

LOW TEMPERATURE ABIOGENIC SYNTHESIS OF DOLOMITE

JÁN BABČAN¹ and JAROSLAV ŠEVC^{2*}

¹Department of Geochemistry, Faculty of Science, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovak Republic

²Geological Institute, Faculty of Science, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovak Republic

(Manuscript received September 8, 2000; accepted in revised form March 15, 2001)

Abstract: Endowed with the theoretical knowledge of carbonate evaporation and the precipitation of CaMg carbonates from aqueous solutions the authors systematically researched the low temperature formation of dolomite-like carbonates. The results obtained at 40 °C indicate that the formation of rhombohedral CaMg carbonates depends on the solid matter/water ratio (solidus index *I_s*). The higher the ratio, the more MgCO₃ enters into the carbonate structure. The results also confirm a gradual transition of these relationships from calcite, through Mg-calcite, Ca-dolomite and Q-dolomite (Quasi-dolomite) to Mg-dolomite (Ca₄₄Mg₅₆). The structure of these synthesised carbonates is disordered, much like their natural counterparts in lagoons, sabkhas, soils etc. When studying Ca-dolomite in the laboratory it was found to restructure into stable dolomite at 100 °C and into calcite at 180 °C. Synthesized dolomite (Ca₅₀Mg₅₀) does not show superstructural X-ray reflections and hence it was denominated as a Quasi-dolomite (Q-D).

Key words: hydrothermal alterations, synthesis, Q-dolomite, dolomite, Ca-dolomite, Mg-calcite.

Introduction

In 1850 Naumann wrote that Arduino was the first to publish his genetic considerations of Ca-Mg carbonates, later termed dolomites. He attributed them to: "... replacement of limestone by agents coming from depth". It is clear that Arduino considered that metasomatic reactions were the main agent responsible for the origin of dolomite. But this was not an isolated opinion. Sometime earlier Heim (1806, cit. in Naumann 1850) also assumed that dolomite was a limestone metamorphosed through "vaporous explosions (Dampfexplosionen)".

The presumption that dolomite developed at relatively high temperatures, was also supported by experimental modelling results. Von Morlot (1847 cit. in Naumann 1850) was probably the first to confirm the metasomatic origin of dolomite when he reacted limestone with "bitter salt" solution (MgSO₄) at 220 °C. Furthermore, Marignac (1847 cit. in Naumann 1850) is alleged to have made a successful experiment using chloride MgCl₂ instead of sulphate, but at the lower temperature of 200 °C.

The view that the secondary origin of dolomite was at the expense of primary CaCO₃ remained practically unchanged until the 1960's. The opinion prevailed that all dolomite formed via metasomatic replacement of calcite or aragonite. In the light of increased experimental results, views as to the mechanisms of this process have shifted away from assuming that it occurs at endogenous — high temperatures to more recently the assumption that it can also take place at low temperatures. However the experiments ruled out the possibility that it could occur below 100 °C which once again contradicts observations made in nature of mineral associations with dolomite.

A breakthrough came with the recent finding of, dolomite-like minerals in littoral sabkhas, lagoons and salt lakes. Until then, attempts to produce dolomite under conditions either corresponding to, or similar to sabkhas were unsuccessful. The only exceptions were Oppenheimer's experiments (1964 cit. in Hsü 1967) which succeeded in changing natural Mg-calcite into dolomite in a synthetic marine environment with the addition of pepton, ferrous phosphate, a hydrous solution of peat and quartz. The temperatures during this experiment ranged between 22 and 25 °C. We note that this genetic model of dolomite was not generally accepted and most authors did not refer to it when dealing with the dolomite problem. Uzdowski (1989) was the only experimenter into synthesized dolomite at temperatures below 100 °C (i.e. 60 and 90 °C).

The genesis of dolomite is a geological problem which has been referred as the "dolomite question" or "the dolomite problem" since the mid 19th century, when Sorby (1856 cit. in Hardie 1987) found dolomite in unconsolidated sediments. The key point to this question was formulated by Friedman & Sanders (1967) and it persisted for a long time in its original form: "to reliably explain the origin of dolomite and dolomitic rocks one can neither use the comparison with natural dolomite, nor the experiments".

It would take a lot of time and space to synthesize only a fraction of previous reviews on the dolomite problem. Such reviews appear from time to time in the literature and we shall mention some studies referring to this problem in the discussion.

