulting from volcanic activity. But metasomatism would be different: “The water penetrates the rocks in capillary openings. By the phenomenon known as adsorption, the film of liquid on the solid contains more than an average amount of material in solution and these films are likely to become supersaturated in advance of the remainder of the solution, so that chemical reactions will be facilitated. In this manner the mineralogical and structural character of rocks may be changed”: Lindgren (1933, p.23). After stressing the importance of water in the processes of metamorphism and metasomatism, Lindgren (1933, p.89) stated: “Solution and precipitation go on continuously; one or the other may predominate at any given place.”

A clear distinction needs to be made between Lyell’s (1833) concept of *metamorphism* and Naumann’s (1828) concept of *metasomatosi*s. In this regard, two useful definitions were given by Lindgren (1933). Metamorphism involves processes, which result in a partial or complete crystallization or recrystallization of solid masses of rocks (for example the change of granite into gneiss, or of mica schist into clay shale). Metasomatism was defined by Lindgren (1933, p.91) as “the process of practically simultaneous capillary solution and deposition by which a new mineral of partly or wholly differing chemical composition may grow in the body of an old mineral or mineral aggregate.” Such a process of metasomatism would leave its traces in the form of pseudomorphs and in the form of the petrification of fossils; the occurrence of metasomatism provides evidence that the rocks involved were subject to *unstable conditions* (as Lindgren, 1933 put it). Korzhinsky (1964, p.1714) gave the following interpretation of the concept: “Present-day geologists understand the metasomatism concept to designate any substitution which alters the chemical composition of a rock, providing the minerals in the older country rock are dissolved and new minerals are deposited almost simultaneously, the rock, therefore, remains a solid throughout the entire process.”

From 1810 to 1900

One of the very first papers describing magnesite from Austria is that by Klaproth (1810), in which chemical analyses of a sample of magnesite from Kraubath, Obersteiermark were recorded. (Samples from this very location had been described macroscopically, but not analyzed chemically, by Karsten, 1808 A.) The analyses by Klaproth (1810) showed the sample to consist of 48 wt.% magnesium oxide (*Bittererde*), 49 wt.% carbon dioxide and 3 wt.% water. Especially this very low water content and its high percentage of carbon dioxide distinguished the magnesite mineral from the magnesia sold by pharmacists (*Magnesia der Officinen* or magnesia alba, i.e., magnesium hydroxide carbonate).

Von Hauer (1852) and Von Hauer & Foetterle (1852) reported on magnesite from the Triebenstein Mountain near St. Lorenzen, Austria. Chemical analyses were performed by Carl von Hauer (1852) on a sample of magnesite from Semmering given to him by Foetterle. One year later Štúr (1853) found magnesite at two other Austrian locations: on the southeastern slope of the Grimming mountain (NW of Trautenfels) and in an area northwest of Triebenstein im Sung. These two sites had previously been explored by Adolph von Morlot, who thought the upper and lower borders of the magnesite deposits there to be rather unclear. (Von Morlot was at that time, much like Franz Ritter von Hauer, Carl von Hauer, Franz Foetterle and Dionýs Štúr employed at the *Kaiserlich-Königliche Geologische Reichsanstalt of Vienna*). Foetterle (1855) related, how he had re-investigated several of the rock samples collected in the area of Bruck an der Mur (Steiermark) and had found these samples to consist of pure magnesite. The magnesite of Bruck an der Mur occurs there intercalated with limestone, which limestone is embedded in schists. Analyses by Carl von Hauer (1854), showed the magnesite to be a very pure form of magnesium carbonate. Foetterle (1855) reminded his readers, that this particular deposit of magnesite was the fifth occurrence of magnesite in Austria: the first two had been described by Von Hauer & Foetterle (1852) and the other two by Štúr (1853).

Miller von Hauenfels (1864) found two different kinds of magnesite in the serpentinite near Kraubat(h): in cracks and fissures a compact kind of magnesite occurred, which was explained to have been deposited from hot, ascending solutions (thermae). The second kind of magnesite was clearly crystalline (*Magnesitspath*), and often occurred in association with talc in crystalline slates. According to Miller von Hauenfels (1864) the latter kind of magnesite must have originated in the manner suggested by Foetterle (1855): that is by way of a reaction between the embedding schists and a magnesia-rich solution. Höfer von Heimhalt (1866) published chemical analyses of rock samples, he had collected near Leoben and Veitsch. The serpentinite masses of Veitsch are interspersed with numerous veins of magnesite, often of considerable thickness and of great extension. Enclosed in the magnesite are pieces of serpentinite rock, which in turn are cut by many thin veins of magnesite. Chemical analysis showed the magnesite of Veitsch to be pure MgCO_3 . The dolomitization of gneiss masses by magnesium bicarbonate solution, in the manner suggested by Nauck (1848) and Scheerer (1866), was explained to have been responsible for the formation of the serpentinite. Karl Ritter von Hauer (1867) analyzed samples of magnesite from Bruck an der Mur, and found the samples to be as pure as those from the very first known Austrian magnesite deposit of St. Katharein an der Laming (North of Leoben). Von Hauer (1867) stressed the possible economical significance of this very pure magnesite, especially its use as heat-resistant bricks for the lining of steel furnaces. The review by Von Zepharovich (1873) included magnesite deposits in the Austrian province of Salzburg (Semmering, Schellgaden, Flachau, Kollmannsegg bei Dienten and Nöckelberg im Schwarzleo Thal); in Steiermark (Mariazell, Katharein, Bärnegg a.d. Mur, Kraubat, Sung am Triebenstein, Trieben, Grimming (near Trautenfels and Irdning); in Kärnten (Waldenstein) and Tirol (Salzberg near Hall, Greiner and Rothenkopf in the Zillertal, Fassa and Pfitsch).

A multitude of field observations had convinced Rumpf (1873 A, B, C), that crystalline magnesite invariably occurs in close contact with shale or with talc- or chlorite slate. Only two other parageneses had become known: the magnesite in the anhydrite of Hall (Austria) and that in the melaphyr porphyrite of Zwickau (Germany). Magnesite had *never* been found contacting limestone or dolomites (according to the field observations by Rumpf that is!). In contrast, the cryptocrystalline variety of magnesite was always found in or near serpentinite rocks. Furthermore, the two different kinds of magnesite, the crystalline and the cryptocrystalline varieties, had never been found next to each other. The two types of magnesite, amorphous and crystalline, therefore had to be genetically quite different from

each other. Much like Bischof (1855), Rumpf concluded, that the concentration of the required Mg-bicarbonate solution and factors such as the rate of crystallization, temperature of the solution and the possible presence of other salts in solution, would determine whether the amorphous or the crystalline form of MgCO_3 would originate. Many (field) observations on crystalline magnesite deposits in Steiermark had been made by Rumpf (1873 B); without exception all of those crystalline magnesites occurred intercalated in clay slates. Two examples were discussed in detail: the magnesite from Sunk (Steiermark) and that from Semmering (Nieder-Oesterreich). Both of these possessed what is known as the *Pinolit* texture.

Rumpf (1876) related, how he had tried to determine the stratigraphic position of the *Pinolit*-magnesite from the Sunk area, and had actually found crinoids fragments in the limestones just below the massive magnesite-containing marbles. It is of considerable importance to realize, how Rumpf (1876) interpreted the origin of the magnesite from Steiermark as having been formed by *thermae* springing up in shallow parts of the sea, and he hinted, that therefore magnesite would have been formed more or less as a sedimentary rock. Rumpf (1876), after studying the magnesite deposits of for example Sunk, Wald, Mautern, Oberdorf and Mixnitz, tended to agree with the existing dual classification of a crystalline and an amorphous kind of magnesite. At the same time Rumpf (1876) stated to never have found any indications for a possible transition of previously existing dolomite into crystalline magnesite, nor had he ever noted any possible metamorphic origin. Ultimately, Rumpf (1876) repeated his suggestion, that the *Pinolit*-Magnesit must have formed from *thermae*. The *thermae* possibly carried magnesium bicarbonate solutions, but most certainly magnesium sulphate would have been present too. A reaction between organic compounds from the black muds (which later changed into black shale intercalations in between the magnesite layers) and the magnesium in solution must have been responsible for the formation of the mineral magnesite.

Meanwhile various authors contributed more and more data on the occurrence of magnesite in Austria. Von Gümbel (1880) observed, that the samples of the *Röthikalk*, he had collected in Switzerland, strongly resembled samples of a carbonate rock (from the *Werfener Schichten*) found near Elmen (in the Kufstein area, Austria). Chemical analysis showed this particular carbonate to consist of magnesium carbonate, with only minor amounts of SiO_2 , Al_2O_3 , MnO and Fe_2O_3 as admixtures. Because Von Gümbel (1880) also was aware of the possible economic value of magnesite for the production of steel, he urged his fellow geologists to investigate the vast deposits of magnesite in the Austrian Alps (thereby repeating the suggestion by Von Hauer, 1867).

Much like Hochstetter (1854) had done previously, Schrauf (1882) studied the area around Křemže (near Budweis; in those days part of the Austrian-Hungarian Empire) and found magnesite, opal and chalcedony in fissures and veins of the host rock, a weathered serpentinite. Schrauf (1882) stated specifically, that there the magnesite had not formed at the same time as the serpentinite, but only much later upon the weathering of the serpentinite. Von Foullon (1884 A) described magnesite crystals with zones of different colour found in the Kaswassergraben (near Großreifling, Ennstal, Steiermark). Von Foullon (1884 B) investigated the magnesite deposit near Dienten, that had been studied previously by Carl von Hauer (1867) and Rumpf (1873 A, B, C; 1874 A, B). The chemical composition of this magnesite was much the same as that reported by the latter two authors, but Von Foullon (1884 B) noted something special in the insoluble residue. Very small crystallites of pyrite and colourless, platy crystallites of the mineral epidote were recognized under the microscope.

Koch (1893) found various fossils, among which *Productus punctatus*, *Spirifer octoplicatus*, *Zaphrentis* sp., *Fenestella* sp., and crinoid stem fragments of Lower

Carboniferous age in the magnesite deposit of the northern Mur area (near Veitsch). However, the fossils had been found mainly in the calcareous shale partings and narrow layers of limestone within the magnesite deposit. Although a few fossils had really been found in the magnesite itself, the fossils from Veitsch were badly preserved, and consisted almost exclusively of crinoid stem fragments. Some of those crinoid stem fragments consisted partly of dolomite and partly of magnesite in one and the same fragment. Vacek (1893) related, how Koch (1893) had concluded on a secondary origin of magnesite from pre-existing limestones being caused by magnesium-rich solutions. Vacek (1893) observed, how the magnesite of the Sattlerkogel / Veitsch deposit not only had underlying limestones, but in places had underlying shale formations. In other words, the field observations by Koch (1893) turned out, not to have been really convincing. Vacek (1893) maintained, that when looking in detail, the multitude of contacts between magnesite and limestone were so very sharp and well-defined, that no transition from limestone into magnesite seemed possible.

From 1900 to 1950

Weinschenk (1900) studied numerous outcrops of crystalline magnesite near Wald im Liesenthal, which appeared to be closely related to the talc-graphite deposits of Mautern in Steiermark. Redlich (1900) reported on a newly found magnesite deposit near St. Martin at the basis of the Grimming Mountain (Ennstal, Steiermark). According to Baumgärtel (1902) the magnesite deposits of the Eastern Alps would have originated from granite intrusions, changing limestone into magnesite and shales into talc deposits. Similarly, Humphrey (1905) explained magnesite formation in terms of a granite intrusion, but added that during the ensuing process of contact metamorphism, solutions would have penetrated along bedding planes, leading to the typical intercalations of dolomite and magnesite layers. In addition, Humphrey (1905) described dolomites containing remains of crinoids together with magnesite and siderite from the vicinity of Turrach (near Reichenau, Austria). Hörhager (1911) was convinced that volcanic activity during the Alpine orogenesis, and especially its inherent hydrothermal solutions, had been the real source of the formation of iron carbonate and magnesium carbonate. Iron-rich solutions would have initiated the formation of iron carbonates, whereas magnesium-rich solutions were responsible for the magnesite masses. At points of overlap between the two different hydrothermal solutions, mixed carbonates would have resulted. At the same time Hörhager (1911) rejected a possible alteration of pre-existing dolomite into magnesite. If such a conversion would have taken place, half the volume of the dolomite would have to be removed in one way or another. As a consequence the remaining dolomite would have to be highly porous, which so obviously was not the case. The well-defined parallel alternations of layers of magnesite with beds of dolomite occurring in the magnesite deposit at the Stangalpe near Turrach (Austria) could, according to Hörhager (1911), be interpreted only as evidence contradicting any suggested gradual conversion of dolomite into magnesite.

The mode of formation of the iron carbonate deposits of the Hüttenberg (Kärnten) was attributed by Baumgärtel (1902) to the conversion of calcium-magnesium carbonates by solutions stemming from volcanic intrusions (ascending solutions, that is). Any suggestion of a possible sedimentary origin of this particular deposit was ruled out; instead Baumgärtel (1902) thought an epigenetic mode of formation (involving the replacement of pre-existing limestone) to be most likely.

Redlich (1903) started out his paper on the origin of magnesite deposits in Austria with noting, that it had become more and more clear, that stratiform ore deposits need not be of a

sedimentary origin. That observation might well be applicable to magnesite and ankerite deposits. North of the main Alpine chain there was a vast system of layered rocks (limestones, shales) and conglomerates, known as the *Grauwackenzone*, which contained many of such stratiform iron- and magnesium carbonates. Because Redlich (1903) had observed the *Pinolit* texture not only in magnesite, but also in iron carbonate (ankerite) ores, he concluded, that both mineral deposits must have formed in an analogous manner. At the same time Redlich (1903) postulated, how magnesite must have formed from pre-existing limestones through a “diffusion” process, much like the way in which dolomite would have formed. (An observation which had previously been made by Höfer von Heimhalt, 1866). In conclusion Redlich (1903) hypothesized, how submarine volcanism would have led to the formation of stratiform mafic rocks and tuffs, and how this volcanism would have ended with thermal springs changing limestones into dolomite or magnesite (as Rumpf, 1876 had suggested).

Two newly discovered deposits of magnesite were described by Canaval (1904): one near the Goldegg Mountain and another near Tragail. Chemical analysis of a sample from the latter location showed it to contain 89 % MgCO_3 , 4 % FeCO_3 plus traces of CaCO_3 . The insoluble residue consisted of quartz, muscovite and a graphite-like substance. Contacting the magnesite deposit of Tragail were layers of dolomite and ankerite. Canaval (1904) was well aware of the replacement theory of Weinschenk (1901) and Redlich (1903), but considered an epigenetic origin for this particular case not entirely unlikely.

Redlich (1907) reported on large masses of magnesite (in Austria) embedded in dolomite, which dolomite originally must have consisted of limestone. All of the minerals occurring in the magnesite deposit of the Sattlerkogel (Veitsch) were listed by Cornu (1908). Magnesite, iron-rich magnesite (breunnerite), dolomite and talc formed the main part of this particular deposit. Finely divided pyrite was nearly always present in the magnesite. Secondary minerals such as quartz, ankerite, aragonite, calcite, and leuchtenbergite were found in the magnesite and the dolomite. Veins of sulphides cutting through the magnesite contained quartz, chalcopyrite and pyrite. Upon weathering of the sulphide veins, a variety of epigenetic minerals would be formed, including malachite, azurite, chrysocolla, limonite and goethite. Cornu (1908) recognized aragonite as well as magnesium sulphate (epsomite) as recently formed minerals at this location. Unweathered magnesite showed a white colour, but the oxidation of the ever-present, fine-grained pyrite gave it a yellowish to yellowish-brown colour. Cornu (1908) stressed, that he had found numerous crinoids stem fragments in the dolomite associated with the Sattlerkogel magnesite. Redlich (1908 A) did not hesitate, and declared the siderite of the Erzberg (Steiermark) could not be of sedimentary origin at all. The siderite must have originated from a pre-existing limestone through a conversion brought about by “iron solutions”.

