Low-temperature synthesis of eitelite, $Na_2CO_3.MgCO_3$

By **J. C. Deelman**, Eindhoven

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Abstract: Up to now eitelite could be synthesized in laboratory experiments only when temperatures of 333 K or more were used. In the present paper experiments are described in which eitelite nucleation took place at 298 K. Essential element in the low-temperature synthesis of eitelite was found to be some form of periodicity. Successful tests involved the periodical addition of a small amount of a magnesium bicarbonate solution to a mixture of sodium carbonate and sodium hydrogen carbonate. In a typical experiment 2 cm^3 of a magnesium bicarbonate solution (containing 0.2 g magnesium hydroxy-carbonate dissolved in 1 dm^3 H_2O with excess CO_2 bubbled through) would flow once per half hour onto a mixture of 5 g Na_2CO_3 plus 20 g $NaHCO_3$. A heat lamp and fan secured the complete desiccation at a constant temperature of 298 ± 2 K during half-hour intervals. After this phase of desiccation another 2 cm^3 of the magnesium bicarbonate solution would flow onto the sodium salts and desiccate again. Subsequent tests revealed that it is not necessary to use a mixture of Na_2CO_3 plus $NaHCO_3$. When using either of these salts the solid in contact with the periodically desiccating magnesium bicarbonate solution eitelite will also form. Several experiments were carried out in an attempt to obtain a static control for the described low-temperature synthesis of eitelite under fluctuating conditions. Tests employing magnesium bicarbonate solutions saturated with both sodium hydrogen carbonate and sodium carbonate were not successful. Even when using a saturated magnesium bicarbonate solution, at the same time saturated with $NaHCO_3$ and Na_2CO_3, no form of magnesium would precipitate. Further tests based on the reaction between a saturated solution of $NaHCO_3$ added to magnesium hydroxy-carbonate were more successful. It was established that for this reaction a minimum temperature of 323 K is required when adding the two ingredients in one action. In a fluctuating system a different minimum temperature was found: When adding periodically small amounts of a saturated $NaHCO_3$ solution to a quantity of magnesium hydroxy-carbonate, eitelite forms already at 298 K. The described low-temperature synthesis of eitelite has far-reaching consequences for the dolomite problem. It has now been established that the so-called dehydration barrier of magnesium cations in aqueous solution can be overcome, at low temperature, through the influence of fluctuations.

Key words: Eitelite, low-temperature synthesis, dolomite.

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* Studies on irreversible geochemical reactions no. 6

Introduction

The double carbonate eitelite, $Na_2CO_3.MgCO_3$, is not often found in large quantities in the sedimentary environment. The mineral is, however, of certain interest because it contains both sodium carbonate and magnesium carbonate in an anhydrous form. Once the mode of formation of eitelite under conditions of low temperature (around 298 K) and low pressure (1 bar total pressure) is known, conclusions could be drawn regarding the dehydration of magnesium cations in aqueous solutions at low temperatures. A number of authors have expressed the view that the difficulty of obtaining an anhydrous form of magnesium carbonate forms the main barrier in the low-temperature nucleation of dolomite (e.g.: "*… daß die Enstehung von Dolomit stark von der Hydratation der in Lösung befindlichen Mg-Ionen abhängig ist*": Usdowski, 1967, p.34; and, "*The most important inhibition must be due to the dehydration barrier of the* Mg^{2+} *ion*", Lippmann, 1973, p.167). Information on the low-temperature dehydration of magnesium cations is therefore of considerable significance with respect to possible answers to the "dolomite problem". The dolomite problem is perhaps one of the most long-standing scientific puzzles to be found. Its enigmatic character has brought despair to scientists ever since the first description of the mineral by Commandeur Déodat de Dolomieu in 1791.

As a mineral, $Na_2CO_3.MgCO_3$, was first described by Milton, Axelbrod & Grimaldi (1955) from the (Eocene) Green River Formation of Wyoming, U.S.A. The mineral was found there in close association with calcite, dolomite, magnesite, norsethite $MgBa(CO_3)_2$, nahcolite $NaHCO_3$, trona $NaHCO_3.Na_2CO_3.2\ H_2O$, thermonatrite $Na_2CO_3.H_2O$, natron $Na_2CO_3.10\ H_2O$, and shortite $Na_2Ca_2(CO_3)_3$ (see also: Milton & Fahey, 1960).