During our studies we recorded evidence of dolomite formation produced through low temperature reactions. The partial results were interpreted and presented at the XVII International Geological Congress in Moscow (Babčan 1984) and in this paper we present the complete data and other

*Corresponding author: kgee@fns.uniba.sk

details about the low temperature abiogenic synthesis of dolomite.

Experiments

Experimental procedures and identification of reaction products

We used varied experimental procedures and therefore detailed descriptions will be given separately for each group. The analytical and mineral determination methods of the products were similar.

In most cases we have characterized the reaction environment before and after the reactions by using the pH values measured with a Radelkies pH-meter with a reproducibility of measurements ± 0.05 units. The contents of the basic chemical components were measured only in solutions (chelometrically). We did not determine the chemical composition of solid reaction products because of their varied mineral compositions. The contents of Ca, or Mg in the reaction products were determined by using the content differences in input materials and in solutions once the experiments were over. The CaCO_3 and MgCO_3 contents in synthesized dolomite were tentatively determined using the Lumsden's (1979) principle, which was extended to include Mg-calcite and Ca-dolomite.

In agreement with Baron (1960) we consider X-ray diffraction to be the only suitable method to determine mineral composition of very fine-grained and heterogeneous carbonate products. X-ray analysis was made on a DRON UM 1 instrument using Cu-radiation, Ni-filter, 30–40 kV and an electric current of 25–30 mA. To ensure the accuracy of the lattice parameter determinations of the newly formed products, NaCl was used as the internal standard.

Because most natural minerals and synthetic precipitates are mixtures of various CaMg carbonates, one of the most reliable methods of determining their CaCO_3 and MgCO_3 content is X-ray diffractometric analysis and the associated $d_{10.4}$ reflection values. The mol % CaCO_3 content in a rhombohedral CaMg carbonate is then calculated using Lumsden's equation

$$N\text{CaCO}_3 = M \cdot d_{10.4} + B$$

where N = mol % CaCO_3 , d is the (10.4) reflection value in angström (Å) and M and B are constants whose values are 333.333 and 911.99 respectively. In contrast to Lippmann

(1973), Reeder (1983) reported that the relation between the lattice parameters and chemical composition is linear only when the CaCO_3 content ranges between 48 and 57 mol %.

The recent classification of unconsolidated carbonates based on low magnesia (<4 mol % MgCO_3) and high magnesia (>5 mol % MgCO_3) content, is insufficient and too broad. In agreement with Lippmann's proposal (1973) we suggest including Ca-dolomite as an independent member of the nomenclature within a given range of $d_{10.4}$ reflexion values. For dolomite, that is Q-dolomite, we outline a field representing the carbonate compositions ranging within $\text{Ca}_{55-45}\text{Mg}_{45-55}$. For carbonates with the composition $\text{Ca}_{45-25}\text{Mg}_{55-75}$ we employ the name Mg-dolomite and with the composition $\text{Ca}_{25-5}\text{Mg}_{75-95}$ the name Ca-magnesite.

Trigonal CaMg carbonates obtained during our experiments, and classified using the system proposed by us are mentioned below (Fig. 1).

Evaporite formation modelling at 50 °C

These experiments were originally aimed at elucidating the problems of magnesite formation in eastern Slovak gypsum-anhydrite deposits (Babčan 1980). We ran experiments with solutions containing 0.4 M CaCl_2 , 0.4 M MgCl_2 , 0.5 M Na_2SO_4 and 1 M NaHCO_3 , while the controls were carried out with the CaCl_2 , or MgCl_2 solutions, separately. The precipitation kinetics were evaluated in relation to the degree of evaporation and to the amounts of Ca, or Mg that entered into reaction products. The procedure included heating all reagents to 50 °C prior to mixing and the addition of NaHCO_3 in its solid form. The amounts of reacted Ca and Mg were calculated by using the difference between the amount added to the experiment and the amount remaining in the solution at a given time. The solid components were separated using filtration and then submitted to X-ray diffraction analysis, microscopic study and DTA. The results are listed in Table 1.

In systems containing dissolved CaCl_2 , the results showed that gypsum crystallized in a very well ordered form immediately after the addition of Na_2SO_4 . X-ray diffraction was sensitive enough to indicate even a small admixture of calcite. However, after 6 hours the gypsum crystals had totally vanished through evaporation. In systems with MgCl_2 the solid phases did not precipitate unless 25 % of the solution was evaporated. This process was accompanied by the formation of nesquehonite. Once the solution gelatinized, hydromagnesite formed.