According to the analyses by Hammer (1909) the magnesite from Stiereck (Ortler Alpen) is rich in iron carbonate (some 17 wt.% FeCO_3). However, much more prominent is the dolomite at this location, which was analyzed to contain some 8 wt.% iron (II) carbonate. Two new Austrian magnesite deposits were described by Redlich (1908 B): one on the Millstätter Alp and the other at Mallnock near St. Oswald. Both deposits of magnesite originally must have consisted of limestone (Redlich, 1908 B). Redlich & Cornu (1908) pointed out, how the paragenesis of talc and magnesite indicates, that magnesia solutions must have changed not only shale into talc, but also limestone into magnesite. After studying the magnesite deposit of the Hinter-Eichberg near Gloggnitz, Sigmund (1909) stated that a sedimentary origin could be excluded at beforehand.

Redlich (1909 B) expressed a need for an adequate classification of the Austrian magnesites, and defined four different types of magnesite. The first type of magnesite, or “Typus Hall”, had been found in anhydrite layers of the salt mines at Hall, Tirol. Breithaupt

(1841) had described this particular magnesite as *Carbonites allotropus*. The magnesite itself had a gray to black colour, and contained a characteristic texture, which Redlich had given the name of “Pinolite-like”, because the small bodies making up this texture resembled the fruits of the pine tree *Pinus pinea*. The mode of formation of this particular kind of magnesite was explained by Redlich (1909 B) as follows: in the overall process of the formation of rock salt, first carbonates would precipitate from the evaporating seawater. After that calcium sulphate, sodium chloride and magnesium sulphate would follow. Once a brine containing predominately magnesium sulphate had been formed, it would react with the previously formed carbonates. In this way aragonite would be transformed into dolomite, and upon prolonged exposure of this dolomite to the concentrated magnesium sulphate solution, it would be changed into magnesite. Evidence in support of this explanation was found by Redlich (1909 B) in the occurrence of magnesite in gypsum deposits found in the Spanish Pyrenee Mountains and in other parts of northern Spain (see: Tenne, 1902). Precht (1882) and Biltz & Marcus (1910) found magnesite in the rock salt from Staßfurt (near Magdeburg, Germany). Much the same paragenesis had been reported from Vauds (Switzerland) by Kenngott (1866). Later Bücking (1911) described magnesite from rock salt in Zipaquira (Columbia) and from the rock salt in the Douglashall mine (near Börde-Hakel, Germany). Bücking (1911) recalled how Ochsenius (1890) had found magnesite in the carnallite deposits of that same salt mine and Görgey (1912 A) had described magnesite in the rock salt deposits of Wittelsheim, France.

The second category of Austrian magnesites was named “Typus Kraubath”, after the town of Kraubath in Steiermark. Here magnesite occurs in sills within nearly every serpentinite or its parent rocks (peridotite and Mg-rich gabbro). Field observations had convinced Redlich (1909 B), that the actual formation of magnesite did not at all coincide with the time of formation of the serpentinite; magnesite formation must have happened much later. Upon the weathering the actual formation of magnesite did not start in the top layers of a soil, but depths of at least 50 cm would be required (at the same time opal and two forms of antigorite would be formed). Large masses of serpentinite without any magnesite present indicated, that magnesite formation would take place simultaneous with the weathering of the mineral serpentine.

Redlich (1909 B) had noted in the field, how the Kraubath kind of magnesite was quite plastic and soft to the touch. Microscopic examination had failed to reveal any crystallites. In conclusion therefore Redlich (1909 B) described his second category of magnesite as “a gel”: definitely not a crystalline form of magnesite (thereby following the much earlier description of the same material as *Thermaterites magnesius* by Breithaupt, 1841). Aragonite and dolomite had been found at Kraubath together with the newly formed magnesite.

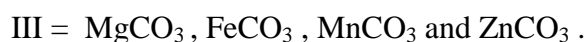
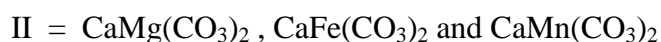
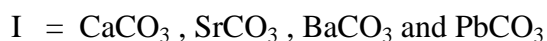
The third type of Austrian magnesite came from the Greiner area in Tirol and had been described originally by Breithaupt (1841) as *Carbonites brachitypicus* or *Eisentalkspat*. The magnesite occurred in close association with dolomite and manganese-rich dolomite. This third type of magnesite from the classification by Redlich (1909 B) was given the name of “Typus Veitsch”. Its formation would be closely related to the metamorphism of limestones, and often this type of magnesite occurred intercalated in black slates (see also: Redlich 1903, 1907, 1908 A, 1909 A). Mineralogical analyses of this very magnesite previously conducted by Von Foulton (1885), had shown the presence of minerals typical of the neighbouring crystalline shales. High percentages of iron carbonate were responsible for the formation of $\text{MgCO}_3 - \text{FeCO}_3$ mixed crystals. The explanation of the mode of formation of the “Typus Veitsch” magnesite given by Rumpf (1876) (i.e., an origin from thermae in the sea) was rejected by Redlich (1909 B); formation during metamorphism seemed much more likely. Large dolomite crystals inside the magnesite, but especially the presence of crinoid fragments

now converted into magnesite or dolomite, would form the undeniable evidence of a secondary conversion of limestone into magnesite and/or dolomite. In the explanation of Redlich (1909 B) this change must have been caused by magnesium bicarbonate solutions reacting with the limestones; large amounts of calcium carbonate must have been removed. Much the same reaction would cause the formation of talc deposits, when silicates in the form of shales were present.

Ascher (1917) criticized the observations made by Redlich (1909 C) on the magnesite found near St. Martin an der Salza, Steiermark. On the basis of his own detailed knowledge of the area and its magnesite (in the *Werfener Schichten*), Ascher (1917) outlined various mistakes made by Redlich (1909 C), not only misinterpretations of field observations but also false suggestions as to the possible industrial significance of the deposit. At the same time Ascher (1917) included various remarks made by the director of the geological survey in Berlin, Germany, contradicting most of the conclusions reached by Redlich (1909 C).

Magnesite formation, much like that of dolomite, would always need relatively high values of the CO_2 -pressure for its formation (as Redlich, 1914 A claimed). When finding calcite, dolomite and magnesite together, such paragenesis would indicate an incomplete stage in the process of metamorphism. According to Redlich (1914 A) an important observation with regard to the mode of formation of magnesite had been made by Leitmeier (1909): after desiccating a quantity of spa water from Rohitsch Sauerbrunn (which spa water is in fact a magnesium bicarbonate solution) nesquehonite and/or lansfordite formed, both of which changed relatively quickly into amorphous magnesite. The formation of amorphous magnesite of the Veitsch type was, according to Redlich (1914 A), invariably associated with serpentinite. Such a serpentinite rock forms upon the weathering of the mineral olivine through the action of CO_2 dissolved in water. This weathering process had been studied in a variety of laboratory experiments (although there only nesquehonite or lansfordite would form). What remained was the question how the CO_2 - containing water would be able to enter into the rock: would rain water seep through the soil and take up large amounts of carbon dioxide there (= *descending solution*)? Or would CO_2 -rich water rise up from deep-seated sources, invariably related to intrusions of basic magmas (i.e., *ascending solution*)? Writing about the mode of formation of the first kind of magnesite, the “Typus Hall”, Redlich (1914 A) did not at all doubt the fact, that this kind of magnesite in salt deposits would have had a “metasomatic” origin.

It should be realized, that Redlich (1914 A) had arrived at his three different models of magnesite formation on the basis of field observations only. The common factor between all three processes was the inherent “metamorphosis of calcium carbonate”. In this regard Redlich (1914 A) stressed the significance of the observations made by Grünberg (1913), who had distinguished three different series of carbonates, which were miscible amongst each other only within their own group:



The three groups of carbonates defined by Grünberg (1913) explained at once, why magnesite so often contained iron carbonate. At the same time Redlich (1914 A) observed, how calcium and magnesium on the one hand, and calcium and iron on the other, were apparently not able to form complete series of mixed crystals. In nature only the mixed crystals of definite composition dolomite and ankerite were known. Pure iron (II) carbonate

(siderite) would have formed in much the same way as magnesite would have formed. (Pichler had documented the close association between iron carbonates and dolomite as early as 1858.) Redlich (1914 A) explained how siderite would have originated upon the interaction of Fe (II) bicarbonate solutions with (pre-existing) solid CaCO_3 , during which reaction ankerite might be formed as well. However, as Redlich (1914 A) noted, the origin of, and the venues for, such iron (II) bicarbonate solutions posed a major problem. In his 1916 paper Redlich returned to the subject of the origin of iron carbonates. The suggestion that all of the ores in magnesite deposits had a “metasomatic” origin (the suggestion of Redlich & Großpietsch, 1913) was reiterated by Redlich (1916). The vast deposit of siderite of the Steirische Erzberg must have been formed in exactly that manner: through “metasomatism”. The presence of a variety of mixed crystals of Mg and Fe (II) carbonate, such as ankerite and breunnerite, provided all of the necessary evidence. In addition to siderite, amounts of dolomite had become known from the Erzberg, at times in the form of zoned crystals of dolomite and siderite. According to the field observations by Redlich (1916) the iron carbonates and the magnesite deposits had formed only after folds and faults originated.

Redlich (1917 A) discussed the paper by Leitmeier (1916 A), but restricted his comments to the crystalline type of magnesite and restricted himself even more by considering only “observations from nature”. The change of limestone into dolomite, and the possible later change of dolomite into magnesite, had been doubted by Leitmeier (1916 A) on the grounds of chemical theory. Redlich (1917 A) countered this point by stressing the significance of his field observation, that at least half of the magnesite deposit of Veitsch consisted of pure dolomite. The suggestion of Leitmeier (1916 A), that depending on the degree to which magnesium chloride solutions would react with pre-existing carbonates, dolomite or magnesite would form, was claimed by Redlich (1917 A) as his own. However, such an explanation would apply solely to the kind of magnesite found in rock salt (“Typus Hall”). The underlying suggestion found in Leitmeier’s (1916 A) paper concerning a possible marine, sedimentary origin of magnesite, was furiously rejected by Redlich. The main argument used by Redlich (1917 A), was that such a suggestion was contradicted by “... *all of the observations ever made on Alpine magnesite deposits*”. In other words: Redlich (1917 A) choose to consider only field observations as worth his while. The laboratory experiments by Leitmeier (1916 A) would have revealed themselves to be wholly inadequate to “explain” the mode of formation of magnesite (at least according to Redlich!). Similarly, the suggestion made by Sigmund (1909), that the Semmering magnesite might be of an “epigenetic” (i.e., not secondary) origin, was rejected by Mohr (1910) on the ground of a most remarkable argument: because all the rest of the Austrian magnesites were of a metasomatic origin, there really could be no exception for the Semmering magnesite.

Most of the magnesite from Kraubath is microcrystalline (*Gel-Magnesit*) as Granigg (1910) pointed out. In addition Granigg (1910) stressed the fact, that the Kraubath magnesite (at least in its type locality) occurs in irregular and rather small quantities, making large-scale exploitation almost impossible and certainly uneconomical. According to Hörhager (1911) there really is a close relation between magnesite and deposits of iron carbonate. However, the possible transformation of limestone into dolomite or into magnesite seemed unlikely, because it required the removal of such vast amounts of calcium carbonate. At the same time, this transformation theory was unable to explain the presence of iron carbonate in the magnesite. According to Redlich (1903) the formation of magnesite and iron carbonate could only be explained in terms of metamorphic reactions. Hörhager's (1911) observations on the regular intercalations of magnesite layers in dolomite sequences at the Stangalpe near Turrach had given the impression, that descending magnesium-rich solutions had partly, but very regularly, changed dolomite layers into magnesite. The deposits of iron carbonate and those of anhydrous magnesium carbonate must have originated during volcanic intrusions of

serpentine and granite. Hot springs would have deposited iron carbonate in the deeper regions and magnesium carbonate in the higher parts. The very fact that the hot magnesium-rich solutions moved downwards through the rock would be proven by the decreasing amounts of magnesite with depth.

Magnesite in the highly metamorphic limestones of Wald and Trieben were described by Heritsch (1912). The *Pinolit* texture found near Triebenstein-Sunk must have had, according to Heritsch (1912), an "epigenetic" origin. Kern (1912) expressed his doubts concerning the often suggested "metasomatic" mode of origin of magnesite, and instead proposed a purely sedimentary origin, whereby the necessary magnesium would have been supplied by metamorphism of diabase and porphyry into green schists. Notably the extreme geographical range of the Austrian magnesite deposits was difficult to understand, when assuming a metasomatic origin (which should have been much more localized). Furthermore the immense quantities of dissolved magnesia could not have been supplied by the solutions involved in metasomatism. In Kern's (1912) view the formation of the Austrian magnesite deposits would be related to processes of post-volcanism, because of the association between magnesites and ultrabasic igneous rocks.

The magnesite deposit of Trens (near Freienfeld im Eisacktal) had been studied by Canaval (1912), who performed not only microscopic, but also geochemical analyses. One of his observations concerned the black material found in the Austrian magnesites. In contrast to the often repeated suggestion, that the black material would consist of graphite, Canaval (1912) found it to be mainly coal with small amounts of pyrite in it. Concerning the mode of formation of magnesite, Canaval (1912) could not agree with the explanation given by Kern (1912). The suggested sedimentary mode of formation would require immense amounts of magnesium bicarbonate solution; in reality, the initial precipitate would have been a cryptocrystalline form of magnesium carbonate, which later changed into crystalline magnesite due to high pressures and high temperatures. Notably the necessary vast amounts of magnesium bicarbonate would make Kern's (1912) theory untenable (that is, according to Canaval, 1912).

Redlich (1912) repeated his theory, that the three different types of magnesite defined by him in 1909 would really represent three different modes of formation. The claim made by Bischof (1847), that not only bicarbonate solutions coming from below, but also CO₂-rich water originating in the soil, would be instrumental in the formation of magnesite, might well be of significance in this regard. Redlich (1912) added that in order for the bicarbonate solution to exert its influence, it should be able to penetrate the underlying rocks through crevices and fissures. Weathering of magnesium silicates (serpentine, olivine) would invariably give rise to (amorphous) silica. This weathering process would lead to the "amorphous" form of magnesite (and to *Gurhofian*, the "amorphous" form of dolomite). Concerning the mode of formation of the "Typus Kraubath", Redlich (1912) stated, that the crystalline form of magnesium carbonate always required high temperatures (as the experiments by Pfaff, 1907 would have shown). This second category of crystalline magnesite was often found in association with salt minerals or with aragonite, dolomite, quartz and/or talc. In contrast to his 1909 (B) tripartite classification Redlich now subdivided the crystalline magnesites into five different classes: 1- "Typus Hall" (magnesite in rock salt); 2 - "Typus Greiner" (iron-rich magnesite from talc slates); 3 - "Typus Veitsch" (magnesite with the *Pinolit* texture); 4 - magnesite from (plutonic) intrusions; and 5 - magnesite formed by "pneumatolysis".

After a detailed investigation of the Veitsch area, Redlich (1913) postulated, how the magnesite there must have been formed long before the large-scale Alpine tectonics had taken place. The local paragenesis of Veitsch consists of magnesite, dolomite, ankerite, aragonite, (idiomorphic) quartz, pyrite, and (only locally during the summer) epsomite (see

also: Cornu, 1908). Redlich & Großpietsch (1913) concluded, on the basis of the mineral paragenesis magnesite, quartz, talc and clinochlore, that the Austrian magnesite deposits must have originated during low-grade metamorphism. Redlich & Großpietsch (1913) had found, and had chemically analyzed, numerous fossils (corals, gastropoda, crinoids and brachiopoda), which consisted of magnesite or dolomite. Finding these fossils, and realizing that all of these once had consisted of calcium carbonate, led to the postulation of a chemical reaction between CaCO_3 and magnesium-rich solutions to initially give dolomite. This dolomite in turn would have reacted with the remaining magnesium-rich solution to give magnesite. Redlich & Großpietsch (1913) expressed their support for the (chemical) observations of Retgers (1891), in that they had not been able to find in nature any carbonates with a composition in between that of dolomite and magnesite. Redlich (1914 A) provided convincing evidence for his theory of a secondary change of calcium carbonate into dolomite, which subsequently had been changed into magnesite in the form the crinoid fragments found by him, which consisted partly of dolomite and, in the very same specimen, partly of magnesite. Redlich (1914 A) called into memory the laboratory syntheses of magnesite by De Sénarmont (1849, 1850, 1851 A, B), De Marignac (1855), Pfaff (1894) and Klement (1894, 1895). Notably the experiments by Schmidt (1913) and Diesel (1911) had clearly demonstrated, according to Redlich (1914 A), how magnesite exclusively forms under high carbon dioxide pressures.