Previous syntheses

Sodium magnesium carbonate had been known from laboratory experiments long before it was found as a mineral. In 1851 De Sainte-Claire Deville found that the anhydrous double carbonate formed when heating a concentrated solution of sodium carbonate with magnesium bicarbonate to boiling point. It also formed upon heating a concentrated $NaHCO_3$ – Na_2CO_3 solution with freshly precipitated magnesium hydroxy-carbonate to 333 – 343 K (Rubinstein, 1925 / 1930; Pabst, 1973). Similarly, sodium magnesium carbonate precipitated from concentrated solutions of $NaHCO_3$ plus Na_2CO_3 reacting with $MgCO_3$ or MgO at temperatures between 333 and 343 K (Rubinstein, 1925 / 1930). According to Von Knorre (1903) the presence of both Na_2CO_3 and $NaHCO_3$ is a prerequisite for successful synthesis. In the reaction nesquehonite, $MgCO_3.3\ H_2O$, may precipitate as an initial phase, but gradually more and more $Na_2CO_3.MgCO_3$ will be formed. The crystals will eventually grow to a size of about 0.3 mm after one week when keeping the solution at a constant temperature of 353 K (Eitel & Skaliks, 1929 A). Eitelite may also form from a solution of only $NaHCO_3$ plus magnesium bicarbonate heated to 353 K (Wilson & Yü-Ch'Ih Ch'Iu, 1934). Addition of NaCl to solutions of both $NaHCO_3$ and Na_2CO_3 plus $MgCO_3$ or MgO will enhance the formation of $Na_2CO_3.MgCO_3$ (Rubinstein, 1926 / 1928). The addition of large amounts of NaCl may even lower the minimum temperature to 323 K (Wilson & Yü-Ch'Ih Ch'Iu, 1934). Sea water heated to 333 K and mixed with sodium carbonate also precipitates the anhydrous sodium magnesium double carbonate (Lucas, 1948). Another possibility to synthesize the double carbonate can be found in adding $Mg(NO_3)_2$ to a concentrated solution of Na_2CO_3 and heating the solution to 373 K for several hours (De Schulten, 1896 A,B).

In his patent on the production of sodium carbonate Urbain (1930 / 1932) claimed to have found a process to form sodium magnesium carbonate from aqueous solution. The starting materials were magnesium carbonate, sodium chloride, and carbon dioxide. In an aqueous solution these ingredients would react to give magnesium chloride plus sodium bicarbonate, according to:

$$MgCO_3 + 2\ NaCl + CO_2 + H_2O \rightarrow MgCl_2 + 2\ NaHCO_3\ .$$

The addition of ammonia would then cause the precipitation of the more or less insoluble sodium magnesium carbonate:

$$MgCl_2 + 2\ NaHCO_3 + 2\ NH_3 \rightarrow 2\ NH_4Cl + Na_2CO_3.MgCO_3.$$

Since Urbain (1930 / 1932) described an industrial process it may be assumed that high CO_2 pressures are required (this must be assumed because Urbain, 1930 / 1932 did not specify the reaction conditions). A comparable industrial process was described by Büchner (1933), who claimed the formation of $Na_2CO_3.MgCO_3$ from a solution of sodium chloride and magnesium hydroxy-carbonate in water subjected to carbon dioxide overpressures of 12 bar during 6 to 7 hours.

High-temperature syntheses of sodium magnesium carbonate were described by Skaliks (1928): Sodium carbonate and magnesium carbonate were melted together under carbon dioxide overpressure. Eitel & Skaliks (1929 B) reported that a minimum temperature of 1113 K was required for melting the two carbonates under carbon dioxide overpressure.

Von Knorre (1903) found that no $Na_2CO_3.MgCO_3$ will form when adding nesquehonite ($MgCO_3.3\ H_2O$) or magnesium hydroxy-carbonate to a concentrated solution of sodium carbonate (an observation that has been confirmed by Eitel & Skaliks, 1929 A). The addition of sodium carbonate to sea water of 293 K does not lead to the precipitation of eitelite; instead calcium carbonate will be formed (Lucas, 1948). In addition, Nikolskaya & Moshkina (1970) reported that no eitelite formed in a solution containing sodium-, magnesium-, and calcium sulfate that had been saturated with CO_2 at 298 K.