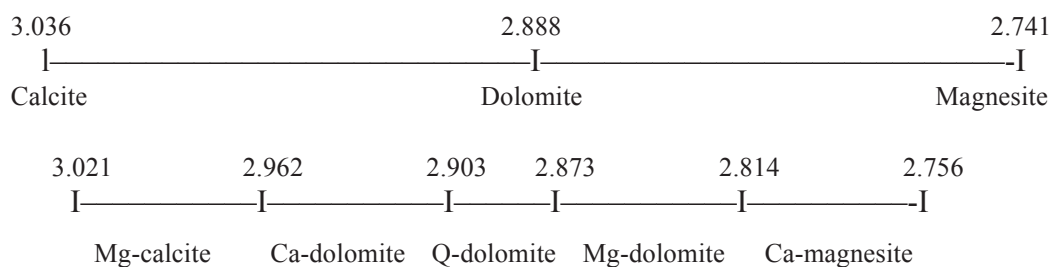


Fig. 1. A system proposed to classify metastable rhombohedral CaMg carbonates ($d_{10.4}$ spacings values are given in $\text{nm} \times 10$).

Table 1: Results of evaporite formation modelling (experiments series No. 742, for more details see text).

% evapo- ration	CaCl ₂ systems		MgCl ₂ systems		CaCl ₂ + MgCl ₂ systems		
	% react Ca	products	% react Mg	products	% react Ca	% react Mg	products
0	78.4	G, C	0	0	62.2	9.9	G, A
25	99.5	C, A	13.2	N	96.0	4.5	A, MgC
50	99.9	C, A	83.4	N	89.9	41.9	MgC, A
75	99.9	C, A	83.1	N	85.3	39.9	MgC, A
100	100.0	C, A	87.4	HM ₁ N	99.9	99.8	CaD, A

A — aragonite, C — calcite, CaD — Ca-dolomite, G — gypsum, HM — hydromagnesite, MgC — Mg-calcite, N — nesquehonite, O — solution without precipitate

Table 2: Reaction results in systems gypsum-MgSO₄-Na₂CO₃ in relation to pH values of the environment (temperature 40 °C, for more details see text).

exper. No.	ml Na ₂ CO ₃	pH in solution		% of reacted Mg	products of reactions
		begin.	end.		
769 a	0	7.18	7.70	0	G, C
b	1	9.31	8.08	1.51	G, A, C
c	2	9.46	8.09	3.11	G, A, C
d	3	9.52	8.13	0.77	G, A, C
e	4	9.41	8.14	1.91	G, A, C
f	5	9.45	8.14	5.68	C, A, HM
g	6	9.49	8.14	16.51	C, HM, A, evid. of QD
h	7	9.51	8.75	24.16	C, A, HM, evid. of QD
i	8	9.64	8.97	35.75	C, A, HM, evid. of QD
j	9	9.81	8.92	56.86	C, A, HM, N, QD
k	10	9.86	8.96	67.66	C, A, HM, QD
l	11	9.83	9.19	76.38	C, A, HM, QD
m	12	9.90	9.24	86.25	C, A, HM, QD
n	14	10.07	9.82	93.89	C, A, HM, QD

Note: Besides of 40 °C we have also experimented at 4, 5, 25 and 100 °C; Abbreviations see Table 2, QD — Quasi-dolomite

In mixed CaCl₂ and MgCl₂ solutions, gypsum co-precipitated with aragonite and as soon as 25 % of the solution was evaporated, Mg-calcite began to precipitate. A remarkable feature was that as a progressive amount of Mg reacted, the d-values of (10.4) reflections in the resulting Mg-calcite shifted towards the Ca-dolomite field ($d_{10.4} = 2.970 \times 10^{-1}$ nm to 2.928×10^{-1} nm).

A study of reactions in the gypsum-MgSO₄-Na₂CO₃ systems at 40 °C

Apart from Cl⁻-SO₄²⁻-CO₃²⁻ systems we also investigated evaporation in other systems, and the results differed considerably. Thus, in a nitrate environment (NaNO₃ was used instead of Na₂SO₄) calcite was the main product, while nesquehonite and brucite were rare. In the presence of NaCl calcite formed almost alone, while hydromagnesite was sporadic and magnesite rare. When we used Na₂B₄O₇, calcite was identified among the products along with an unidentified calcium borate and hydromagnesite.