A new deposit of magnesite (near St. Erhard in the Breitenau region) was found by Sigmund (1914), who thought it to be of sedimentary origin, because it was as well bedded as the magnesite from the Eichberg mountain in the Semmering area. If the theory of Koch (1893) and Redlich & Cornu (1908) would be correct, the infiltrating magnesia-rich solutions responsible for the (secondary) change of pre-existing limestones must have left clear traces behind in the form of magnesium salts at the junctions of the many bedding planes of the original rock. Thus, the absence of such a framework of interrelated magnesite veins crossing the bedding planes showed, that no secondary conversions by circulating solutions could have taken place. Sigmund (1914) observed the well-defined bedding of the magnesite in the large quarry of St. Erhard and concluded from this fact, that the magnesite there, much like that of the Semmering area, had to be of a primary, that is *sedimentary* origin. The presence of widely distributed, but small and local occurrences of dolomite contributed more evidence in this regard (Sigmund, 1914). Such local nests of dolomite greatly reduced the economical value of the magnesite rock, because they lowered the strength of the burnt product, making it impossible for use as kiln lining. The crinoids now consisting of magnesite described by Redlich (1914 A) provided, in the view of Sigmund (1914), additional and convincing evidence of a possible sedimentary origin. Because of the tectonic disturbances that took place after the deposition of the (sedimentary) magnesite, the correct interpretation of field observations had become rather complicated.

Redlich (1914 B) studied the magnesite - breunnerite - siderite deposits enclosed in shales near Gloggnitz am Hart in the Semmering area, and explained how magnesite and talc must have originated in much the same manner. There where the infiltrating magnesia solutions were able to react with silica, talc had formed. The magnesite itself, invariably associated with dolomite and limestone, would have been formed in the manner described by Redlich & Cornu (1908). Close relations between magnesite and nickel ores such as the nickel silicate called garnierite, were suggested by Kraft (1915). The formation of magnesite would have taken place according to Kraft (1915) during the weathering of serpentinite; at first hydrated magnesium carbonate would have formed a colloidal precipitate, but during the later stages of its formation metasomatism would have played an important role.

Leitmeier (1916 A), thereby following Rumpf (1876), expressed as his conviction, that magnesite (and dolomite as well) may well have originated in the marine environment.

Leitmeier (1916 A, B) could not agree with the explanation given by Redlich (1903, 1909 B, 1914 B) concerning the metasomatic mode of formation of magnesite. In Leitmeier's view descending solutions of magnesium chloride rich in carbon dioxide would react with pre-existing limestones to give magnesite. Even so, elevated temperatures as well as high pressures would be required. The initial reaction products might well be magnesium calcite (the *Linck'sche Mischsalz*) or hydrated magnesium carbonates, which later would dehydrate into anhydrous magnesium carbonate.

Writing on the iron ores of Eisenerz in Steiermark, Redlich (1916) concluded on a metamorphic origin not only for the iron ores (siderite, ankerite), but also for the smaller amounts of magnesite found there. The irregular distribution of magnesite would point toward penetration through fissures and faults of the limestone. Even so, the origin and the nature of the solutions carrying magnesia were not clear to Redlich (1916).

Leitmeier (1917) responded to the criticism by Redlich (1917), whose major complaint was that Leitmeier's laboratory experiments had nothing to do with "the reality as seen in the field". The suggestion made by Leitmeier (1916 A) of a marine (i.e., sedimentary or authigenic) origin for magnesite was rejected by Redlich, because only magnesite in rock salt might have originated in such a manner but certainly not the two other types of magnesite. However, Leitmeier (1917) did not want to attribute that much importance to a classification of magnesite based only on field observations. The (field) evidence in the form of crinoid fragments (partly) consisting of magnesite, cited by Redlich in support of his suggestion of the conversion sequence calcite – dolomite – magnesite, was seriously doubted by Leitmeier (1917). No convincing examples of crinoid fragments *from magnesite layers* had been described up to that moment. Renewed analyses of magnesite samples with crinoids, samples given by Redlich to Leitmeier, all revealed considerable amounts of incorporated calcium carbonate: the mineralogy was dolomite and not magnesite. Redlich (1918) wanted to have the last word in his discussion with Leitmeier, and reiterated, that observations made in the field always held priority over any and all geochemical considerations. Contrary to the conclusion of Leitmeier, that magnesite deposits must have had an origin in the sedimentary environment, Redlich (1918) declared all magnesites to have an "epigenetic, metasomatic" origin. In this regard, Redlich (1918) considered the crinoid ossicles now (partly) consisting of dolomite and/or magnesite as the best evidence in favour of his view of a secondary conversion. Without any doubt, these crinoid fragments originally had consisted of calcium carbonate. Not everyone would disagree with the views of Redlich. For example Machatschki (1922), writing on the magnesite deposits of the Kaswassergraben near Großreifling, subscribed to Redlich's suggestion of a metamorphic change of calcium carbonate and dolomite into magnesite. Especially the presence of fissures filled with magnesite in the dolomite of the Kaswassergraben area had convinced Machatschki (1922) of such a conversion by way of magnesium-rich solutions.

Two magnesite deposits of Hohenburg (Kaintaleck, Austria), originally described by Kittl (1920), were revisited by Redlich (1921). The first deposit (at Wiesergut) contained exceptionally pure magnesite with little or no calcium or iron. The second deposit at Arzberg (near Neuberg) contained dolomite and limestone in addition to magnesite. In the interpretation of Redlich (1921) both magnesite deposits must have originated in an epigenetic manner and certainly not as sediments. Originally Redlich had thought epigenetic to mean metamorphic, but later he became convinced, how not only external solutions would have changed the pre-existing limestones, but that additionally solutions circulating through numerous fissures must have contributed to significant changes in mineralogy.

Genetic relations between calcium carbonate, dolomite and magnesite have been indicated by Angel (1924). Microscopic examination of dolomite thin-sections had shown sporadic fossil fragments, granoblasts of dolomite crystallites together with intergranular

graphite-like material. The dolomite crystals often showed bi-axial optics; Angel (1924) claimed this phenomenon to have been caused by high pressures during burial. Irregular patches of dolomite had been found inside the magnesite. In many instances it was easy to recognize magnesite in the field because of its *Pinolit* texture. The presence of a black, graphite-like intergranular substance in between the macroscopic *Pinolites* made the determination of the magnesite much easier. Magnesite was usually macrocrystalline, but microcrystalline magnesite had been found as well. The latter kind of magnesite was found in association with weathered serpentinite rocks. Angel (1925) explained the formation of magnesite in the Austrian Gleinalpen to be the result of two different metamorphic reactions. The first step involved a reaction of the mineral olivine with carbon dioxide and water to give serpentine plus magnesite. The second step would involve the change of enstatite reacting with carbon dioxide and water to give talc plus magnesite.

According to Mohr (1925) magnesite had to be of metamorphic origin, although low-grade metamorphic, as witnessed by the presence of minerals such as edpidote, chlorite, talc and possibly even albite and zoisite. Therefore magnesite formation would require a certain minimum pressure and a minimum temperature. Another argument in favour of a metamorphic origin would be the complete absence of occurrences of modern magnesite (or dolomite) in the sedimentary environment. A third argument was the absence of any magnesite in Paleozoic rocks, which lacked any traces of metamorphism. There was only one difficulty: when assuming the metamorphic (or metasomatic) conversion of limestone or dolomite into magnesite, a very large amount of calcium carbonate needed to be removed. Any supply of magnesium-rich solutions was unlikely according to Mohr (1925), because nowhere any evidence of magnesium-carrying veins had ever been found. The conversion as such must have consisted of a selective removal of calcium carbonate from pre-existing dolomite or limestone. Proof of this kind of removal of calcium carbonate could be found in the view of Mohr (1925) in the countless (thermal) springs carrying calcium bicarbonate in solution, which were active even at that moment.

The often observed relation between the Austrian magnesites and the mineral talc was emphasized by Rózsa (1925 A). A distinct spatial differentiation of the carbonate minerals calcite, dolomite and magnesite would exist in most magnesite deposits. The mineral talc is invariably found immediately near the dolomite layers. The source of the silicate necessary for the formation of talc is to be found in the shales contacting the dolomite. At times, talc was not only found in the magnesite masses, but also in the dolomite. In other words, the occurrence of talc within the large-scale Alpine magnesite deposits was, according to Rózsa (1925 A), primarily related to the contacting shale formations. Rózsa (1925 B, C) re-interpreted the formation of magnesite in terms of a primary marine sediment. Especially the often observed interlayered sequences of limestone, dolomite and magnesite could not be explained through any secondary changes. However, Rózsa (1925 B, C) could not exclude the possible effects of submarine eruptions during Paleozoic times, when these carbonates had been formed. In his field studies Rózsa (1925 B, C) had never been able to detect any calcium carbonate in magnesite, and similarly never any magnesite in limestone. Calcite and magnesite seemed mutually exclusive; dolomite always appeared as an "intermediate". Rózsa (1926) repeated his observations on the "primary" nature of the Austrian siderite - dolomite - magnesite deposits, and added, that for example the small-scale alternations between limestone and dolomite can not be explained by any "secondary" process: these oscillations pointed toward a sedimentary origin. Fine laminations, often visible as colour differences in the magnesite deposits, contributed evidence of periodical changes for example in amount of rainfall, not only in the case of magnesite, but also as recorded in the laminations of limestones and dolomites.

The close relations between Austrian magnesites and tectonics were highlighted by Schwinner (1925), after he had studied the local geology of the area near the Brenner Pass. For example, the magnesite of Turrach must have been formed after the large-scale Alpine tectonics had ended. In addition Schwinner (1925) proclaimed, how all magnesite deposits of the same nature must have formed during only one geological event of possibly restricted extension. In other words, it would be difficult to maintain, that all Austrian magnesite deposits would have one and the same origin. For example the magnesites of Turrach and Steinach showed no traces of any tectonical deformation in clear contrast to many other Austrian magnesite deposits. The relations between tectonics and magnesite were re-investigated by Petrascheck (1926), who noted how the gold-containing quartz veins of the Hohe Tauern mountains cut through the schistosity of the gneiss masses and therefore these quartz veins had to be younger than the orogeny itself. At various other locations in the Austrian Alps much the same relations exist: in general ore formation would post-date tectonics. Exactly this view was now applied by Petrascheck (1926) to the formation of magnesite deposits: following Schwinner (1925), magnesite as well as siderite deposits had to be of post-tectonic origin. Redlich (1926 A) could not agree more: magnesite could not have had a sedimentary origin, but must have been “epigenetic” and definitely formed after the main tectonic events in the Alps had ceased.

Microscopic studies of magnesite samples from Kraubath convinced Clar (1928), that the name *Gel-Magnesit* could no longer be used, because all of such samples were seen to consist of very small crystallites. Therefore Clar (1928) suggested to replace the term gel magnesite with *dichter Magnesit* (= compact magnesite). Only three years later, Halla (1931) confirmed Clar's observation, and stated that the three different classes of magnesite introduced by Redlich (1909 B), could not be maintained because **no** form of amorphous magnesite existed at all (Halla, 1931 based his interpretation on X-ray diffraction).

Clar (1928) claimed magnesite formation not have been one of numerous metamorphic reactions, but instead it had to be the result of the weathering of serpentinite rocks (as Leitmeier, 1914 had suggested). Formation of magnesite at Kraubath would be the result of a reaction of serpentinite rock with CO₂-containing water. Subsequently Clar (1928) discussed the three different theories on magnesite formation of that time. The first theory explained magnesite formation in terms of a process of metamorphism (Angel, 1925; Angel & Martiny, 1925). The second theory explained magnesite formation to be the result of descending CO₂-rich solutions, which theory had been advanced by Kraft (1915), Krusch (1912) and Von Zur Mühlen (1920). Both Redlich (1914 B) and Leitmeier (1914) had rejected this theory of the descending solutions; main arguments were, that not all serpentinite rocks contained magnesite; the absence of a regular distribution pattern; the lack of modern magnesite deposits; and the low content of dissolved carbon dioxide in groundwater. Clar (1928) found the third theory on the formation of the Kraubath magnesite deposits to be the most convincing, thereby following the suggestion made by Leitmeier (1914, 1915) of the secondary conversion of nesquehonite. As shown by Leitmeier (1909) in his experiments, magnesium carbonate trihydrate (and not the anhydrous form of magnesium carbonate) is what precipitates from a magnesium bicarbonate solution. Clar (1928) gave two arguments in favour of the third theory. In the first place the association of magnesite with siliceous nickel ores. At the same time Clar (1928) had seen in his thin-sections clear examples of the role of ascending CO₂-rich solutions. The usual fine-grained character of the compact magnesite of Kraubath must have its origin in the dehydration of MgCO₃·3 H₂O as claimed by Leitmeier (1914). Apparently, not everyone thought the arguments of Clar (1928) to be quite convincing. For example, Petrascheck (1928), without taking the trouble to cite any evidence, declared all magnesites from the Austrian region of Steiermark to have had a metasomatic origin. In his reaction, Clar (1931) once more cited his detailed microscopic analyses in

support of the idea, that magnesite (at least the magnesite of Breitenau) had nothing to do with tectonics. Especially the thinly-bedded and evenly laminated texture had to be of a primary origin. Post-sedimentary metasomatic or metamorphic effects had not been observed by Clar (1931).

The close relations between magnesite and siderite were pointed out by Petrascheck (1926, 1932). Because of the irregular nature of the bedding planes, magnesite as well as siderite could not have originated as sediments. The formation of talc, in many instances an accessory, would have taken place concomitant with the formation of magnesite. In a number of instances the horizontal transition of one into the other could be recognized in the field. Where traces of bedding planes could be recognized, these had to be of sedimentary origin overprinted during metasomatism. Major tectonic events must have occurred *prior* to the formation of magnesite and siderite. Petrascheck (1932) repeated his view, that the Austrian magnesite deposits post-dated the Alpine orogeny. Field studies had shown how the magnesite deposits lacked any well-defined stratigraphic position. Siderite deposits showed much the same lack. At beforehand Petrascheck (1932) rejected any possible formation of magnesite in the sedimentary environment (which had been suggested for example by Rózsa, 1925 B). What really precipitated in the sedimentary environment was magnesium hydroxide carbonate. The necessary high concentrations of magnesium bicarbonate could not be found in any normal sedimentary environment and therefore Petrascheck (1932) claimed, that magnesium hydroxide carbonate could occur in lakes only. The possible change of any magnesium hydroxide carbonate into magnesite during metamorphosis could be excluded, because all of the Austrian magnesite deposits are intercalated with marine sediments (and not with lacustrine sediments). Nevertheless, Petrascheck (1932) had to admit that magnesite often possessed distinct bedding, usually parallel to the bedding planes of the contacting limestones or shale. Obviously, this bedding phenomenon is of primary origin. However, Petrascheck (1932) claimed, that no such relation between primary bedding and magnesite formation would exist. The cause of bedding planes in magnesite deposits had to be found in the original bedding planes of the pre-existing limestones. The only exception would be the magnesite from Hall in Tirol. The formation of iron (II) carbonate deposits by way of CO_2 - rich weathering (i.e., descending) solutions would not be possible according to Petrascheck (1932), because oxidation of Fe^{2+} to Fe^{3+} would lead to the precipitation of iron oxides and/or hydroxides such as limonite. From this very comparison Petrascheck (1932) drew the conclusion, that the formation of the related magnesite deposits could not have taken place by “descending” solutions (i.e., during the weathering process). In addition, Petrascheck (1932) described crinoid stem fragments only partially replaced by magnesite, whereas others consisted of dolomite, and wondered about the rather irregular behaviour of the replacement process during metasomatism.