Up to date there is only one known claim as to the low-temperature synthesis of eitelite: in Gmelin's *Handbuch* (Mg, Bd.27 B, pp.438-439) (Pietsch, 1939) a paper by Obuchow & Gordon (1935) is cited stating that mixtures of magnesium carbonate and sodium carbonate in water would precipitate the anhydrous double carbonate. The formation of sodium magnesium carbonate would depend on the solids present (and, as the authors of Gmelin's *Handbuch* so aptly remarked, the actual form of the magnesium compound used by Obuchow & Gordon, 1935, was not specified), on the reaction time, and on the temperature (398 K in one instance). Because the original Russian text appeared in the *Zurnal Prikladnoj Chim.*, and was not accessible to the present author, the claim that eitelite would have been formed at 308 K could not be verified. On the other hand, there is the statement by Rubinstein (1925 / 1930) that MgO or $MgCO_3$ will not react with aqueous solutions of Na_2CO_3 or $Na_2CO_3.6\ H_2O$ unless heated to 333 K.

Experimental

The low-temperature nucleation of eitelite was first noticed in an experiment wherein small quantities of a magnesium bicarbonate solution were periodically added to a mixture of sodium carbonate and sodium hydrogen carbonate. In experiment MZ-38 a pure magnesium bicarbonate solution was used, that had been prepared by dissolving 0.2 g magnesium hydroxy-carbonate in 1 dm^3 demineralized water by bubbling excess CO_2 through it (the magnesium hydroxy-carbonate had been produced by Merck GmbH, Darmstadt, W.Germany, under article number 5828. Gasometric analysis of a random sample of this particular lot showed that it contained 71 wt.% $MgCO_3$, and titration on Mg^{2+} revealed that it contained 72 wt.% $MgCO_3$). Once per half hour 2 cm^3 of the magnesium bicarbonate solution streamed into a small plastic container (measuring 6.5 x 14 x 1.5 cm) with 5 g Na_2CO_3 anhydr. and 20 g $NaHCO_3$ in it, both initially as dry powders. A heat lamp in combination with a fan secured the complete desiccation of the 2 cm^3 of magnesium bicarbonate solution during each half hour interval. Temperature was a near-constant 300 ± 2 K. After 7 days the precipitate formed was X-rayed: trona ($NaHCO_3.Na_2CO_3.2\ H_2O$), anhydrous Na_2CO_3, and eitelite were found.

The next experiment to produce eitelite at low temperature was test M-49, in which a pure magnesium bicarbonate solution flowed periodically onto a mixture of sodium hydrogen carbonate and sodium carbonate. In the small plastic container placed under the heat lamp plus ventilator, 5 g Na_2CO_3 anhydr. mixed with 20 g $NaHCO_3$ were spread. Once per half hour 2 cm^3 of a pure magnesium bicarbonate solution (with 0.2 g magnesium hydroxide-carbonate per dm^3 water) would stream into the container. During each following half hour the magnesium bicarbonate solution would desiccate. The temperature near the surface was a constant 300 ± 2 K. After 15 days the salts present were analysed. X-ray diffraction demonstrated that eitelite, trona, and natron ($Na_2CO_3.10\ H_2O$) were present. After washing away the more water-soluble salts, and filtering off the remainder, pure eitelite was found.

An exact duplication of test M-49 was performed as experiment MZ-42. Here too, a pure magnesium bicarbonate solution would periodically desiccate in contact with a mixture of sodium carbonate and sodium hydrogen carbonate. In the small plastic container 5 g Na_2CO_3 anhydr. And 20 g $NaHCO_3$ were spread out. Once per half hour 2 cm^3 of the magnesium bicarbonate solution, containing 0.2 g magnesium hydroxy-carbonate per dm^3 dissolved with excess CO_2, would stream onto the powder in the container. A constant temperature of 298 ± 2 K secured the desiccation of the small quantities of the magnesium bicarbonate solution during each half-hour interval. After 2 weeks eitelite, trona, and Na_2CO_3 anhydr. were found in X-ray diffraction. Two more tests were conducted, using the same ingredients under identical conditions, to verify the observations made. Tests MZ-47 and MZ-48 were exact duplicates of experiment M-49, and in these two tests too, eitelite was formed at a temperature of 298 K.