Because the above mentioned experiments indicated the distinct influence of a sulphate environment upon the formation of Mg-calcite; we carried out a series of experiments using sulphates — natural gypsum (from Kateřinky near Opava, Czech Republic) and MgSO₄ solution instead of chloride compounds. In contrast to the mixed chloride-sulphate environments, in these environments the Mg-calcite developed even at 5 °C. The experimental results achieved in the sulphate-carbonate systems, were very interesting, because of their changing pH values.

The basic material was finely powdered gypsum (651 mg) suspended in 40 ml of 0.1 M MgSO₄ (92.25 mg). One ml of a 0.75 M Na₂CO₃ solution with pH 10.69 was added to each batch of solution. To preserve roughly equal volume and mass concentrations of MgSO₄, the volume of water was reduced. These systems were then left for 14 days to react at 40 °C. The pH of the resulting suspensions was measured, the solid components were filtered away and then finally submitted to X-ray diffraction analysis. We measured the contents of unreacted Mg in the solution. A summary of the results is given in Table 2. The sequence of minerals corresponds to visually estimated abundances from X-ray records. In experiments with high concentrations of Na₂CO₃ and high pH, the formation of Q-dolomite was evident.

Thermodynamic presupposition of dolomite formation

Observations of nature clearly show that dolomite associates with other minerals in the sediments. In the majority of cases, it is unlikely that this is occurring under elevated temperatures. Dolomite formation should be easily reproduced in the laboratory but surprisingly there is a lack of experiments confirming this. As stated above, the only low temperature dolomite synthesis achieved at 25 °C was that, reported by Oppenheimer & Master (1965), which, however has, not been widely accepted.

Apart from natural observations, theoretical calculations also clearly indicate that it should be easy to produce dolomite in a lab. With this in mind we checked theoretical calculations that confirm this presumption using thermodynam-

Table 3: Presumed reaction types leading to formation of dolomite and their equilibrium constants.

Number	reaction type	log K
1	$2 \text{CaCO}_3 + \text{Mg}^{2+} \rightarrow \text{CaMg}(\text{CO}_3)_2 + \text{Ca}^{2+}$	-1.28
2	$\text{CaCO}_3 + \text{Mg}^{2+} + \text{HCO}_3^- \rightarrow \text{CaMg}(\text{CO}_3)_2 + \text{H}^+$	-3.25
3	$2 \text{CaCO}_3 + \text{MgSO}_4^0 \rightarrow \text{CaMg}(\text{CO}_3)_2 + \text{CaSO}_4^0$	-1.08
4	$\text{Ca}^{2+} + \text{Mg}^{2+} + 2 \text{HCO}_3^- \rightarrow \text{CaMg}(\text{CO}_3)_2 + 2 \text{H}^+$	-5.21
5	$\text{CaCO}_3 + \text{MgCO}_3 \rightarrow \text{CaMg}(\text{CO}_3)_2$	+1.90
6	$\text{CaCO}_3^0 + \text{MgCO}_3^0 \rightarrow \text{CaMg}(\text{CO}_3)_2$	+8.86
7	$2 \text{CaCO}_3^0 + \text{Mg}^{2+} \rightarrow \text{CaMg}(\text{CO}_3)_2 + \text{Ca}^{2+}$	+9.04
8	$2 \text{CaCO}_3^0 + \text{MgSO}_4 \rightarrow \text{CaMg}(\text{CO}_3)_2 + \text{CaSO}_4$	+11.24
9	$2 \text{CaCO}_3^0 + \text{MgSO}_4^0 + 2 \text{H}_2\text{O} \rightarrow \text{CaMg}(\text{CO}_3)_2 + \text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$	+11.42
10	$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O} + \text{Mg}^{2+} + 2 \text{CO}_3^{2-} \rightarrow \text{CaMg}(\text{CO}_3)_2 + \text{SO}_4^{2-} + 2 \text{H}_2\text{O}$	+10.89
11	$\text{Ca}^{2+} + \text{Mg}^{2+} + 2 \text{CO}_3^{2-} \rightarrow \text{CaMg}(\text{CO}_3)_2$	+15.45

Table 4: Experimental results for No. 840 series.

exper. No.	Temp. °C	Gypsum g	Na ₂ CO ₃ g	MgSO ₄ g	H ₂ O ml	pH		products
						begin.	end.	
a	25	6.15	6.42	1.24	520	9.85	9.14	A, CaD _{2.943}
b	25	6.15	6.42	2.48	520	9.40	8.85	A, MhK
c	25	6.15	6.42	4.95	520	9.40	8.85	N, A
d	40	6.15	6.42	1.24	520	9.72	9.06	QD _{2.894} , HM, A
e	40	6.15	6.42	2.48	520	9.35	8.70	QD _{2.877} , A, HM,
f	40	6.15	6.42	4.95	520	9.14	8.60	A, HM, QD _{2.894}

Note: Abbreviations see Table 2, MhK — monohydrocalcite CaCO₃·H₂O

ic probability. We calculated equilibrium constant values (from the Gibbs energies) for 11 reactions postulating either direct, or indirect syntheses of dolomite (Table 3). The data used for these thermodynamic calculations were obtained from the monographic volumes of Garrels & Christ (1965), Naumov et al. (1971) and Melnik (1972).