In many instances magnesite deposits do show bedding planes parallel to the contacting limestones, dolomites and shales. In the explanation of Petrascheck (1932) this bedding phenomenon would be caused by very thin intercalations of graphite, by alternations in colour or by differences in grain size between individual layers. Any effects of rhythmic deposition or diffusion processes were excluded by Petrascheck (1932). The bedding phenomenon was also found in siderite deposits, but there alternations between dolomite and siderite were involved. In clear contrast to the case of magnesite, Petrascheck (1932) explained the bedding of siderite to be primary, i.e., of sedimentary origin. There would be a close relation between the Alpine deposits of magnesite and siderite and other ore deposits (such as copper, nickel, lead and zinc). After repeating his earlier observation, that magnesite is not confined to any specific stratigraphic horizons, Petrascheck (1932) once more denied the possible formation of magnesite as a sediment. Accepting the secondary conversion of calcite or dolomite into magnesite implies a considerable loss of volume (24.3 % in the case

of the conversion of calcite into magnesite). As a consequence all metasomatic magnesite deposits had to be quite porous. Petrascheck (1932) claimed to have found evidence of (at least former) porosity in virtually all magnesites and siderites in the form of microscopic textures. Often dolomite could be seen to fill out the primary porosity.

The Alpine magnesites of Austria had to have a metasomatic origin according to Himmelbauer (1933). Evidence in the form of crinoids having been changed into magnesite indicated a secondary origin, but the complete disregard of magnesite deposits for any bedding planes could only be seen as evidence in favour of metasomatism. The close association with iron carbonate deposits and the presence of Cu, Sb and As minerals in virtually all magnesites contributed further evidence as to the latter's metasomatic origin. After having analyzed the magnesite deposit of the Entachen Alm, Friedrich & Peltzmann (1937) suggested on the basis of especially its graptolite fauna, that the limestones from which later the magnesite originated during metasomatism, must have been of Paleozoic age. Clearly, the initial limestones pre-dated the tectonics, plutonism and metamorphism of all of the Alpine events.

Numerous macrofossils found in a shale intercalation in the magnesite deposit of Veitsch have been described by Metz (1937). Fossils found included the brachiopoda *Productus gigantoides* and *Orthis (Schizophora) resupinata*.

Schwinner (1937) was not at all convinced of the possible relations between magnesite deposits and intrusions of granite; instead he thought a close relation to exist between magnesite and basic magmatic rocks such as diabase, amphibolite and serpentine. Furthermore no clear correlation between magnesite deposits and Alpidic tectonics would exist; instead the tectonics involved would have taken place in the Carboniferous era. After the metamorphosis of olivine-rich rocks into serpentinite, still following the explanation given by Schwinner (1937), magnesia-rich groundwater moving downwards ("descending") would have been responsible for the actual formation of magnesite. In his later papers Schwinner (1942, 1949) described, how he had been unable to detect any relations between the Austrian magnesite deposits and deposits of metallic ores (such as Pb, Zn and As). The local formation of certain ore deposits and for that matter of magnesite deposits too, would have to be closely related to the local composition of the intruding plutons.

The formation of the Austrian magnesites has been attributed by Angel (1939 A, B) to metamorphism, but he could not discover any relation between magnesite and siderite deposits. The closely related geochemical behaviour of magnesium and iron would prevent the separation into different ore bodies. Finding separate ore bodies of magnesite and of siderite had to mean, that the two had been deposited separately in location or in time. Angel (1939 A) did not hesitate to attribute the formation of the magnesite deposits of the Gleinalpen to metamorphic reactions. Previously existing marls, limestones and dolomites had been the source of vast amounts of carbon dioxide, and this carbon dioxide must have been instrumental in the formation of magnesite. The very mechanism responsible for the origin of magnesite had to be the reaction of serpentinite rocks of magmatic origin, reacting during metamorphism with carbon dioxide and water. According to Angel (1939 B) the magnesite deposits of the Erzberg, as well as its vast reserves of iron ore (iron sulphide as well as iron carbonate), must have had a metamorphic origin. That is to say: originally a metamorphic assemblage had been formed (involving lenses of peridotite within a variety of other metamorphic rocks), which locally would have been changed into magnesite by way of metasomatism.

The Austrian magnesite deposits are tectonically situated deeper than iron-copper deposits (Metz, 1938). When the two kinds of deposits would be near to each other, the magnesites would be seen to contain more iron. Metamorphism certainly had influenced both kinds of deposits, and therefore metamorphism had to be younger than ore deposition;

metamorphism in itself being the result of large-scale tectonic events. Two different zones of metamorphism could be distinguished. Metz (1938) had noted, much like Brinkmann (1928) and Petrascheck (1932), how the degree of metamorphism depended on burial depth. Magnesite in combination with talc was found exclusively in the more highly metamorphosed rocks. Siderite deposits are both tectonically and geographically separated from the former two. In short, Metz (1938) could only confirm the relations between magnesite formation and metamorphism indicated by Clar & Friedrich (1933). With respect to the possible origin of the vast amounts of magnesia, Metz (1938) considered basic rocks, possibly altered during metamorphism, to be their ultimate source. Schwinner (1942) also discussed the relations between the tectonics and ore deposits of the Eastern Alps, and started out with the general observation, that the petrology of a certain area would be determined to a large degree by the properties of the underlying magma. In this regard the Eastern Alps of Austria should be regarded as representing one petrologic unit. The magnesite deposits of the region were all related to (ultra-) basic magmas, which had been changed into mainly serpentinite rocks.

The relations between magnesite and metamorphism have been discussed in some detail by Clar (1945). One would have to try and find the more simple solution to the problem of the metamorphic origin of magnesite. There would be no need to postulate the removal or the addition of large amounts of solutions and/or dissolved compounds (*Stoffwechsel* instead of *Stoffzufuhr* as Clar, 1945 observed). Moreover, there really was no need for speculations concerning the possible presence of deep-seated magma chambers. The local intrusions by plutonic rocks all were known to be much later than the origin of the magnesite deposits. Such deposits of magnesite must have been formed by thermal water. The exact age of magnesite formation remained problematical, because its relation to tectonics was not at all clear. The suggestion that the formation of all Alpine ore deposits, including magnesite, had to be the result of magma intrusions, was rejected by Clar (1945). As indicated earlier by Clar & Friedrich (1933) and Friedrich (1937) metamorphism also must have played an important role in addition to the magma intrusions and hydrothermal solutions connected with such intrusions. The origin of magnesite would form a good example, because the intruding magma in this part of the Alps was of a granitic nature, and not of the required Mg-rich, ultrabasic kind. Therefore Clar (1931), much like Schwinner (1942) after him, concluded, that hydrothermal solutions could not have been able to supply the magnesium needed to form the vast amounts of magnesium carbonate. However, Schwinner (1946) could not agree with the suggestion of an overall unity (of time and place) of events leading to the different Alpine ore deposits as suggested by Clar (1945). It would be hard to imagine, how an acid magma could ever be held responsible for the deposition of magnesite.

No distinction could be made according to Petrascheck (1945) between the origin of the Alpine magnesite and siderite deposits and that of the other ore deposits (such as lead-zinc, gold and silver, copper and zinc). All of these had to be the result of magmatic exhalations during the various tectonic intervals, which had influenced the area. Notwithstanding the fact that the corresponding pluton had not been discovered, Petrascheck (1945) argued that numerous large faults, steep boundary layers and porous sequences would offer the required vistas for *ascending* ore solutions. In other words, the origin of magnesite would be related to magma intrusion rather than the often invoked metamorphic processes.

Turner (1947) noted, how the Austrian magnesite deposits often possessed the shape of a lens, and that these rather isolated masses of magnesite were usually bordered by glide planes typical of tectonical movement (much the same conclusion had been formulated by Redlich, 1935). In short, there were complications due to multiple intervals of tectonic deformations. At the same time Turner (1947) reiterated the conclusion reached by Schwinner (1937), that magnesite deposits occurred most often near ultrabasic plutonic rocks,

and that such magnesite deposits were not at all related to iron carbonate (as had been suggested by Metz, 1938).

An overview of the geology of the iron- and magnesium deposits of the Eastern Alps was published by Metz (1948). The iron carbonate deposits of for example the Erzberg were much easier to interpret than the closely related magnesite, because these siderite deposits showed clear evidence of their secondary origin from limestone formations. Not so, however, in the case of the magnesite deposits, which in most cases had become separated from their source-limestones. In addition, the magnesite had been affected by the tectonics of the Alpine orogeny, much more than the siderite. In general the magnesite deposits of the Eastern Alps were closely related to Carboniferous limestones. At the same time the large-scale tectonic deformations proved, that the magnesites must have formed before the tectonic deformations took place (in 1937 Schwinner had drawn the very same conclusion). In summary, Metz (1948) stated that the Austrian magnesite and siderite deposits had undergone a low degree of metamorphism. Mobilization of magnesium from (ultra-) basic rocks would have been the ultimate cause of magnesite formation. Similarly, a large supply of iron causing siderite ore formation must have become available from the breakdown of iron silicates during metamorphism. In 1949 Metz described the close relation between magnesite and talc (of the magnesite deposit at Mautern). Talc would have originated from the metamorphic change of shales, and the large amounts of carbonate ions freed in that process were responsible for the actual formation of magnesite.

Schwinner (1949) pointed out, that no correlation could be found between Austrian magnesite, magma and any orogeny. The Austrian (crystalline) magnesite had been formed upon the alteration of peridotite to serpentine. Similarly the formation of large masses of iron carbonate was not the result of intrusion by magma, but rather the result of the accumulation of iron set free upon the conversion of garnet, staurolite and biotite into chlorite.

Although Spangenberg (1949 A) discussed the magnesite deposit of Zobten (Silezia), he arrived at important conclusions with regard to the mode of formation of magnesite in general. The deposit of Zobten had first been described by Von Zur Mühlen (1920). Concerning the mode of formation of this type of magnesite, Leitmeier (1914) and Redlich (1914 B) had expressed their doubts concerning the assumed role of *descendant* CO₂ -containing solutions. And Clar (1928) had concluded on an active role for *ascending* CO₂ -rich solutions. Thus Redlich (1934) stated that the majority of scientists would favour the theory of *ascending* CO₂ -rich solutions. In other words, the Austrian magnesite deposits would have originated in hydrothermal reactions from olivine, enstatite or serpentinite rocks. According to Redlich (1934) it was in particular the absence of high amounts of CaO, FeO and/or Al₂O₃ , that provided the most convincing argument for the *ascendant* theory. With respect to this very argument Spangenberg (1949 A) commented, that up to that moment there was no real evidence, that such magnesites were free from FeO. The possibility of oxidation of embedded ores such as pyrite into iron (II) oxides during the activities of *ascending* solutions had, according to Spangenberg (1949 A), never been adequately investigated. In short, there was little or no reason to include magnesite formation in the usual sequence of hydrothermal ore formation. Nevertheless Spangenberg (1949 A) (on the basis of his detailed mineralogical studies) claimed a hydrothermal origin for the magnesite deposit of Zobten, and added, that ultimately *ascending* (hydrothermal) CO₂ -rich solutions were responsible. Spangenberg (1949 B) went into some detail concerning the weathering reactions of the mineral olivine in the ultrabasic host rock at Zobten. Von Braunmühl (1929) as well as Redlich (1934) had invoked *ascending* CO₂ -rich solutions to explain the formation of magnesite during the weathering of ultrabasic rocks. In addition Spangenberg & Müller (1949) pointed out, how the weathering of olivine implies the removal of MgO as well as that of SiO₂ . Ultimately Spangenberg & Müller (1949) invoked a mechanism described as

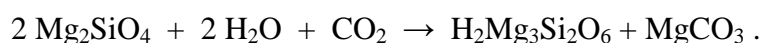
metasomatosi to explain volume changes accompanying the formation of magnesite and, to a lesser extent, that of silica.

1950 to the present

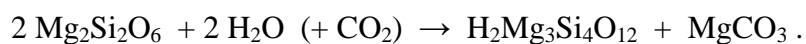
The origin of the crystalline (“Typus Veitsch”) Austrian magnesite was discussed by Rohn (1950). Any suggested relation between magnesite and the sandstones of the *Grauwackenzone* could not be maintained according to Rohn (1950), because only a very small part of that zone actually consists of magnesite. The geographic distribution of magnesite within this vast sandstone-shale complex allowed for only one conclusion: all of the magnesite deposits shared a common mode of formation. Their origin was apparently not related to any specific stratigraphic position. One of the few factors in common was that the magnesite always occurred concordant within sedimentary sequences. But there were more arguments pointing toward a possible sedimentary origin, as for example Leitmeier (1916 A, 1917) had stressed. Considerable differences must have existed in local conditions, as witnessed for example by variation in the amounts of iron, calcium and talc. Often these variations were in the form of zones parallel to the bedding planes. Such local variations contradicted in a way the much-sought-after general explanation for the mode of formation of magnesite. In addition there were serious arguments against any suggestion of an origin by way of metasomatism. For example the field relations with respect to the impermeable shale layers, which must have prevented the direct contact between pre-existing limestones or dolomites and magnesium-rich solutions. Furthermore, no intermediate stages in the conversion of dolomite to magnesite had ever been found. Similarly no reactions between the hypothetical magnesium solutions and other rocks had ever been described. After giving all of these arguments in favour of a sedimentary origin, Rohn (1950), somewhat surprisingly, concluded, that the Austrian crystalline magnesite must have formed as the result of submarine volcanic eruptions. Especially the high-temperature laboratory syntheses of magnesite by De Sénarmont (1851 A), conducted at temperatures around 423 K, were cited in favour of this conclusion. Rohn (1950) suggested that during submarine volcanic eruptions temperatures between 2,273 and 3,273 K might well be reached; more than enough to allow for the formation of magnesite.

Friedrich (1951) devoted considerable attention to the question, whether the magnesite deposits of Austria had had a sedimentary or a metasomatic origin. The possible formation of magnesite as a sedimentary mineral, first suggested by Redlich (1909 B), could not be excluded at beforehand. Originally, Redlich (1909 B) had suggested such a mode of formation of magnesite in highly saline environments. Much like Redlich (1909 B) authors such as Rumpf (1876), Kern (1912), Leitmeier (1916 A), Rózsa (1925 B) and Rohn (1950) all tended toward a possible formation of magnesite in the sedimentary environment. The argument of Rohn (1950), that all Austrian magnesites consisted of relatively small and irregularly-distributed bodies enclosed in limestones or in dolomites, was not taken seriously by Leitmeier (1951). Both limestone and dolomite contained a high percentage of carbonate anions and therefore the large-scale chemical reactions typical of metasomatosi only needed to replace calcium ions by magnesium ions. The sedimentary origin of the Austrian magnesites would become understandable only, when all of the magnesites would occur in the same stratigraphic position. Since that was definitely not the case, Leitmeier (1951) thought a metasomatic origin to be the better explanation. In addition the absence of any clear signs of bedding, the absence of (horizontal) grading into dolomite or limestone, and the relations with talc deposits, were convincing enough for Leitmeier (1951) to disregard any

possible sedimentary origin. Much less certain was Friedrich (1951) about the relations between magnesite and siderite. There had been authors like for example Redlich (1914 B) and Petrascheck (1926, 1932), who were convinced that the formation of these two minerals was closely related. However, in the opinion of Angel (1939 B) and Metz (1938) magnesite and siderite were not really related in their mode of formation. In favour of the point of view of Redlich and Petrascheck are for example the close geochemical relations between magnesium and iron. Many siderite deposits contain large amounts of magnesium, and large amounts of iron were invariably found in magnesite. Even the banded textures found in some magnesites had their counterparts in siderite deposits. Exactly these close geochemical ties between iron and magnesium were emphasized by Angel (1939 B): the two would be so closely related, that separation would be virtually impossible. As a result siderites and magnesites must have formed at different moments, or at least geographically separated. Near the end of his review paper Friedrich (1951) devoted his attention to the question of the source of the magnesium ions. Several authors (among them Schwinner, 1925 and Petrascheck, 1932) held basic plutonic rocks (gabbro's, diabases, peridotites) responsible, whereas Clar (1945) and Friedrich (1936) thought solutions formed during a later process of metamorphism to be more likely. Especially the presence of elements such as Cr, Ti and P would indicate a truly basic rock like peridotite, to be the ultimate source of the magnesium ions (Leitmeier, 1917, 1951). The olivine mineral of these ultrabasic rocks would be the source of the magnesium ions for the formation, provided a reaction involving water and carbon dioxide takes place according to:



In other words, the olivine mineral would change into serpentinite plus magnesite. But such a reaction with water and carbon dioxide would also change the enstatite – bronzite minerals of the ultrabasic rocks; in that case talc plus magnesite would result according to:



Notably the latter reaction would, still following Friedrich (1951), explain the often observed paragenesis of magnesite and talc. Friedrich (1951) was somewhat puzzled by the fact, that world-wide many occurrences of peridotite – serpentinite rocks were known, but that not all of these occurrences involved deposits of magnesite and/or talc. Apparently there had been very specific factors in the Alpine orogenesis, which had to be responsible for the formation of the magnesite deposits of Austria.