It could be questioned in how far it is necessary to use a mixture of both sodium carbonate and sodium hydrogen carbonate. In experiments MZ-49 and MZ-50 this question was investigated. Once again 2 cm^3 of the magnesium bicarbonate solution (with 0.2 g magnesium hydroxy-carbonate per dm^3 water dissolved with excess CO_2) would stream in half-hour rhythm into the plastic container. In experiment MZ-49 only 2 g $NaHCO_3$ were placed in the plastic container. Fan and heat lamp ensured desiccation at a constant temperature of 298 ± 2 K. After 14 days the contents of the small container were X-rayed: $NaHCO_3$ and eitelite were found (see Fig.1). After washing and filtering off, followed by air drying, pure eitelite was obtained. In experiment MZ-50 an identical set-up was used, the same temperature, the same magnesium bicarbonate solution, the same half-hour rhythm, but this time 2 g anhydrous Na_2CO_3 were spread out in the plastic container. After 14 days of interrupted desiccation, natron plus eitelite were found.

Static controls

Unequivocal evidence that certain mineralogical changes are the result of periodical fluctuations is obtained only when making a comparison with static controls. Static controls use the same solutions as the ones used in the syntheses involving fluctuations, but lack the artificial introduction of periodicity (Deelman, 1980).

In a number of instances, however, it will be difficult to devise an adequate experiment as a static control. For example, it will be very difficult to imitate the conditions that are created when each half hour a small quantity of a magnesium bicarbonate solution flows onto $NaHCO_3$ or Na_2CO_3 or a mixture of both, and desiccates completely. It is clear that the small quantity of solution goes through a whole range of concentrations. What concentrations of $NaHCO_3$ and Na_2CO_3 are to be used in a static control? Obviously, the solution to be used should contain 0.2 g magnesium hydroxy-carbonate per dm^3. But will the 2 cm^3 of magnesium bicarbonate solution be saturated with $NaHCO_3$ and Na_2CO_3 as soon as it streams out over the dry powdered solids? Or will the magnesium bicarbonate solution reach saturation with sodium hydrogen carbonate and some form of hydrated sodium carbonate at some later stage of desiccation? All these questions are quite essential, but it may well be virtually impossible to answer these at beforehand. Therefore, once more, the empiric approach was used.

Experiment MZ-37 can be considered to be a static control based on expelling the excess CO_2 that was responsible for the dissolution of magnesium hydroxy-carbonate. This approach was chosen in order to avoid the difficulty of tracing a very small quantity of a magnesium salt in an enormous excess of $NaHCO_3$ and Na_2CO_3. Supersaturation with the latter two salts was thought to be a realistic requirement for this static control. To 1 dm^3 of the pure magnesium bicarbonate (containing 0.2 g magnesium hydroxy-carbonate) 75 g $NaHCO_3$ and 100 g Na_2CO_3 anhydr. were added. A plastic tube, at the end of which a small bubble device (as used in aquariums), connected to a small air pump was immersed into the solution. In order to secure complete removal of carbon dioxide a fan was placed closer to the beaker. The air pump was activated for several hours. After that time a white precipitate had been formed. This precipitate was filtered off from the saturated solution, washed with demineralized water, and air dried. X-Ray diffraction could not reveal any trace of a magnesium salt: only $NaHCO_3$ was found.