Three important conclusions can be drawn from these calculations:

1. The highest equilibrium constant corresponds to reaction No. 11. We postulate that the input of all components into the reaction are in ionic form. However, owing to distinct hydration properties of both ions, and especially of Mg²⁺ the reaction is unrealistic.

2. Most reactions in purely carbonate systems are thermodynamically improbable, while the systems with sulphate participation are much more probable.

3. The high thermodynamic probability of systems with soluble neutral molecules (CaCO₃⁰, MgCO₃⁰, MgSO₄⁰) is a remarkable feature.

In view of these conclusions our experimental work was focused on creating reaction conditions that would comply with the criteria stated on pps 140 and 141. A sulphate environment was established using gypsum and magnesium sulphate (reactions Nos. 8 to 10). To prepare soluble undissociated CaCO₃⁰ and MgSO₄⁰ molecules, we used our experience from the evaporite study, especially the preparation of evaporation experiments, when gypsum crystals formed, immediately after the solutions were mixed and after 6 hours of evaporation the gypsum was totally replaced by aragonite and Mg-calcite. We presuppose that dissolved CaCO₃⁰ and MgCO₃⁰ molecules form as a transitional product during the formation of crystalline CaCO₃ and MgCO₃·3H₂O on account of original gypsum and epsomite.

The first series of experiments conducted using these pre-conditions brought remarkable results (listed in Table 4). Nev-

ertheless, we assume that they are accidental, because the repeated experiments deviated to some extent from the original ones, especially from those conducted at 40 °C. Many carbonates formed within these systems, but the dolomite reflections are clearly visible on the X-ray records. The experiments lasted 14 days and the repetitions (841 series) took 10 more days. The results of repeated experiments, made at 40 °C differed, mainly in the order in which the minerals were represented in the products.

Experimental results in systems with changeable component vs. water ratios

In the next series of experiments we changed both the content of gypsum and the amount of magnesium sulphate and water. The water appeared to be crucial, because when its amount in a given system dropped, the d_{10.4} reflections of rhombohedral carbonates shifted toward lower values (more MgCO₃, Table 5).

We prepared for testing a mixture of solid basic materials — gypsum, epsomite (MgSO₄·7H₂O) and Na₂CO₃ in the amounts corresponding to molal ratios 1 : 1 : 2. The mixture was thoroughly stirred, ground in an agate mortar and constant amounts were then inserted into glass ampules. Water (as shown in Table 5) was then added. The ampules were then welded together and constantly stirred. They were kept for 7 days at a temperature of 40 °C. After this period the ampules were opened, and the pH of the suspension and X-ray diffractograms of the solids were measured. The results are listed in Table 5.

In the next series of experiments we changed the contents of gypsum and epsomite in the original materials. Calcite was the only mineral that formed in the presence of pure gypsum at 40 °C in systems similar to those of No. 868 of the experiment series, while hydromagnesite and magnesite formed in Mg systems.

Table 5: A review of results No. 868 series.

No of experim.	ml H ₂ O	pH	components	d-values (nm×10) of main lines
a	7	8.26	MgC, CaD	2.970, very weak 2.919
b	4	8.18	CaD, MgC	2.922, 2.988
c	2	7.79	CaD, CaD-QD	2.907, 2.943
d	1	undeterm.	CaD, C, HM	2.918, 3.035, 6.27
e	0.5	undeterm.	QD-MgD, MgC, HM	2.870, 2.990, 6.30

Table 6: A review of results No. 872 series.

No. of experim.	CaCl ₂ g	MgSO ₄ .7H ₂ O g	Na ₂ CO ₃ g	pH	ml H ₂ O	products d (nm×10) of main lines
a	0.30	0.28	0.24	8.01	6.07	CaD-QD _{2.904}
b	0.39	0.35	0.30	7.68	3.92	QD _{2.896} , MgC _{2.993}
c	0.48	0.44	0.38	6.83	2.42	QD _{2.896}
d	0.46	0.41	0.35	undet.	1.11	C _{3.044}
e	0.46	0.41	0.35	undet.	0.55	MgD _{2.854} , C _{3.010}

In the experiments in which CaCl₂ was used instead of gypsum the products were similar to those identified in previous sulphate-carbonate systems. The used components, their amounts and reaction results are listed in Table 6.