After reminding his readers, that Gómez de Llarena (1951) had explained the formation of magnesite to be a sedimentary process, Leitmeier (1953) claimed, that this very explanation might well account for the formation of the magnesite “Typus Veitsch” in general. The sedimentary mode of formation was the more likely, since Rózsa (1925 B) had indicated seawater to be the major source of magnesium ions. After citing Goldschmidt's (1922) definition of “metasomatism”, Leitmeier (1953) refrained from invoking it as an explanation for magnesite deposits, because the concept did not contribute specific information on any possible process involved. Most publications suggesting metasomatism as the cause of magnesite formation had revealed little or nothing on the actual nature of the reactions involved (Leitmeier, 1953). The theory advanced by Mohr (1925) would be much more to the point, because it explained formation of magnesite from pre-existing dolomite by way of the dissolution of calcium carbonate from the mineral dolomite. However, Leitmeier (1953) wondered, how such a large-scale secondary change of dolomite might take place since major changes need to be invoked. Quantitatively, the total amounts of magnesite were

always subordinate to the vast amounts of dolomite found, and from this observation Leitmeier (1953) concluded, that the process of magnesite formation “was much rarer” than that of dolomite formation. Ultimately, Leitmeier (1953) concluded on the initial deposition of nesquehonite ($\text{MgCO}_3 \cdot 3 \text{H}_2\text{O}$) from seawater followed by dehydration into magnesite during an increase in (burial) pressure. In this regard the designation “metamorphic sedimentary rocks” coined by Angel (1924) may well be applicable, as Leitmeier (1953) put it. The presence of fossils in magnesite, found even by Leitmeier himself, consisting partly of dolomite, proved that the original magnesite deposit must have consisted of calcium carbonate and had been changed into dolomite and after that into magnesite.

Angel & Trojer (1953) discussed in detail some 30 different samples of Austrian magnesite. Almost all of their mineralogical observations pointed toward a metasomatic and/or metamorphic origin (thereby confirming the observations made by Petrascheck, 1932, 1945 and Redlich, 1935). Finding minerals such as talc, leuchtenbergite, chlorite and sericite of course must be considered as convincing evidence for a metamorphic origin.

The origin of the Austrian magnesite deposits has been compared with that of the iron carbonate (siderite) deposits by Meixner (1953), who concluded that the close connection between the two (as had been originally suggested by Redlich, 1903 and Petrascheck, 1932) was essentially correct. According to Redlich (1903, 1907, 1914 A) the origin of magnesite as well as that of siderite relies entirely on the secondary change of pre-existing limestones, described initially as “metamorphosis”, but later Redlich used the word “metasomatosis”. Convincing evidence was found by Redlich & Großpietsch (1913) in the partial replacement phenomena of fragments of crinoid stems, which now consisted of dolomite and/or magnesite, but which must have formed as pure calcium carbonate. Although Leitmeier (1917) had expressed doubt about this observation, Redlich (1935) renewed his claim citing more factual evidence. (Criticism on the work of Redlich, 1935, in particular on his interpretation of the structural geology of the Spitzkofel magnesite, was published by Awerzger & Angel, 1948). In their theory of the “metasomatic” replacement of calcium carbonate, Redlich (1907) and Redlich & Großpietsch (1913) had suggested a two-step reaction: first dolomite would form, which later would be transformed into magnesite. Much the same process would change calcium carbonate into iron (II) carbonate in two different steps: first into ankerite, and later into siderite. However, what the suggested theory of “metasomatism” by Redlich cannot explain, is the fact, that in one instance the mysteriously percolating solutions would deliver magnesium and in another bivalent iron. Or did these “metasomatic” solutions carry magnesium as well as iron (II)?

Many field observations seem to indicate, that limestone must have been the original material, which later underwent conversion into magnesite or siderite. Meixner (1953) emphasized the need to assume fundamentally different conditions for the (secondary) formation of magnesite or siderite. Based on a multitude of geochemical analyses, Meixner (1953) concluded, that real kinship exists between the deposits of Austrian magnesite and those of siderite. The views expressed by Angel (1939 B) and Leitmeier (1951), that from a geochemical point of view such a close relation was rather unlikely, were not shared by Meixner (1953).

Petrascheck (1953) recalled how Redlich (1935) had chemically analyzed crinoid stem fragments from the brown-coloured magnesite of the Häuselberg and found these to contain 43.34 (wt.) % of MgO . So many crinoids stem fragments consisting of dolomite and/or magnesite had meanwhile been found, that any doubts about the possibility of the *magnesitization* of pre-existing limestone had been effectively removed (as Petrascheck, 1953 put it). An astonishing observation on the actual occurrence of microfossils in many samples of magnesite from Sunk or Fieberbrunn was made by Petrascheck (1953): when dissolving some magnesite samples with hydrochloric acid, silicified microfossils of marine

origin were found (including sponge spicules, echinodermata fragments and aquatic fungi). Taking this technique one step further, Petrascheck applied it to free the minerals present as insoluble residues. In this manner data were obtained, concerning the question raised by Friedrich (1951) as to the specific moment at which magnesium and iron would have been introduced. The minerals in the insoluble residues were predominantly pyrite, (alpha-) quartz, rutile and a black, graphite-like material of vegetable origin. The occurrence of pyrite in magnesite as well as in siderite proved, according to Petrascheck (1953), that these two carbonates could not have been formed in the sedimentary environment. Ultimately Austrian magnesite and siderite had to be so closely related, that both must have been formed during the Alpine metallogenesis, which in turn did not have its origin in the presence of a pluton of basic rocks in the deep underground (Petrascheck, 1953). Later, Petrascheck (1963) pointed out, how not only the Austrian magnesite deposits, but also those from the Balkan, Greece and Turkey, were closely related to centers of Alpidic magmatism. In Austria the occurrences of magnesite (and other ores as well) were part of the Alpidic metamorphosis. The Austrian magnesite deposits all had to be, without exception, of metasomatic origin (Petrascheck, 1963).

The small gas bubbles within liquid inclusions of minerals (which originally had been discovered by Sorby, 1856, 1858) were studied in great detail by Correns (1954), because of their possible use as "paleothermometers". When assuming, that the liquid inclusions are of primary origin and have not been altered during later events, their significance in environmental reconstruction becomes clear. Exactly this point was stressed by Burruss (1987): fluid inclusions in carbonate rocks might well be affected by re-equilibration during burial. In that case homogenization temperatures would correspond to the maximum temperature during burial. Another complicating factor is the uncertainty about the pressure within the liquid inclusion (at its time of formation that is). Even so, relatively simple equipment such as a heating stage on the optical microscope enabled reasonable estimates of the temperature during the time of formation. The actual composition of the liquid inclusion can be determined by spectroscopy (e.g., Vogelsang & Geissler, 1869; Königsberger & Müller, 1906).

A multitude of observations on the various magnesite deposits of the Salzburg area (Austria) were interpreted by Leitmeier & Siegel (1954) in terms of evidence in favour of a sedimentary mode of formation. The significance of finding fossils partly consisting of magnesite and partly of dolomite was stressed once again. The close association between magnesite and dolomite, in the field or in thin-section, implied according to Leitmeier & Siegel (1954), a very close genetic relationship.

In 1956 "the magnesite problem" was described by Ney as follows: do the Austrian deposits of crystalline magnesite have a hydrothermal-metasomatic origin, or are they essentially of a sedimentary origin and were they subsequently overprinted during metamorphism? Ney (1956) stressed, that any knowledge from laboratory syntheses (up to that moment only high-temperature syntheses!) had to be supported by "facts as seen in the field." In this regard it is most useful to realize how, according to Ney (1956), the hypothetical metasomatic reactions of ultrabasic rocks with circulating bicarbonate solutions giving rise to magnesite, lacked any experimental verification. In addition such large-scale metasomatic reactions must have left clear evidence in the form of mineralogical changes in rocks other than limestone and dolomite. Such evidence from the field had not become known. Notwithstanding the convincing observations presented by Ney (1956), the hypothetical "metasomatic" origin of Austrian magnesite would remain a favourite explanation for many years to come. For example Zschucke (1956), after having studied in great detail the magnesite deposit at Breitenau, Steiermark, attributed the conversion of dolomite into magnesite as having been brought about by conditions comparable to those

found in the experiments of Schloemer & Nacken (1953). However, the temperature of 473 K and the pressure of 25,000 kPa used in the experiments by Schloemer & Nacken (1953), place this particular process in the realm of hydrothermal rather than "metasomatic" changes. At the same time, Zschucke (1956) described to have found several (but overall very few) samples of laminated magnesite of clear sedimentary origin.

Observations on the banded (even laminated) texture of magnesite deposits were presented by Clar (1954 A). Microscopic analyses pointed to an origin in terms of crystal growth (*postsedimentäre Neukristallisation*) instead of a (primary) sedimentation process. This (secondary) change of dolomite into magnesite appeared to have taken place in a rhythmic manner. Even to such a degree, that Clar (1954 A, p.64) used the expression of “.... **an alternation between dissolution and deposition**” [original German text: “.... (ein) **Wechselspiel von Lösung und Absatz**”].

More on the overall mode of formation of Austrian magnesites was published by Clar (1954 B). The concept of an “Alpine metallogenesis” of Petrascheck (1926, 1932, 1945), which according to Friedrich (1951) had to include the magnesite-talc-leucophyllite deposits as well as the siderite deposits, was reconsidered. As Clar had concluded before, he could not attribute magnesite formation to magma intrusions; instead magnesium supply was seen to be closely related to the separation of serpentine from ultrabasic rocks (as Angel, 1939 B, Friedrich, 1937 and Metz, 1938 had suggested).

According to Friedrich (1958, 1959) the postulated sedimentary origin for the crystalline magnesites (*Spatmagnesite*) could not be correct. No traces of the assumed nesquehonite precursor (a hypothesis advanced by for example Leitmeier, 1951, 1953 and Leitmeier & Siegel, 1954) had ever been described. Moreover, a multitude of observations all pointed to a truly metasomatic (replacement) origin under conditions of nonequilibrium (in the sense of Raguin, 1961). The often observed paragenesis of limestone, dolomite plus magnesite could, according to Friedrich (1959), not provide any indication concerning its mode of formation. All of the Austrian magnesites must have been formed by way of hydrothermal metasomatism. Even so, Friedrich (1958) had shown, how many samples of these (hydrothermal) magnesites contained relict textures (even structures) typical of limestones and dolomites. The presence of local concentrations of crinoids and other fossils now consisting of magnesite was considered to prove the "metasomatic" origin of the magnesite.

An essential, but generally neglected, point was raised by Clar (1956): **whether or not grain-to-grain contacts as seen with the light microscope in thin sections of compacted carbonate rocks (such as for example Paleozoic limestones) actually can be interpreted in terms of a sequence of events**. When seeing a magnesite rhomb penetrating neighbouring dolomite or calcite grains, the question could be raised whether the magnesite has partly replaced that other particle (and therefore was formed later), or whether the magnesite particle had been mechanically forced into neighbouring softer grains during the compaction of the rock as a whole. One would expect clear evidence of either process, but in general no such distinction can possibly be made (see for example Friedrich, 1968 A). In addition Clar (1956) doubted, whether the secondary conversion of limestone or dolomite into magnesite would have left any evidence in the form of relict grain boundaries. Notwithstanding, Clar (1956) tended to follow the usual explanation for the formation of the Austrian magnesite in terms of hydrothermal metasomatism, but he could not at all exclude an initial sedimentary origin of at least some of those magnesite deposits.

After considering a variety of laboratory observations on the high-temperature / high-pressure syntheses of magnesite and dolomite, Ney (1956) arrived at the conclusion that hydrothermal solutions may well be able to change a limestone into dolomite, but never be able to change a limestone or a dolomite into a deposit of magnesite. Ney (1956) found

another convincing argument against the theory metasomatic replacement in the absence of any “incomplete” stages of the assumed process. Therefore, Ney (1956) could only agree with Leitmeier (1953), that most of the (Austrian) magnesite deposits must have had a primary, sedimentary origin that had been overprinted during metamorphism. The most convincing argument in favour of the origin of magnesite in the sedimentary environment, according to Ney (1956), had been given by Leitmeier & Siegel (1954). Those two authors had described in detail the magnesite deposit of Entachenalm (near Hintertal), and revealed a complete, and gradual, transition of a black, saline-type magnesite (*Typus Hall*) via a brown, cavernous magnesite (*Typus Kaswassergraben*) into a grey, fine- to coarse grained crystalline magnesite. Earlier Leitmeier & Siegel (1954) had described, how a number of Austrian magnesites had become known, which lacked any indications of a possible metasomatic origin (thereby implying formation in the sedimentary environment). The magnesite of Entachenalm studied by Leitmeier & Siegel (1954) contains graphite and coal, which also occur in the underlying *Grauwacke Schiefer*. Microscopic examination showed the graphite - coal to be made up of plant remains. In addition the microscope revealed petrological details typical of sediments.

Vohryzka (1960) stated, that the magnesite from the serpentinite of Kraubath had been formed by *ascending* solutions during tectonic movements (much like Clar, 1928; Von Braunmühl, 1929; Redlich, 1934; and Petrascheck, 1945). The magnesia-rich fluids had found ample pathways through the many fault systems. In addition, minor amounts of magnesite would have been (re-)deposited upon the weathering of the serpentinite rocks. At first Schroll (1961) had reported on the presence of magnesite in the anhydrite deposits of Lauffen (Austria) on the basis of his chemical analyses only. However, additional research with differential thermal analysis and with X-ray diffraction showed unmistakingly the presence of magnesite (in addition to dolomite and calcite). Concerning the possible mode of formation of this magnesite in anhydrite deposits Schroll (1961) expressed his support for the idea of Friedrich (1959), in that obviously any “syngenetic” formation had to be ruled out.