A new experiment was designed to check the actual role of periodicity in the low-temperature nucleation of eitelite. In experiment MZ-40 again 1 dm^3 of demineralized water was used, in which 0.2 g magnesium hydroxy-carbonate had been dissolved with the aid of carbon dioxide. To this solution were added 100 g $NaHCO_3$ and 300 g Na_2CO_3 anhydr. These large amounts of sodium hydrogen carbonate and sodium carbonate added ensured that the solution was saturated with both at the outset. With the aid of a heat lamp and a fan the solution was slowly evaporated at a constant temperature of 300 K. Because of the fact that the solution was virtually supersaturated with the two sodium salts at the outset, it took less than one day to change the solution into a thick, paste-like substance. In order to avoid the possibility that this time too no magnesium salt would be detected, a new addition of 1 dm^3 of the magnesium bicarbonate solution was made. Like before, this bicarbonate solution contained 0.2 g magnesium hydroxy-carbonate per dm^3. After two days of desiccation another dm^3 of the magnesium bicarbonate solution was added to increase the total amount of magnesium present. After another two days once again: In total 5 dm^3 of the magnesium bicarbonate solution were desiccated while supersaturation with both $NaHCO_3$ and a form of Na_2CO_3 was being maintained. It cannot be denied that in a strict sense, therefore, experiment MZ-40 was not a static test at all. The only defence can be that perhaps 1 g of magnesium hydroxy-carbonate will be easier to detect in a mixture of about 400 g sodium salts than only 0.2 g. After complete desiccation of the last addition the mass of salts was washed with demineralized water, and the more water-soluble residue was filtered off. X-Ray diffraction could only reveal the presence of trona and sodium hydrogen carbonate.

Experiment MZ-43 was an additional attempt to perform a static control test. Obviously the quantity of magnesium hydroxy-carbonate had to be increased. In the previous two static controls only 0.2 g, respectively 1.0 g, of that compound had been used in contact with a solution supersaturated with both $NaHCO_3$ and a hydrated form of Na_2CO_3. This time the solution would have to be saturated with magnesium bicarbonate, too. To 30 g of magnesium hydroxy-carbonate 1 dm^3 of demineralized water was added. After mixing the water was enriched in CO_2 by way of adding a quantity of dry ice. Additions of dry ice were furthermore made during the following days, so that the solution would certainly be saturated with CO_2. The remainder of the magnesium hydroxy-carbonate powder was filtered off, and after drying at the air, was weighed. It could be established that 6 g of magnesium hydroxy-carbonate had been dissolved into the solution. Added were then 100 g $NaHCO_3$ and 300 g Na_2CO_3 anhydr. After mixing, air was used to expell the carbon dioxide. This time a small aquarium pump was used to slowly bubble air through the solution. Temperature during experiment MZ-43 was a near-constant 298 ± 2 K. Bubbling air was continued for 14 days; after that time the precipitate formed was filtered off and washed with several dm^3 of demineralized water. The phases formed in this experiment were trona, $NaHCO_3$, anhydr., and thermonatrite. No form whatever of magnesium could be detected in several samples that were subjected to X-ray diffraction.

A further attempt to design static control tests was based on the observations of De Sainte-Claire Deville (1851) and Pabst (1973). Those two authors had stated that eitelite forms when heating a concentrated solution of $NaHCO_3$ with magnesium hydroxy-carbonate to a temperature of 333 K. In experiment MZ-53 said mixture was desiccated at a constant temperature, but not only at 333 K, at several other temperatures as well. The procedure was such that in all cases a supersaturated solution of $NaHCO_3$ was prepared (supersaturated at that particular temperature) prior to mixing it with magnesium hydroxy-carbonate. In the first test of this series 100 g of $NaHCO_3$ were dissolved in 300 cm^3 water kept at a temperature of 343 K (according to Weast, 1971, a maximum of 16.4 g will dissolve in 100 cm^3 water at 373 K). The solution was kept for 24 hours at that temperature with the result that much of the water evaporated. The remaining liquid would therefore certainly have reached supersaturation. Of this solution 100 cm^3 were decanted off, and added to 2 g magnesium hydroxy-carbonate. The mixture was placed in a thermoconstant box and kept at 343 ± 1 K. After only 36 hours the water had evaporated, and the dry mixture of solids could be analysed after crushing and powdering. It was found that eitelite, Na_2CO_3 anhydr., and magnesium hydroxy-carbonate were present. When performing an identical test at a temperature of 333 K (experiment MZ-53 B) the precipitate would consist of eitelite, trona, and magnesium hydroxy-carbonate. The same three compounds were found when performing the experiment at 323 K. However, the precipitate formed after 3 days of desiccation at 313 K did not contain any eitelite. In that case trona, sodium hydrogen carbonate, and magnesium hydroxy-carbonate were found. Desiccation at a temperature of 303 K led to the formation of trona plus hydromagnesite (not fully equivalent in its X-ray diffraction pattern with the magnesium hydroxy-carbonate used as an ingredient).