The experiments corresponding to the results listed in Tables 5 and 6 confirm that the solid matter/water ratio has a crucial effect upon the formation of rhombohedral CaMg carbonates. Some problems occurred in experiments Nos. 872d and 872e. Despite being similar, calcite formed in the former and Mg-dolomite + calcite in the latter. These anomalies occurred in samples with the addition of CaCl₂ in which minimal water was used. This feature developed because the CaCl₂, which we used in the reaction contained surplus constitutional water, thus, we had to use a concentrated solution in which the CaCl₂ content was analytically determined to exactly measure the amount of water in the reaction mixture.

Experimental results in systems with precise amount of water in the reaction environment at 40 °C

The results of previous experiments indicated that it is mainly the amount of water in the environment that influences the composition of the reaction products. Because not only the solid substances (CaSO₄.2H₂O, MgSO₄.7H₂O), but also solutions (saturated CaCl₂ solution) released water to the reactional environment we made calculations for each experiment separately to exactly determine the amounts of water. The solid matter/water ratio was expressed by solidus index Is, calculated according to the formula:

$$I_s = \frac{\text{solid matter (g)}}{\text{sum water (g)}} \times 100$$

The results of these experiments are listed in Table 7 and are shown graphically in Fig. 2. The graph illustrates how the d values of (10.4) reflections depend on the solidus index of rhombohedral metastable CaMg carbonates. At the same time the graph shows how a gradual thickening contributes to the formation of products from calcite to Mg-dolomite.

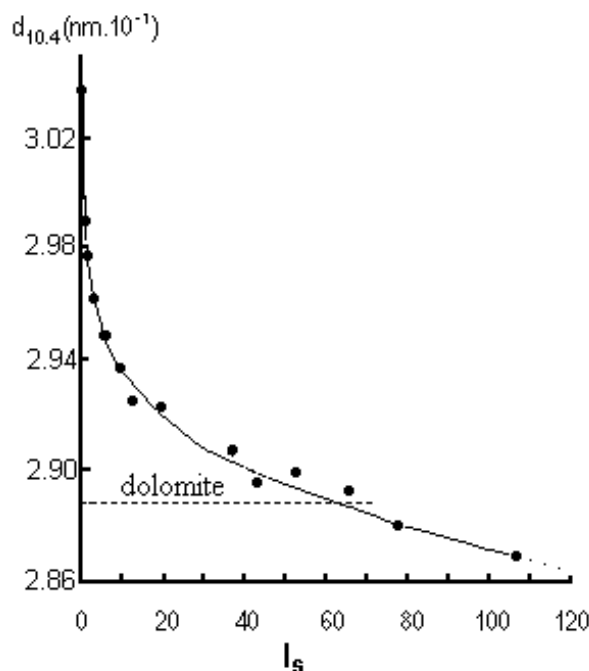


Fig. 2. Relationship between d_{10.4} reflexions from synthetic rhombohedral CaMg carbonates and solidus index.

Hydrothermal alteration of synthetic Ca-dolomite

According to Malinin (1970), calcite has minimal solubility in water at 150 °C. This information lead us to believe that it may be a key to the transition problem between unstable CaMg carbonate and stable minerals. Therefore, we made a series of tentative experiments with 4 synthetic carbonate mixtures of aragonite, Mg-calcite, Ca-dolomite and water emplaced the glass ampules, sealed and then exposed to elevated temperatures. After 11 days of exposition at 100 °C and 5 days of exposition at 180 °C we observed distinct changes in all but one sample (No. 831e): at 100 °C the Ca-dolomite was replaced by Q-dolomite and at 180 °C by calcite, as shows by the d values of (10.4) reflections in Table 8.

Table 7: Experimental results in system with exactly adjusted solid matter/water ratio.