Angel (1962) was quite convinced, that the dolomite as well as the magnesite of the *Grauwackenzone* could only have formed by way of metasomatism and that these carbonates had not been deposited as sediments. The process of metasomatism would have changed pre-existing limestones first into dolomite; often only partly. In order for the secondary change to take place, large amounts of calcium carbonate had to have been removed and magnesium to be supplied. How this large-scale replacement would have taken place, was not clear to Angel (1962), the more because in many instances no further reaction took place after dolomite had been formed. If the supply of magnesium continued, the dolomite would be dissolved again and magnesite would have formed. In other words, magnesite would have replaced dolomite, and Angel (1962) had actually observed such a replacement in many of his thin sections. In the words of Angel (1962) metasomatism is a replacement process taking place in steps and with a certain direction (*“Metasomatose ist also ein Verdrängungsvorgang, der sich in ganz bestimmter Richtung und in Etappen vollzieht”*: Angel, 1962, p.523). As one of the very few students of the process of metasomatism, Angel (1962) considered its actual mechanism in some detail. Only tectonic movements within the pre-existing limestones could have opened up the necessary many thoroughfares for the magnesium solutions. However, the formation of talc in pre-existing shales upon the reaction with magnesia-rich solutions was difficult to understand, because shales are quite impermeable. In the explanation of Angel (1962) shales and other impervious rocks would have played an important role in stopping the magnesia-rich solutions from moving out of the partly-converted limestones again, and so would explain why in some places dolomite had been formed and in other places magnesite.

In his 1963 paper Friedrich cited numerous observations in support of his explanation of the origin of the magnesite deposit of Kaswassergraben in terms of metasomatism.

Numerous thin-sections appeared to contribute textural evidence contradicting any possible suggestion of a sedimentary origin. In several instances field relations as well as thin-section textures indicated replacement of pre-existing dolomite by magnesite. Even remnants of calcium carbonate within dolomite relicts documented the replacement of calcium carbonate by dolomite as a first step in the process of magnesitization. At the same time Friedrich (1963) had found more indications proving the process of magnesite formation to be quite separate from that of siderite formation.

Large quantities of nodular magnesite concretions in the shales of the Werfener Schichten near Leogang, Austria were described by Siegel (1964). The very fact that the magnesite nodules were enclosed in shale, excluded any possibility of a metasomatic origin. Because no traces of any halite or anhydrite were present, an origin in a saline environment could be excluded as well. A number of textures found in the magnesite nodules, suggested similarity with the gel-like magnesite of the Kraubath type. In conclusion, Siegel (1964) suggested, that hydrothermal solutions pouring into a marine environment would have been responsible for magnesite formation in the Werfener Schichten. Mostler (1966) described nine different species of conodonts from the dolomite / magnesite layer of the Sauberger Kalk, Entachen Alm (near Saalfelden, Austria). Apart from these conodonts Mostler (1966) found *Orthoceras* sp., crinoid ossicles, echinodermata remains and calcispheres in the red-coloured dolomite / magnesite. Petrascheck (1966) could only agree with the statement of Schwinner (1942), that the Austrian magnesites must have been formed between the Variscian and the Alpidic orogeny. Not so much magma intrusions, but rather their proximity to serpentinite rocks (as suggested by Schwinner, 1938) formed the most likely explanation for their formation.

Laboratory syntheses of magnesite were described by Johannes (1966 A), involving the reaction between dolomite powder and a solution of MgCl_2 at temperatures between 473 and 673 K at 2×10^5 kPa pressure. In subsequent laboratory experiments Johannes (1966 B) observed a reaction between magnesite and quartz to give talc plus carbon dioxide at temperatures between 623 and 673 K under a pressure of at least 2×10^5 kPa. Johannes (1967 A) described, how he had performed numerous hydrothermal experiments (at 2×10^5 kPa pressure and high temperatures), which led him to conclude, that serpentinite will readily react with CO_2 even at relatively low $p\text{CO}_2$ values. The reaction products are talc and magnesite, which formed at temperatures above 553 K. Quartz instead of talc, together with magnesite, formed in the experiments, when ultrabasic rocks such as dunite, forsterite and serpentinite reacted with large amounts of CO_2 at temperatures between 573 and 673 K. Only in the absence of carbon dioxide, serpentinite could be considered to be stable. Applying the results from his experiments to the mode of formation of Austrian magnesites, Johannes (1967 A) observed, that because those magnesites contain free quartz, they must have been formed during metamorphic reactions at temperatures between 573 and 623 K and at pressures corresponding to burial depths not exceeding 7 to 8 km. Although Johannes (1967 B) claimed his laboratory syntheses of magnesite (and dolomite) as providing ultimate insight into metasomatic reactions, that claim might well be doubted. In all of these hydrothermal tests pressures of 1×10^5 kPa or more were used, and temperatures ranged from 573 to 723 K. Such p, T conditions deserve the description of “metamorphic” rather than “metasomatic”.

Two conclusions can be drawn on the basis of these experiments. In the first place Johannes (1967 B) observed, how under high pressure and high temperature conditions, bicarbonate solutions are not able to transport magnesium in solution or to convert calcium carbonate into magnesite. In the second place: under such p, T conditions magnesium chloride solutions are quite capable of changing the mineralogy of solid calcium carbonate: first dolomite will form, later changing into magnesite. Johannes (1967 C) commented on the paper by Rosenberg & Mills (1966) on the possible reaction of CO_2 -solutions at temperatures

of more than 473 K with dolomite. Their conclusions were founded on the laboratory experiments by Rosenberg & Holland (1964), in which phase relations between calcite, dolomite and magnesite were studied in $\text{CaCl}_2 - \text{MgCl}_2 - \text{CO}_2$ solutions at temperatures between 548 and 693 K. According to Johannes (1967 C) it was not possible to draw conclusions concerning the actual formation of magnesite from dolomite from those laboratory experiments. "The proposed mechanism for emplacement of magnesite is probably also not in agreement with observed field relations, once the 180 different well investigated occurrences of magnesite in the eastern Alps are considered. In these cases calcite was as a rule replaced by dolomite and later on, dolomite by magnesite": Johannes (1967 C, p.148). Later, Johannes (1969 A) described laboratory experiments on the formation of mixed crystals of siderite and magnesite. Mixed crystals involving magnesite required temperatures of at least 623 K at a pressure of 1×10^5 kPa. Johannes (1969 B) listed numerous results from his high pressure / high temperature experiments in the system $\text{MgO} - \text{SiO}_2 - \text{H}_2\text{O} - \text{CO}_2$. One of the conclusions reached was, that the often-found assemblage of talc plus magnesite requires temperatures of 623 to 823 K at 2×10^5 kPa pressure. A number of geologic examples were given, where the outcome of the high pressure / high temperature experiments could be applied. For example the magnesite deposit at Tux (Austria) contains talc as well as chlorite (Angel & Trojer, 1953), and therefore temperatures in excess of 573 K and pressures of at least 30,000 kPa must have been involved (Johannes, 1969 B).

Experiments by Johannes (1970) indicated two possible ways in which magnesite deposits might develop. The first mechanism consisted of CO_2 -metasomatism; the second would involve magnesium-metasomatism. Numerous experiments showed the parageneses quartz + magnesite and talc + magnesite to be largely independent of the CO_2 pressure. But the parageneses of enstatite + magnesite and anthophyllite + magnesite could only exist at high pressures of CO_2 . In contrast the parageneses serpentinite + magnesite indicated low carbon dioxide pressures. Magnesium metasomatism most likely had to involve magnesium chloride solutions. Depending on pressure, temperature, salinity and CO_2 pressure, the parageneses calcite + dolomite or dolomite + magnesite would originate. Both metasomatic reactions required high temperatures (573 to 973 K) as well as high pressure (2×10^5 to 7×10^5 kPa). On the basis of his hydrothermal syntheses Johannes (1970) stated specifically, that the formation of magnesite at temperatures below 473 K was not at all possible, and that the formation of magnesite from normal seawater was out of the question.

Höll & Maucher (1967) reported to have found conodont fossils in several of the small intercalations of calcite within the dolomite - magnesite of Tux (Tirol). Throughout the whole of the Tux dolomite-magnesite deposit crinoids were found; their determination was not possible, however. Apart from volcanic influences during the time of deposition, which had to be held responsible for the formation of for example the occurrence of the mineral scheelite, Höll & Maucher (1967) stressed the far-reaching impact of the Variscian as well as the Alpine orogeny on the Austrian dolomite-magnesite deposits.

Friedrich (1968 A) recalled the existence of two fundamentally different explanations for the formation of magnesite: 1) the metasomatic theory (Redlich, Clar, Meixner, Angel) and 2) the sedimentary theory (Gómez de Llarena, Leitmeier, Siegel). In his 1968 (A) paper Friedrich described a multitude of observations made with the (optical) microscope, which taken together had convinced him, that magnesite could not have originated in the sedimentary environment, but must have formed through "metasomatosis". Even the well-known example of crinoid stem fragments (from the Sattlerkogel), now partially consisting of magnesite, was explained to have formed through the process of metasomatosis. The partial dolomitization of crinoid fragments must have taken place during the process of diagenesis. The presence of ankerite in the same samples would have little or nothing to do with the formation of magnesite. In a second paper published that same year Friedrich (1968 B)

emphasized, that two different genera of Austrian magnesite existed, the formation of which were related to the Variscian or to the Alpidic orogeny. With regard to the crystalline Austrian magnesites Friedrich (1968 B) repeated his interpretation of a "metasomatic" origin.

Magnesite nodules from the Lower Triassic *Werfener Schiefer* red beds found near Innsbruck and Saalfelden, were studied by Eisbacher (1969). Previously, the same nodules had been investigated by Angel & Trojer (1955), who had interpreted their origin in terms of primary magnesite concretions formed in a highly saline environment. Somewhat cautiously Eisbacher (1969) postulated an origin for these magnesite nodules predominantly in the sedimentary environment, but with subsequent changes during tectonic movements.

An extensive review on the formation of the Austrian magnesite deposits, based especially on the microscopic properties of such deposits, was published by Friedrich (1969). The conclusion reached on the origin of magnesite was the same as that reached in his previous publication (Friedrich, 1959): magnesite could not have formed as a sedimentary mineral, but could have formed only through a process known as metasomatism. Friedrich (1969) confirmed all of the detailed observations made by Angel & Trojer (1953), but he added more on the process of metasomatism (or *Neumetasomatose*) as it had been defined by Raguin (1961). Of course, such a process might well work out in irregular ways in pre-existing rocks. The hydrothermal experiments by Rosenberg & Holland (1964) (conducted at temperatures from 548 to 693 K) had contributed valuable insights into the phase relations between calcite, dolomite and magnesite, and had elucidated the close relation between magnesite and dolomite. In addition, the high-temperature experiments by Johannes (1966 A, B) had done much to understand the role played by talc and quartz in systems involving magnesite. According to Friedrich (1969) all of these laboratory experiments only confirmed his observations made in the field. The geochemical differences between top and bottom of magnesite layers intercalated in dolomite layers, nor the ooid-like textures found by Haditsch (1968 A), could be used in support of a sedimentary origin of magnesite. Partial replacement of macrofossils by dolomite and/or by magnesite would not really support any sedimentary origin, because the replacement during metasomatism might as well have taken place in a very irregular way (as Friedrich, 1969 claimed). Particularly the Carboniferous limestones of Austria would have been susceptible to metasomatic conversion into magnesite. The cause being, at least according to Friedrich (1969), that at the time of actual metasomatism these limestones were still relatively young and therefore had been "easier" to convert into magnesite. After their initial metasomatism the magnesite deposits would have become folded and torn up into irregular sheets during the Variscian orogenesis; after that a second interval of magnesium supply and conversion of limestones into magnesite would have taken place.

As one of very few authors working on magnesite formation, Friedrich (1969) took the trouble to study in detail the origin of magnesite in salt deposits. After comparing the small amounts of magnesite in anhydrite, gypsum or halite deposits with the relatively small intrusions of melaphyr or tuff in the saline deposits, Friedrich (1969) explained this type of magnesite to have formed in much the same way as the fluorite, copper and lead ores present in small amounts in the rocksalt deposits: by way of magnesium-containing hydrothermal solutions. In order to make his argument against a sedimentary origin of magnesite even more convincing, Friedrich (1969) mentioned the fact that the world oceans contain extremely large amounts of magnesium salts, but that no modern deposits of magnesite had become known. (This statement by Friedrich disregards factual evidence on modern deposits of magnesite published prior to 1969.) Nonetheless, Friedrich (1969) admitted that in publications by Angel (1962) and by Schroll (1961), magnesite had been described from truly saline deposits (of geological age). After discussing at some length the relations between magnesite, anhydrite, gypsum and rock salt, Friedrich (1969) concluded, that magnesite

formation had nothing to do with calcium sulphate or any other salt minerals. Having (indirectly) attributed the origin of all (crystalline) Austrian deposits to metasomatism, Friedrich (1969) devoted some thoughts to the possible source of the large amounts of magnesium. Basic (or even ultrabasic) magma must have been the source, and not individual masses of granite, andesite or peridotite. Such a deep-seated magma source did not necessarily form all magnesite in one action, and there may well have been several episodes of magnesite formation.

Magnesite in the anhydrite-gypsum deposit of Wienern am Grundlsee (Steiermark) was identified by Haditsch (1968 B) using X-ray diffraction. Haditsch (1969) emphasized the contrasting views with regard to the origin of the *Spatmagnesite* (the coarsely crystalline type of magnesite). On the one hand, the idea of a sedimentary origin had been advanced, but on the other hand a metasomatic origin was generally considered to be much more likely. Even a compromise seemed possible: the magnesites may have formed in the sedimentary environment, but underwent considerable changes during subsequent orogenesis. Many indications for a sedimentary origin had become known from the Asturreta deposit (northern Spain), as for example Gómez de Llarena (1950, 1951, 1953, 1954, 1955, 1957, 1959, 1960 A, B, 1962, 1964, 1965) had suggested on numerous occasions. Haditsch (1969) emphasized, how not only the magnesite deposit of Asturreta showed an intrinsic lamination; much the same phenomenon had been encountered in the contacting silica-rich rocks (lydites).

Despite the many details revealed in the papers by Gómez de Llarena, and despite his remarkable laboratory experiments on the crystallization of alum and of sodium thiosulphate, Haditsch (1969) felt the need to reject the suggested sedimentary origin for magnesite. Even after studying the magnesite from Dienten (near Zell am See, Austria), which possesses a comparable lamination, Haditsch (1969) was convinced, that the Asturreta magnesite as well as the Dienten deposit must have had a metasomatic origin. This conclusion was based primarily on textures seen in thin section, indicating a distinct sequence in the formation of calcite, dolomite and magnesite, which sequence would exclude any (syn-) sedimentary origin.

Siegel (1969) suggested the existence of a well-defined stratigraphic sequence leading up to layered magnesite deposits. Notably the Entachen deposit would show all of the characteristics of such a sequence. No indications of leaching after deposition could be discerned in the Entachen magnesite. At the same time several observations point toward an organic-rich, reducing environment at the time of formation (as witnessed by the absence of sulphates). The fact that this magnesite would have been formed in a marine environment, was illustrated by measurements of its chlorine content. The magnesite from Kraubath is known to contain around 25 ppm chlorine; the magnesite of Entachen as much as 200 ppm; and of course the magnesite from the salt deposits of Hall (Tirol) contains the highest amounts of chlorine. Many similarities exist, still following Siegel (1969), between the saline magnesite deposits of Hall and those of Entachen. Because the rock salt must have prevented any possible occurrence of circulating solutions typical of “metasomatism”, the magnesite of Entachen would have been formed without any such circulating solutions. Instead the processes (and brine compositions) typical of a hypersaline environment would have led to the formation of magnesite. In 1984 Siegel claimed, that magnesite formation would require a negative Eh (i.e., reducing conditions) as well as a high Mg/Ca ratio (often caused by the precipitation of gypsum/anhydrite).