The described observation of eitelite forming in the (static) experiment MZ-53 at 323 K contradicts the statement of Rubinstein (1925 / 1930) that the minimum temperature would be 333 K. On the other hand, it shows that perhaps the claim of Wilson & Yü-Ch'Ih Ch'Iu (1934) that eitelite can be formed at a temperature as low as 323 K might well be founded. However, the latter two authors had added large amounts of NaCl to their reactants. The observation that eitelite forms in a static experiment at 323 K from a saturated solution of $NaHCO_3$ mixed with magnesium hydroxy-carbonate was double-checked. Experiment MZ-54 was an exact duplication of experiment MZ-53 C. Once again a saturated solution of $NaHCO_3$ was prepared (saturated at 323 K), and to 100 cm3 of this solution 2 g magnesium hydroxy-carbonate were added. After a few days of static desiccation at a constant temperature of 323 ± 1 K the dry, powdered precipitate was X-rayed. Trona, magnesium hydroxy-carbonate, and, quite clearly, eitelite were present.

Perhaps the described reaction between a saturated solution of sodium hydrogen carbonate and magnesium hydroxy-carbonate could be used to devise an adequate static control for the low-temperature synthesis of eitelite. As a first step to investigate this possibility a saturated solution of $NaHCO_3$ was prepared (saturated at room temperature of about 293 K). To 1 dm^3 of demineralized water 100 g $NaHCO_3$ were added, and from this stock solution only 400 cm^3 were used in experiment MZ-56. Once per half hour some 2 cm^3 of the saturated $NaHCO_3$ solution would stream into a small plastic container and desiccate there in contact with 2 g magnesium hydroxy-carbonate. Desiccation was secured through the use of a heat lamp and fan. From the remainder of the saturated $NaHCO_3$ solution another 400 cm^3 were taken and used in the static control test (MZ-57). In the static control test the saturated $NaHCO_3$ solution would also desiccate with 2 g magnesium hydroxy-carbonate, but the difference with experiment MZ-56 was that here all of the 400 cm^3 $NaHCO_3$ solution was added in one action. The mixture was poured into a broad, large plastic container that would facilitate desiccation at room temperature. This container was placed quite near to the set-up of MZ-56, in a well-isolated and darkened room. Temperature near the surface was in both tests a virtually constant 298 K.

After 9 days the precipitates formed were analysed. In experiment MZ-56 (the dynamic test) trona, eitelite, and $NaHCO_3$ were present. In experiment MZ-57 (the static control test) only trona and $NaHCO_3$ could be detected. No trace of eitelite could be found in the end products of the static control. Not only because no trace of magnesium hydroxy-carbonate could be detected in the X-ray diffractograms, but also because of the mere quantity of salts obtained, differential dissolution was used once again. After washing the precipitates with demineralized water, and drying at room temperature, the residues obtained were X-rayed. The residue from the static control test (MZ-57) consisted of the initial ingredients: and magnesium hydroxy-carbonate. The residue of the dynamic test (MZ-56) contained eitelite as well as $NaHCO_3$.

Conclusions and discussion

In the experiments described in the present paper eitelite synthesis at a temperature of 298 K has been performed. Up to this moment eitelite synthesis required a minimum temperature of 323 K (Wilson & Yü-Ch’Ih Ch’Iu, 1934) to 333 K (Rubinstein, 1925 / 1930; Lucas, 1948; Pabst, 1973). The described experiments constitute most probably the first low-temperature syntheses of the mineral eitelite: No descriptions of low-temperature synthesis could be found in the *Chemical Abstracts*, 1907 – 1983, in the *Mineralogical Abstracts*, 1956 – 1983, nor in the literature included here as references.

Tests MZ-49 and MZ-50 have shown that eitelite nucleation at 298 K can take place when small quantities of a magnesium bicarbonate solution react periodically with either $NaHCO_3$ or with Na_2CO_3 anhdr. This observation contradicts the statement of Von Knorre (1903), who claimed that successful synthesis required the presence of both $NaHCO_3$ and Na_2CO_3.