No of experim.	solidus index Is	pH	products	d _{10.4} values in nm×10
868e	106.7	undeterm.	HM, A, MgD-QD, MgC	2.870, 2.990
874b	77.5	undeterm.	QD, MgC	2.881, 2.985
868d	65.4	undeterm.	HM, QD, CaD	2.893, 2.939
874c	52.6	undeterm.	QD	2.899
867d	43.2	7.52	QD, MgC	2.896, 2.976
868c	36.9	7.79	CaD-QD, CaD	2.907, 2.944
868b	19.7	8.18	HM, CaD, MgC	2.922, 2.988
866a	12.7	7.95	A, CaD	2.924, 2.933
874f	9.7	8.30	CaD, MgC	2.936, 2.979
866b	6.2	8.05	CaD, A	2.948
874g	5.6	8.50	CaD, A	2.947
866c	3.1	8.16	CaD-MgC, A	2.960, 2.972
866d	1.6	8.35	MgC, A	2.975
874i	0.9	8.94	MgC, A	2.988
866e	0.4	8.82	MgC, A	2.988
874j	0.2	8.62	MgC, A	3.004
879k	0.04	9.23	C	3.035

Note: Abbreviations see Table 2

Table 8: The results of hydrothermal alteration of synthetic Ca-dolomite and Mg-calcite.

Exp. No.	components of orig. sampl.	d _{10.4} nm×10	products 100 °C	d _{10.4} nm×10	products 180 °C	d _{10.4} nm×10
831a	A, CaD	2.94	A, D	2.90	A, C	3.05
831b	A, CaD	2.94	A, D	2.89	A, C	3.03
831c	A, MgC	2.97	A, D	2.90	A, C	3.04
831e	A, MgC	2.96	A, CaD	2.92	A, CaD	2.91

Note: Abbreviations see Table 2

Discussion

The results presented in the attached tables, as well as the diagram of relation solid matter/water clearly indicate that the entry of magnesium into the structure of rhombohedral CaMg carbonates not only depends on the substance concentration, but mainly on the water content in the reactional environment. Provided that a given environment contains enough Ca, Mg and CO₃ ions, rhombohedral carbonate minerals with chemical composition corresponding to calcite through Mg-calcite, Ca-dolomite, Q-dolomite to Mg-dolomite may form at relatively low temperatures. The formation of these individual substances at equal incipient concentrations of the mentioned compounds depends on the amount of available water. The lower the amount of water in relation to other compounds, the more Mg enters the structure of the newly formed carbonates. When the solidus index exceeds 65, not only the products chemically corresponding to ideal Q-dolomite (Ca₅₀Mg₅₀) are formed, but also the Mg richer members, such as Mg-dolomite (Ca₄₅₋₂₅Mg₅₅₋₇₅).

The mechanism of these processes is not yet fully understood. But a clue to the explanation in agreement with Usdowski's opinion (1994), may be due to the properties of the magnesium atom, or ion. Obviously, the entry of Mg into the crystal structures with calcium is prevented by a large number of water molecules that form a hydration envelope around the Mg²⁺ ion. The values of the heat of hydration clearly indicate how big the differences are between the hydration properties of Ca²⁺ and Mg²⁺ ions. For Ca²⁺ it is 1510 kJ.mol⁻¹, for Mg²⁺ 1828 kJ.mol⁻¹ (Gažo et al. 1974). It

seems probable that both, high salinity and increased temperatures, lower the hydration of Mg²⁺ ions to enable Mg to enter reactions with Ca, accompanied by the formation of mixed CaMg structures.

However, there is another important point which we have already mentioned in relation to thermodynamic calculations — the formation of nondissociated soluble CaCO₃⁰ and MgCO₃⁰ molecules. The transition of a chemical component from one solid mineral form into another may take place when transitional members form, such as the above mentioned undissociated molecules in the presence of water. As an example we note the change of gypsum into calcite in our experiments, when it seems probable that as soon as the gypsum dissolves, the Ca²⁺ ions react with available CO₃²⁻ ions to form undissociated CaCO₃⁰ molecules, from which first nuclei and then crystals of calcite form when the concentration reaches the required level. Should there be MgCO₃⁰ molecules that in similar way the mixed CaMg minerals would form. The possible participation of CaCO₃⁰ and MgCO₃⁰ molecules in reactions of carbonate formation are also cited by Brady et al. (1996) and Pokrovsky (1998).