Samples from the magnesite deposit of Tux (Tirol) were studied by Wenger (1971) with the petrographic microscope: measurement of the optical axes of magnesite (and dolomite) crystallites indicated primary growth, which definitely took place *before* any tectonic deformations. Earlier, in 1964, Wenger had expressed his conviction, that the magnesite of Tux had been formed from contacting limestones and dolomites by way of

metasomatosis. According to Lesko (1972) magnesite of the Kraubath-type (i.e., fine-grained and virtually iron-free magnesite) originated during the weathering of serpentinite rocks under oxidizing conditions. No process of metasomatism would be involved, neither would it be involved in the formation of the medium- to coarse grained, iron-containing magnesite of the Veitsch-type. Both types of magnesite would have been formed during the weathering of silicate minerals rich in magnesium, such as serpentine. Magnesite of the Veitsch-type would have been formed under reducing conditions from H_2S , CO_2 and NH_4 rich solutions. Such solutions would have been responsible for the presence of pyrite and carbon fragments in the magnesite. The following stages could be recognized in the formation of magnesite from serpentine: dissolution; separation of dissolved species; precipitation of calcium and magnesium; deposition and lithification of the thus formed precipitates, followed by the possible recrystallization of some of the precipitates. The latter process, recrystallization, would be responsible for the change of initially precipitated magnesium hydroxide, through a stage of hydrated carbonates into anhydrous magnesium carbonate.

Magnesite forming a cement in between the grains of a sandstone has been described by Petrascheck (1972). As a result of the weathering of a neighbouring serpentinite this magnesite may well have been formed in the granular network of the sandstone. Petrascheck (1972) had to conclude, that any specific conclusion on the possible role of "descending solutions" was not possible, because the magnesite had been found in elongated, narrow veins and fissures, which obviously were the result of tectonic movements. At the same time Petrascheck (1972) admitted, that magnesite deposits with a clear sedimentary origin had become known, for example those of Kaswassergraben and Entachen.

The iron carbonate deposit of Pitten (Austria) was studied by Tufar (1972). A multitude of minerals, including magnesite, can be found there. The relations between the Austrian deposits of iron (II) carbonate and magnesite had been discussed earlier at great length by Petrascheck (1932) and many authors have taken that particular publication as their guideline. In it Petrascheck (1932) had devoted considerable attention to the siderite of Pitten. Based on microscopic analyses of the various ores, Tufar (1972) concluded on recrystallization, secondary changes and replacement mainly due to metamorphism. In conclusion, Tufar (1972) tended to follow the point of view of Angel & Trojer (1953, 1955), Höll & Maucher (1967) and Wenger (1971), that these ore deposits may well predate the Alpidic orogeny.

Additional observations on the magnesite from Sunk / Trieben were published by Siegel & Felser (1973). After having excluded any possible metasomatic origin for the contacting dolomite layers, the conditions during the formation of magnesite were described as essentially poisonous toward every form of life. The absence of fossils and the black colour pointed toward anaerobe conditions. Decomposition of organic remains must have caused high concentrations of dissolved CO_2 and H_2S . No indications were found for any kind of precursor such as nesquehonite. A completely different interpretation of the Austrian Paleozoic rocks enriched in metals (Fe, Mg, Cu, Sb, W, Hg and U) was reached by Schulz (1974). Ore formation must have taken place during numerous hydrothermal intrusions. However, later metamorphic reactions caused considerable problems regarding an adequate interpretation. Notwithstanding, the vast magnesite deposits of the eastern Alps were described by Schulz (1974) as having had a " ... synsedimentary, syndiagenetic - metasomatic origin with a hydrothermal supply".

The petrological analyses by Vavtar (1976) of samples from the magnesite deposit at Hochfilzen (Tirol) revealed only one deformation interval; not two as suggested by for example Petrascheck (1945). The magnesium needed for forming this particular magnesite, would have been supplied by submarine volcanism, as witnessed by nearby tuff layers. Although Vavtar (1976) was inclined to invoke "metasomatism" as the ultimate cause of the Hochfilzen magnesite, he stressed that the possibility of a synsedimentary or "paradiagenetic"

origin could not be excluded at beforehand. Special mention should be made of the finely laminated (mm-scale) red-coloured magnesite observed by Vavtar (1976) in the Rettenwand area, near Hochfilzen.

The magnesite deposits enclosed in the Austrian *Grauwackenzone* are not at all confined to one specific stratigraphic horizon as Felser (1977) noted. Many of the magnesites occur as stratiform deposits in between shale, limestone or dolomite. From analyses of the contacting formations an intra- to supratidal paleo-environment can be deduced. However, Felser (1977) could not find any clear indications concerning the mode of formation of magnesite, but tended to agree with Siegel (1969), in that deposition must have taken place in a rather "specific environment". At the same time evidence had been found, indicating, that in many cases metamorphism had left its traces in the magnesites in the form of changes in texture and geochemistry.

According to Zachmann (1977) the discussion surrounding the origin of magnesite had been influenced especially by the publications on the Eugui deposit by Gómez de Llarena. Up to the 1950's there was general agreement among the (Austrian) scientists, that the Alpine magnesites had been formed by a process described as metasomatism. The experiments by Johannes (1970) were generally considered to provide support for such an interpretation.

The origin of the Austrian magnesites has been explained by Oberhauser (1978) in terms of an Alpidic thermic event related to Triassic volcanism. Tufar (1978 A) applied the method described by Yermakov et al. (1965) and Cunningham (1977) to liquid inclusions in minerals such as baryta and magnesite from Austria. The very small amounts of solution freed when crushing the rock samples, could be chemically analyzed, and were found to consist of magnesium and sodium cations combined with bicarbonate and chloride anions. No iron nor any heavy metals were detected. As a direct result of these analyses, Tufar (1978 A) had to reject the suggestion of for example Meixner (1953), that the magnesite and siderite deposits of Austria had been formed in an identical manner. Tufar (1978 B, 1980) described magnesite together with dolomite, gypsum and anhydrite from the Myrthengrabe am Semmering (Niederösterreich). Much like Schwinner (1946), Tufar (1980) interpreted the dolomite, anhydrite, magnesite deposits as representing a syngenetic - sedimentary sequence. "The geological environment of the Myrthengrabe evaporite deposit clearly excludes an epigenetic influx of "hydrothermal" Mg solutions originating from a (hypothetical) deep-seated magma reservoir. On the contrary, it also offers important evidence for a primary, syngenetic accumulation of magnesium during the time of formation of the deposit and its country rocks": Tufar (1980, p.134).

According to Haditsch & Mostler (1979) most of the Austrian magnesites are closely associated with a black dolomite and fossil-rich limestones (with especially abundant crinoids, but also with ostracodes and foraminifera). Because of the often observed paragenesis magnesite – quartz – muscovite – chlorite, Haditsch & Mostler (1979) concluded on low-grade metamorphism. The intercalated dolomite layers would have formed from the initial limestone deposits by way of a process of dolomitization at a temperature of 503 K, and subsequently this dolomite would have been changed into magnesite at a temperature of 623 to 723 K.

Magnesite together with calcite, aragonite and dolomite was found by Niedermayr et al. (1979) in sandstones and conglomerates of the *Grödener Schichten* in the Gailtaler Alpen, Kärnten. The carbonates occurred as cements in finely laminated layers within the sedimentary rocks, filling up cracks and fractures, and as well-developed crystals in pore spaces. Most probably dolomite and magnesite originated from aragonite and/or calcite upon interaction with highly saline, magnesium-rich solutions. According to Niedermayr et al. (1979) the formation of magnesite must have taken place immediately after the formation of the dolomite. Within the shales and sandstones of the *Werfener Schichten* in the Villach –

Spittal – Lienz area fine-grained magnesite was identified upon X-ray analysis; the mineral magnesite even occurs as a cement in the clastic sediments. The magnesite crystallites are generally very fine grained or microcrystalline, and occur together with aragonite, calcite and dolomite. According to Niedermayr et al. (1980) this fine-grained magnesite must have been formed in highly saline solutions from pre-existing carbonates (such as calcite or dolomite). High Mg/Ca ratio's of the brines must have been caused by the precipitation of gypsum (which occurs in numerous instances within the *Werfener Schichten*). After detailed investigation of several new deposits of magnesite in shales at the basis of the *nördliche Kalkalpen*, Niedermayr et al. (1981) suggested an intra- to supratidal environment for its (low-temperature) formation. In addition, Niedermayr et al. (1981) stated, that the very mode of formation of magnesite in rock salt formations remained an unexplained mystery. According to Babčan (1980) magnesite found in rock salt clearly could not have formed by way of a process known as "metasomatism", but this magnesite probably had been formed initially as magnesium hydroxide carbonate to be changed later into magnesite. Earlier, Babčan (1975) had found in his laboratory experiments, that the formation of dolomite from calcite plus a concentrated solution of magnesium chloride requires a minimum temperature of 373 K; that a mixture of dolomite plus magnesite forms in this experiment at 423 K and, that pure magnesite would require a minimum temperature of 473 K.

Magnesite layers (of up to 1 cm thick) intercalated with gypsum layers from the southern slopes of the Dobratsch Mountain (Villacher Alpen, Kärnten) have been described by Strehl et al. (1980). Because of its association with limestone and dolomite Strehl et al. (1980) suggested an origin for this magnesite by way of a secondary conversion of pre-existing calcium carbonate in a hypersaline environment. Tufar (1981) claimed most of the ore deposits of the Eastern Alps to have had a syngenetic origin (contemporary with the deposition of the pre-metamorphic rocks). In particular the magnesite deposits gave the impression of having been of syngenetic origin; even so Tufar (1981) called for some caution, because carbonates (as well as sulphides) could easily be changed upon only a slight degree of metamorphism. In addition Tufar (1981) provided an explanation for the often invoked "metasomatism" phenomenon: because carbonate rocks such as magnesite and siderite are easily affected by secondary chemical processes, such as metamorphism, in the field the impression of a process described as "metasomatism" would be created.

Morteani et al. (1982) pointed out, that there were essentially two different schools of thought concerning the mode of formation of the Austrian magnesite deposits. The first school of thought had tried to explain the formation of (sparry) magnesite in terms of a metasomatic, if not hydrothermal replacement process. Papers by Petrascheck (1926, 1932, 1972), Clar (1956), Angel & Trojer (1953, 1955), Angel & Weiß (1953), Friedrich (1959, 1963, 1969) and Oberhauser (1978) had advanced that particular theory. The second theory suggested formation of magnesite in the sedimentary environment; papers by Leitmeier (1953), Leitmeier & Siegel (1954), Siegel (1955, 1964, 1969), Gómez de Llarena (1953), Ney (1956), Lesko (1972), Höll & Maucher (1967), Tufar (1972, 1974) all had suggested the latter mode of formation. Apart from the obvious controversy, there had been a serious debate about the exact moment at which the metasomatic / hydrothermal event would have taken place. Attempts were made by Morteani et al. (1981, 1982) to use measurements of rare earth elements in magnesite samples from various locations in Austria to explain the mechanism of formation. However, the results obtained were not at all conclusive. Even so, Morteani et al. (1982, p.629) expressed as their conviction that at least the crystalline magnesite deposits of Austria must have formed "... from metamorphic solutions".

The technique of determining formation temperatures from fluid inclusion homogenisation measurements was used by Bone (1983) to investigate the formation of different Archaen magnesites, and temperatures below 423 K for at least one group of such

magnesites were found. During Alpine and/or Hercynian regional metamorphism temperatures up to 823 K and pressures around 7×10^5 kPa must have been reached (Dulski & Morteani, 1989). At least during the Alpine phase of metamorphism an intense interaction between water and rock masses took place. Measurements of fluid inclusions in the contacting gneiss complexes showed CO₂ contents of 15 to 20 vol.% (Dulski & Morteani, 1989). As observed in the hydrothermal experiments of Johannes (1970), olivine will react with CO₂ and H₂O to give serpentine and magnesite. Excess free CO₂ will lead to a reaction with serpentine to give magnesite plus talc.

Schulz (1986) reminded his readers, that for example Höll & Maucher (1967), Siegel (1969), Lesko (1972), Siegel & Felser (1973) and Tufar (1974, 1981) had concluded on a marine origin for the Austrian magnesites. According to Schulz (1986) it had been Ladurner (1965), who had proven that the suggested "metasomatic" origin of these magnesites could no longer be maintained. Especially the microtectonics of the magnesite at Bürglkopf near Hochfilzen showed, how this magnesite had initially been deposited in the sedimentary environment, but that subsequently it had been enriched during metamorphism (possibly with the aid of thermal springs). Schulz & Vavtar (1977) found sedimentary structures in the sparry magnesite of the Rettenwand mine (near Hochfilzen), which consisted of a primary alternation of magnesite laminae with ones consisting of sericite and hematite.

On the basis of his analyses of strontium isotope analyses of Austrian siderites, ankerites and magnesites, Frimmel (1988) concluded on a sedimentary origin for magnesite and a hydrothermal origin for the Austrian siderites and ankerites. At least two different stages of metamorphic overprinting were recognized by Frimmel (1988). Although most Austrian magnesite deposits bear the traces of metamorphism and Alpidic tectonics, there are a few locations, where the original sedimentary magnesite (and dolomite) remained relatively undisturbed. One such location was described in great detail by Niedermayr et al. (1979, 1989): the magnesites of the Gröden Formation in the Gail Valley, Kärnten. Shrinkage cracks, laminations and algal mats all point toward **deposition in the intra- to supratidal environment**. Niedermayr et al. (1979, 1989) concluded that, because magnesite was obviously not a product of primary sedimentation, this magnesite must have formed during a later stage described as "diagenesis". Accepting this interpretation made it easy to find the actual source of the large quantities of magnesium: not deep-seated hydrothermal sources, but rather normal seawater would be sufficient to change calcium carbonate into magnesite. The sedimentary environment of the Gröden Formation must have consisted of a coastal sabkha, which would have been greatly influenced by sea-level fluctuations (Niedermayr et al., 1989).

Tufar et al. (1989) stated that notably the Radenthein magnesite deposit was part of a "strongly metamorphically overprinted sequence", and therefore used the term "magnesitic marble". The Radenthein magnesite contains numerous, very small (micrometer size) fluid inclusions. From these inclusions homogenization temperatures can be obtained; three different groups of temperatures were measured. The first group showed temperatures around 303 K; the second group temperatures between 473 and 513 K, and the third group showed temperatures in the range of around 543 K. Despite the effects of regional metamorphism which are now obscuring the original sedimentary features, the magnesite would have been formed in rhythmic sedimentary sequences. "The conspicuous regularity of the rhythmic sequences in the banded magnesite indicates a climate-induced annual stratification": Tufar et al. (1989, p.162). Even so, Tufar et al. (1989) speculated, how the initial precipitates would have consisted of hydrous magnesium carbonates, which later would have been transformed into the anhydrous magnesium carbonate. Subsequent events in the form of metamorphic overprinting had been recorded in the Radenthein magnesite in the form of its numerous fluid

inclusions, which served well to establish the temperatures, which must have occurred during the process of metamorphism.

In the explanation of Tufar et al. (1989) there are two main reasons for the prolonged and at times "overheated" discussions on the origin of the Austrian magnesite deposits. In the first place, no large-scale deposits of modern magnesite had become known. And in the second place, many convincing pieces of evidence had become known, illustrating the "secondary" conversion of dolomite into magnesite, which would support the assumed "epigenetic hydrothermal" and "metasomatic" reactions. Such hypothetical reactions would require magnesium-rich solutions, which remained unknown for the time being. An "influx of mineralizing solutions" would have to be considered, still following Tufar et al. (1989), in close relation with the possible origin of the Austrian siderite deposits. However, as the laboratory experiments by Johannes (1970) had shown, there is no relation at all between iron and magnesium carbonate formation (which fact had been stressed by Tufar, 1972, 1974). In addition Tufar's (1978 A) own analyses of fluid inclusions in the Radenthein magnesite had shown the absence of any dissolved iron compounds.

On the basis of their analysis of rare earth elements Kiesel et al. (1990) concluded on a metasomatic origin of the magnesite deposit of Oberdorf/Laming. The amounts of rare earth elements found in the magnesite had originated in the contacting clay/shale formations. At the same time Kiesel et al. (1990) concluded, that limestones and/or dolomites were the original (sedimentary) deposits, which later had been changed into magnesite by "magnesium-rich solutions", derived from nearby serpentinites.