The low-temperature nucleation of $Na_2CO_3.MgCO_3$ requires a fluctuating system. In the described low-temperature experiments (MZ-38, M-49, MZ-42, MZ-47, and MZ-48) fluctuations were introduced in the form of periodical changes in concentration. Although various attempts were made, it was virtually impossible to design a static control for those tests in which magnesium bicarbonate solution had been added to large amounts of $NaHCO_3$ and/or Na_2CO_3. The final static control was found in a somewhat different experiment based on the use of a saturated solution of $NaHCO_3$ and magnesium hydroxy-carbonate. Originally, this reaction had been described by Sainte-Claire Deville (1851) as leading to eitelite formation when conducted at a temperature of 333 K. First it was established in a series of (static) tests that the actual minimum temperature for this reaction is 323 K (experiments MZ-53 A, B, C, D, E). When conducting the same experiment at 313 or 303 K no eitelite would form. The final static control was conducted with a saturated solution of sodium hydrogen carbonate that would be added to a relatively small quantity of magnesium hydroxy-carbonate. In experiment MZ-56 the sodium hydrogen carbonate solution was added in small quantities once per half hour to 2 g magnesium hydroxy-carbonate powder. In experiment MZ-57 the saturated $NaHCO_3$ solution was added in one action to 2 g magnesium hydroxy-carbonate. The temperature near the surface in both instances was 298 K. Duration of both tests was the same. Only in the test with artificially introduced fluctuations eitelite would form at 298 K. No eitelite was found in the static control test.

The low-temperature nucleation of eitelite, $Na_2CO_3.MgCO_3$, possesses a rather unique aspect in that both sodium carbonate and magnesium carbonate are united into the mixed crystal in an anhydrous form. Ever since the observations of Berzelius (1821) and Frtizsche (1836) it could only be confirmed that $MgCO_3$, after being dissolved into water with excess CO_2, will not precipitate again in its anhydrous form under low-temperature (and low-pressure) conditions. Thus far no low-temperature syntheses of magnesite have become known. Sodium carbonate shows a comparable behaviour. It usually precipitates in the form of one of the three hydrates: $Na_2CO_3.10\ H_2O$ (decahydrate), $Na_2CO_3.7\ H_2O$ (heptahydrate), or $Na_2CO_3.H_2O$ (monohydrate) (see also: Jorissen, 1910; Rosenstiehl, 1911; Wegscheider, 1912). From a supersaturated solution of sodium carbonate kept at a temperature below 305 K the decahydrate will crystallize (Loewel, 1851; Wells & MacAdam, 1907; Caspari, 1924). The heptahydrate crystallizes from supersaturated solutions at temperatures between 305 and 308.57 K (Ketner, 1902; Wells & McAdam, 1907; Caspari, 1924). Sodium carbonate monohydrate (the mineral thermonatrite) precipitates from a supersaturated aqueous solution when the temperature is higher than 308.57 K (Well & McAdam, 1907; Caspari, 1924). The anhydrous form of sodium carbonate can be synthesized by heating $Na_2CO_3.10\ H_2O$ or $NaHCO_3$ to temperatures between 523 and 573 K (Lunge, 1897). The industrial production of anhydrous sodium carbonate can take place at temperatures above 380 K (Lynn, 1930 / 1933; Cocksedge & Burns, 1934 / 1936). A patent granted to the Solvay Company (1936 / 1936) describes the dehydration at a temperature of 378 K (under atmospheric pressure). Adding large amounts of sodium chloride to a supersaturated solution of sodium carbonate will lower the dehydration temperature even to 373 K (Keene & Julien, 1935 / 1938).

The described low-temperature synthesis of eitelite has an interesting consequence for that enigmatic puzzle of the earth sciences, the dolomite problem. It has been suggested that the “sorting out” of calcium carbonate into monolayers alternating with monolayers of anhydrous magnesium carbonate requires fluctuations in free energy (Deelman, 1975, 1981). An amazing multitude of indications exist pointing towards a direct correlation between the occurrence of (Recent) dolomite and the predominance of fluctuations in that particular environment. The paragenesis of eitelite and dolomite is yet another indication of the overruling importance of fluctuations. The Green River Formation, from which the mineral was first described, exhibits a number of geological indications that point toward a depositional environment of a playa-lake. Several authors have come to the conclusion that cyclic deposition along with seasonal changes in the chemistry of the playa-lake must have occurred at the moment of deposition of the Green River Formation (Bradley, 1973; Eugster & Hardie, 1975; Lundell & Surdam, 1975; Surdam & Wolfbauer, 1975). As shown in the laboratory experiments eitelite nucleation requires such fluctuations, and this provides the first *mineralogical* evidence that the Green River Formation formed "… on a broad playa fringe, in a shallow-water lake which underwent frequent periods of desiccation" (Lundell & Surdam, 1975, p.493).