Zachmann & Johannes (1989) pointed out, that *Gel-Magnesit* and *Magnesit Typus Kraubath* are but synonyms for the same kind of cryptocrystalline magnesite. The origin of such cryptocrystalline magnesite was attributed to the weathering of ultrabasic rocks by rain and ground water with a high content in biologically produced carbon dioxide (compare the observations made earlier by Wildman et al., 1968). Pohl (1991) distinguished only two kinds of magnesite: the crystalline Veitsch type and the often cryptocrystalline Kraubath type. The crystalline magnesite must have formed in an evaporitic environment as intra- to supratidal deposits. Contrary to the often repeated metasomatic or even hydrothermal mode of formation, Pohl (1991) did not hesitate to ascribe a syngenetic origin to the magnesite deposits of the Veitsch type. A different mode of formation was suggested for the cryptocrystalline magnesite of the Kraubath type. This particular magnesite must have formed either as veins in ultramafic rocks during weathering processes (at ambient temperature) or as the result of hydrothermal processes (at slightly elevated temperatures).

Much like Tufar (1978 A), Prochaska (1999) applied the technique of chemical analysis of the ultra small amounts of liquid inclusions to samples from Austrian magnesites. As described for example by Hall & Friedman (1963), Bottrell et al. (1988) and Banks & Yardley (1992), the crush-leach technique involves crushing small amounts of rock sample to a fine powder and extracting the freed solution during the last stage of grinding. Consistent results, being reproducible within a few percent, were obtained by Prochaska (1999) upon analysis of some 800 samples of Austrian magnesites. The measurements gave very high salinities for the solutions from the "saline magnesites" from Hall and those from the Kaswassergraben. The dark-coloured dolomite contacting the magnesite at the Kaswassergraben also possessed very high salinities in its fluid inclusions. Other magnesite samples (for example those from the Veitsch area) were measured to contain enclosed solutions of normal salinity. Normal salinity was indicated also by the fossil content of the magnesites, dolomites and limestones from the Veitsch deposits. From the chemical analyses of the closely related Austrian siderite deposits Prochaska (1999) drew the conclusion, that the enclosed solutions were in fact concentrated seawater brines and not hydrothermal solutions. The measurements made, also allowed for an interesting conclusion with regard to

dolomite formation. Crushed samples from the Austrian *Hauptdolomit* possessed normal seawater salinities, and not the salinities of highly concentrated brines. Nevertheless, the liquid inclusions from other dolomite and even limestone samples turned out to be concentrated brines. Prochaska (2000) repeated his conclusion, based on these chemical analyses of fluid inclusions in magnesite samples, that the magnesite had originally been precipitated from highly concentrated brines. Such brines most likely had been formed from shallow marine basins. At the same time Prochaska (2000) suggested, that these brines would have been involved in metamorphic reactions, because the magnesite deposits were neither stratabound nor stratiform. In 2012 Prochaska explained the origin of the Austrian magnesites as being "metasomatic-epigenetic", having been caused by concentrated brines invading in a pattern, which would follow the original lithology of the host rock. Ebner & Prochaska (2001) published a detailed analysis of the magnesite deposits at Sunk (Hohentauern). The magnesite there originally must have consisted of limestones and dolomites, which contained numerous (Carboniferous) corals and brachiopoda. The sparry magnesite of Sunk appears to have formed during the Alpidic orogeny, and was influenced by metamorphism more or less at the same time. According to Ebner & Prochaska (2001) the magnesite of Sunk may well have originated under sedimentary conditions; at least certain intervals of the stratigraphic sequence provide evidence of episodes of desiccation. For example the underlying finely laminated dolomite with mud cracks and *Londsdaleia* corals, described by Haditsch (1968 A) and Siegel & Felser (1973), suggested an interpretation in terms of the subtidal environment.

A variety of (amongst others) Austrian magnesites (including those from Kaswasser, Breitenau, Entachen-Hochfilzen, Veitsch, Tux-Lannersbach, Radenthein and Ochsner) was analyzed by Schroll (2002) with respect to the distribution of their ^{13}C and ^{18}O isotopes. Stratabound magnesites (for example those from Veitsch) and the magnesites associated with evaporates (Kaswasser/Hall) may well have originated in the sedimentary environment. On the other hand, magnesites such as those from Hochfilzen and Breitenau are of undisputed metamorphic origin. As Schroll (2002) explained, the magnesite associated with ultramafic rocks occurs in the form of crypto- to microcrystalline, white coloured concretions in soils or sediments overlaying, or adjacent to, such ultramafics. Formation must have taken place under the influence of rain water and dissolved carbon dioxide under low-temperature conditions (and atmospheric pressure).

CONCLUSIONS

After the discovery of anhydrous magnesium carbonate as a mineral by George Mitchel and its analyses by Lampadius (1800) and Klaproth (1807), some confusion ensued concerning the name to be used for the new mineral. Ultimately, it was Karsten (1808 B), who gave magnesite its name and Klaproth (1810) was the first to present the correct chemical analysis.

One of the first scientists to report on magnesite found in Austria, was Klaproth (1810). Some 50 years later, the first explanations for the formation of magnesite were published by Miller von Hauenfels (1864). Two possible origins were distinguished: a crystalline kind of magnesite would have been formed by a chemical reaction between schists and a magnesia-rich solution. The second kind of magnesite was very fine grained and occurred in fissures and cracks in serpentinite rocks; it was thought to have originated from hot, ascending solutions. Soon a third kind of magnesite was found: magnesite occurring in anhydrite or in rock salt.

As early as 1789 De Fourcroy had noted his in laboratory experiments, how anhydrous MgCO_3 would **not** precipitate from a magnesium bicarbonate solution at room temperature. Subsequently, numerous authors have confirmed this fundamental observation. The importance of the fact, that the dissolution / precipitation reaction in the case of magnesite is not reversible, rarely has been recognized as such, but nevertheless is of fundamental importance.

One of the very first statements on a possible low-temperature formation of magnesite has been made by Schrauf (1882): the magnesite formed during the weathering of a serpentinite, must have originated under low-temperature conditions. The same conclusion was later reached by Leitmeier (1914) and Clar (1928). Magnesite occurring very close to limestone beds (with crinoid fragments in it) was described by Rumpf (1876). This close association between magnesite and a fossiliferous limestone seemed to suggest, that magnesite had been formed under more or less the same conditions as those under which the limestone itself had been deposited. In the course of time more and more indications were found supporting a possible relation with limestone, but in particular with dolomite. For example Koch (1893) related to have found fossils consisting partly of dolomite and partly of magnesite (in one and the same specimen), much like Redlich (1907, 1914 A) and Humphrey (1905). Similarly, Redlich & Großpietsch (1913) had found a variety of fossils (corals, gastropoda, crinoids and brachiopoda) consisting partly of dolomite and partly of magnesite. Although magnesite usually does not contain any fossils (which can be understood, when realizing the life-threatening high salinities and temperatures around 313 K: see Hobbs & Xu, 2020), Leitmeier (1953) described fossils, consisting partly of magnesite and partly of dolomite. Friedrich (1959) found fossils, especially crinoid stem elements consisting of magnesite, embedded in a dolomite rock. Friedrich (1959) included photographs and stated to have seen such fossils consisting partly of dolomite and partly of magnesite in the collection of the Mineralogical Institute of the Montanuniversität Leoben, Austria.

Most probably Sigmund (1909) was the first to suggest a possible sedimentary origin for magnesite. Hörhager (1911) and Kern (1912) both were convinced of a possible sedimentary origin of magnesite, especially because the usual explanation in terms of a "metasomatic" reaction would require unrealistically large amounts of magnesium chloride solutions. Similarly, Leitmeier (1916 A) maintained, that magnesite might very well originate in the sedimentary environment. It was Rózsa (1926), who claimed that certain thinly laminated siderite - dolomite - magnesite deposits must have had a sedimentary origin. The origin of those fine laminations had to be found, according to Rózsa (1926), in periodical changes in for example the amount of rainfall. The importance of **periodicity** in the formation of magnesite in the sedimentary environment clearly has been hinted by Gevers (1930) and Ney (1956), and ultimately was proven in the low-temperature syntheses of magnesite by Deelman (1999), Alves dos Anjos et al. (2011) and Hobbs & Xu (2020).

Redlich (1909 B) concluded on a possible step-wise conversion of limestone → dolomite → magnesite on the basis of his observations of magnesite found in Austrian rock salt deposits. In addition Redlich (1914 A) suggested the gradual conversion of calcium carbonate into dolomite and even magnesite, upon prolonged contact with a solution of magnesium chloride. This suggestion has never obtained verification in reproducible low-temperature laboratory experiments (so much for all of the "dolomitization" theories).

No attempt at all has been made in the present chapter to explain each and every regional occurrence of magnesite in Austria. Not the regional geology of Austria was the subject as such, rather the history of various explanations given to the formation of magnesite was. This review of the history of research into Austrian magnesite deposits has opened up the possibility to recognize a number of misunderstandings and even a few misinterpretations. To give only one example: according to Ebner & Prochaska (2001) five

different types of magnesite would exist, which were described as “genetically different types of magnesite”. The first three types of magnesite are those of the classification by Redlich (1909 B); however, those three categories were based entirely on the texture as seen in the field. (Whether or not the three categories really represent different processes of formation remains to be demonstrated!) Therefore, the five different classes of magnesite by Ebner & Prochaska (2001) show, that their classification has little or nothing to do with the genesis of magnesite, but instead relies on one macroscopic property only, that is on texture. Without any attempt at an explanation Ebner & Prochaska (2001) thus went from classification to interpretation. Of course, much the same argument goes against the often cited classification of Redlich (1909 B).

From 1800 onwards various interpretations of the origin of (Austrian) magnesite have been published; interpretations based on field observations. However, theories based solely on field observations are, by definition, open to multiple interpretations. To mention only example: the longstanding discussion on either *descending* or *ascending* Mg-rich solutions as being the source of magnesium ions needed for the formation of magnesite. Most of the interpretations of the origin of magnesite in Austria have been based on the microscopic analysis of thin-sections. However, as remarked by Clar (1956), during thin-section analysis the mistake usually made, is to interpret grain-to-grain relations in terms of a sequence-of-events. Twenty years after this fundamental observation made by Clar (1956), it was shown to be of fundamental importance; direct evidence came from dry-compaction laboratory experiments (Deelman, 1975, 1976). Such dry-compaction experiments have shown, how the often assumed "diagenetic" geochemical reactions play little or no role in changing the microtexture of sediments into compacted ("lithified") sedimentary rocks.

Extremely useful facts concerning the mode of formation of magnesite were found in physico-chemical analyses of brine enclosed in magnesite crystals by Tufar (1978 A), Tufar et al. (1989) and Prochaska (1999). The temperature measurements by Tufar et al. (1989) have shown, how the magnesite samples studied had originated at temperatures as low as 303 K in combination with an original salinity of 180 to 240 promille (recalculated from the 265 to 261.7 K freezing points given by Tufar et al., 1989). The first reproducible low-temperature syntheses of magnesite took place at a temperature of 313 K and a salinity of 110 promille (Deelman, 1999).

Modern magnesite found in 1930 by Gevers in the Etosha Pan (Namibia), has never been seriously considered in any theory on the formation of magnesite. Much the same happened to the descriptions of the vast amounts of Recent magnesite from the Russian Kara Bogaz Gol (which had been described by Vakhrameeva, 1956; Polyakov, 1959; Sedelnikov et al., 1968; Andriyasova et al., 1973 and Gerasimenko & Mikhodyuk, 2009). Until recently, papers on the possible mode of formation of magnesite have repeated over and over the incorrect observation, that no occurrences of modern magnesite would be known.

A totally unwarranted neglect is encountered with regard to magnesite found in rock salt deposits. (For example Schwinner, 1937 in his attempt to provide an explanation for all of the known Alpine occurrences of magnesite, disregarded all "unusual" magnesite, including that found in rock salt.) Papers on magnesite from Austria generally tend to overlook one of the categories of magnesite mentioned by Rumpf (1873 B): the magnesite found in the rock salt of Hall (Austria). Magnesite found in the rock salt deposits is of essential importance, because it demonstrates how upwards or downwards moving, truly hypothetical, "metasomatic" solutions can not have been instrumental in the formation of magnesite, simply because rock salt is quite impermeable. Görgey (1912) emphasized the occurrence of a multitude of small-scale laminations in the rock salt deposits (of Wittelsheim, Alsace, France), where magnesite had been found. Such fine laminations extending over

large areas must have been the result of periodical brine refills; not sudden and quick, but rather taking place as a natural rhythmic event.

During the years 1916 and 1917 an epoch-making dispute took place between Karl August Redlich (1869-1942) and Hans Leitmeier (1885-1967), initially on the actual mode of formation of the mineral magnesite, but it soon touched on the scientific principles used in geology. Leitmeier (1909) had noted in his laboratory experiments, how a magnesium bicarbonate solution (at room temperature and atmospheric pressure) would precipitate hydrous magnesium carbonate only and not any magnesite. In a first reaction to Leitmeier's observations Redlich (1914 A) claimed, that magnesite could only be formed by "metasomatic" processes. The how and why of such a process of "metasomatism" were not revealed. (A fundamental argument against the hypothesis of "metasomatosis" has been contributed by Lesko, 1972: essential questions concerning the role of process of weathering, the possible role of diffusion and ultimately the reaction mechanism as such have never been answered.) The suggestion by Leitmeier (1916 A), that possibly dolomite and magnesite might well have been formed in the sedimentary environment, was countered by Redlich (1917 A) with an *ex cathedra* statement: such an idea was contradicted by all of the observations ever made on Alpine magnesites. After 1917 many scientists have tended to subscribe to the phenomenological approach of Redlich, and relied far too much on field observation and its inherent hypothetical and unwarranted interpretations.

The Alpine rocks of Austria have been subject to a truly complex tectonic history, and it is therefore that mere field observations are in most instances insufficient to explain the formation of individual deposits of magnesite. In the light of reproducible laboratory syntheses of magnesite at temperatures around 313 K (Deelman, 1999; Alves dos Anjos et al., 2011; Hobbs & Xu, 2020) a large number of field observations will need critical re-examination. Gradually it has become clear, that many deposits of magnesite must have had an origin in the sedimentary environment. Ultimately these reproducible syntheses proved all those authors to be in the right, who had ever opted for a "sedimentary" mode of formation of magnesite [e.g., Rumpf (1876), Rózsa (1925 B), Leitmeier (1916 A, B; 1951, 1953); Leitmeier & Siegel (1954); Gómez de Llarena (1953); Ney (1956); Siegel (1955, 1964, 1969); Siegel & Felser (1973), Lesko (1972); and Schulz & Vavtar (1977)]. At the same time, it really cannot be concluded, that no high-temperature formation of magnesite could ever have taken place. For example: on the basis of the presence of certain accessory minerals known to be of metamorphic origin, found by Mohr (1925) in Austrian magnesite, the conclusion seems undeniable that that particular magnesites may well have originated as a metamorphic rock. Similarly, Rózsa (1925 A) emphasized the often found association between magnesite and talc. Even the possibility of a deposit of magnesite formed originally in the sedimentary environment, but later subject to metamorphic temperatures and pressures, cannot be denied at beforehand. In each and every instance exact knowledge of all of the minerals present should lead to reasonable conclusions.

There is a very clear relation between the low-temperature formation of dolomite and that of magnesite. Starting point for any consideration should be, that the hypothetical process once known as "dolomitization" does not exist (because under static conditions calcium carbonate will **not** take up any magnesium at temperatures around 298 K and therefore will **not** change into dolomite). As a consequence there is no need at all to suppose, that a hypothetical process once defined as "metasomatosis" will act in much the same way: under static conditions (in a closed system at 298 K and atmospheric pressure) dolomite will **not** be changed into magnesite. Often the experiments of Johannes (1966 A, B; 1967 A, B; 1969 A) are mentioned in support of the assumed "metasomatic" transition of dolomite into magnesite. However, all of the experiments by Johannes led only to the formation of magnesite under conditions of high

temperature (473 K and higher) and high pressure (2 kbar and more). In fact, the experiments by Johannes illustrate the successful **metamorphic** change of dolomite into magnesite.

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