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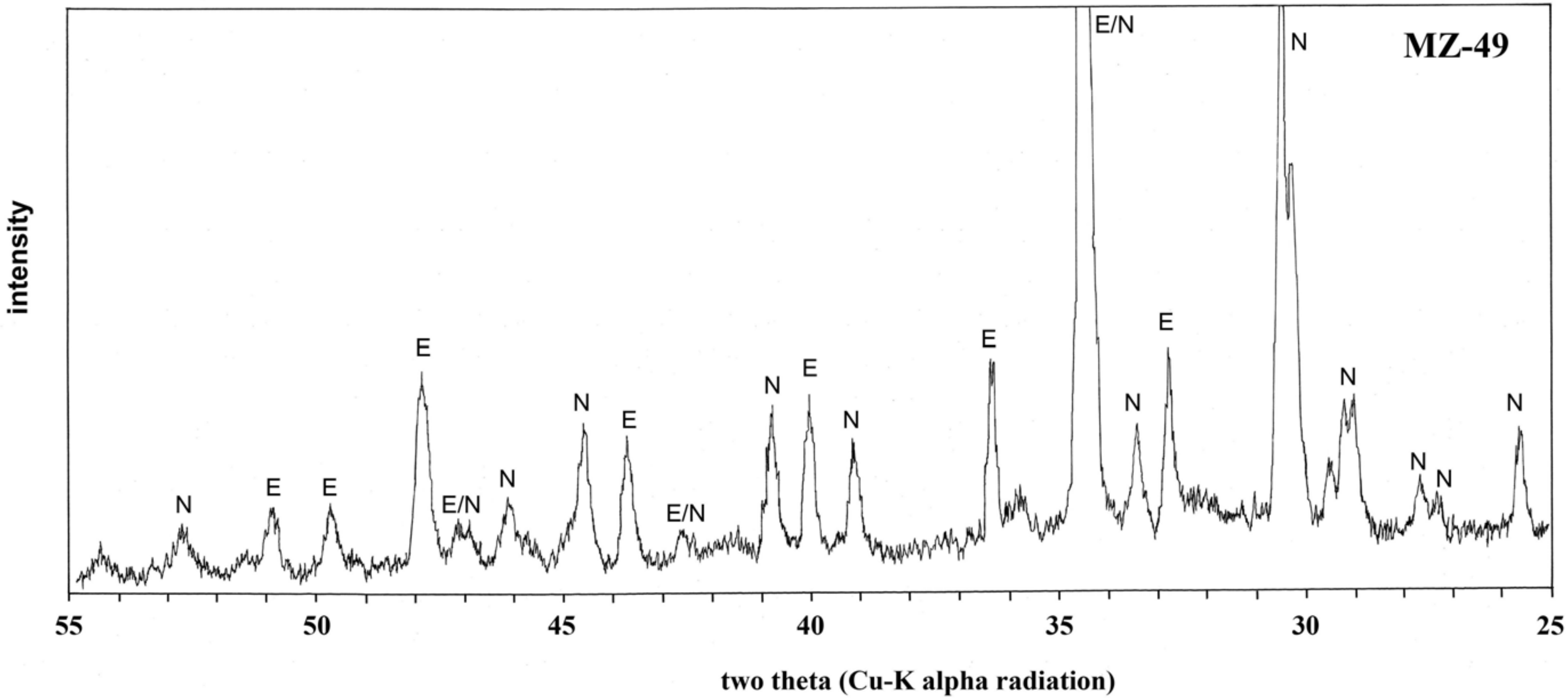

Fig.1. Eitelite synthesized at 298 ± 2 K plus sodium hydrogen carbonate from experiment MZ-49; E = Eitelite and N = sodium hydrogen carbonate (original X-ray diffractogram).

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