Several remarkable features applicable to this problem were recorded during research into the kinetics of CaMg carbonate precipitation from water solutions (Babčan et al. 1992). From purely chloride Ca and Mg solutions (with molar Ca/Mg ratio 3:1) and from mixed chloride-sulphate solutions of a similar composition only calcite precipitated from two minutes to as much as 1 hour of reaction with CO₃²⁻ at temperatures of 5 °C and 25 °C (the amount of reacted Ca was 87 to 89 %). After 24 hours the only reaction product

was Mg-calcite (with 8 mol % MgCO_3), while the original calcite completely vanished. We cannot assume that Mg entered the solid structure of the original calcite, but we can assume that the original calcite dissolved and then reacted in the form of CaCO_3^0 with available MgCO_3^0 . The MgCO_3^0 molecules obviously form with a slow reaction time as the crystals with a carbonate Mg structure first appeared after 10 days. These kinetic experiments enabled us to see that to produce Mg-calcite the amount of Mg entering its structure depended on temperature. At 25 °C it was on average 8 mol % and at 50 °C it was already almost 20 mol %, although, these values indicate that the setting is equilibrated, as suggested before by Berner (1974 cit. in Drever 1982).

Another important pre-condition of CaMg carbonate formation is the pH value in the environment, which ranged in our experiments between 7.5 and 10. In an environment with a high salt content the dissociation of adequate compounds is reduced to correspond to pH values lower than those listed in Table 7. In dense systems ($I_s = 50-100$) the pH of the environment could not be measured.

Despite finding that some experiments made at 25 °C appeared promising (Table 2), we finally decided to use the temperature of 40 °C (± 2 °C) because firstly we expected a faster rate of reactions and secondly, because of similar processes taking place in nature at some localities (Persian Gulf etc.).

Most of our experimental results simulated the processes of CaMg carbonate precipitation from various systems, ranging from brines to strongly concentrated brines such as those of coastal lagoons (Persian Gulf, Bahamas, Qatar, Southern Australia etc.), sabkhas (Arabian Peninsula), soils (calcrusts, dolocrusts) and crusts covering historical buildings made of limestone.

Several data referring to this problem in the literature could not be confirmed by our experimental results. For instance, the assumption of De Boer (1977), Folk & Land (1975), Friedman & Sanders (1967), Hardie (1987), Kukul (1986), Leeder (1982), Lippmann (1973), Rosen et al. (1989), Tucker et al. (1990), Usdowski (1989, 1994), that a high Mg/Ca ratio is necessary to produce carbonates with a high content of MgCO_3 component could not be confirmed. In our experiments we obtained the products with various contents of CaCO_3 and MgCO_3 (Table 7) using an equal ratio between starting substances. However, we should note that the Mg/Ca ratio does not characterize given reaction conditions realistically. The Ca/Mg ratio corresponds to the initial content of Ca and Mg compounds and it changes immediately after the addition of CO_3^{2-} compounds into the system. Most of the calcium immediately reacts and the formation of CaCO_3 changes the real reaction environment to a completely different environment relative to the theoretical, or original environment.

To characterize the low temperature reaction environment we use the solidus index I_s , a value that can easily be calculated during laboratory experiments. For natural systems an adequate variable may be the value of total salinity, as confirmed, for instance, by the experiments of Erenburg (1961) and Glover & Sippell (1967) who obtained the richer MgCO_3 products in an environment with higher concentrations of NaCl during

the synthesis of CaMg carbonates. Kazanskij (1976) reports that in sediments from the Balchaš Sea the Ca-dolomite (according to Kazanskij protodolomite) appeared in depressions in which the salinity of water was 4.6–5.3 g/kg.

In the highly concentrated coastal lagoons, sabkhas etc., no environments with individual Ca^{2+} , Mg^{2+} , or CO_3^{2-} ions are expected to occur. They are present as undissociated molecules, molecule associates, hydrates etc. Therefore the calculations postulated by several authors, such as solubility calculations, equilibrium constants etc., cannot be made. For instance we do not use values of ionic strengths for the characterization of a medium.

Although, there are indications to explain the nature of this problem, the question of how the unstable CaMg carbonates change into stable ones with ordered structure, still remains unanswered. Some of specialists assume that the mentioned change is a matter of time (Purser et al. 1994). However, there is evidence that the unstable Mg-calcite with 20 to 40 mol % MgCO_3 remained unchanged in the Tertiary limestones of the Swiss Jura (Kübler 1958). On the other hand, another remarkable finding was the well ordered dolomite in the Coorong Holocene sediments (Rosen et al. 1989). Even more interesting was the find of stoichiometric transparent dolomite (besides Ca-dolomite) within the weathering crusts (patinas) on limestones used in historic buildings (Rodríguez-Navarro et al. 1997)

Remarkable there have also been results from experimental research into the recrystallization kinetics of synthetic CaMg carbonates (with 41.7 mol % MgCO_3 , in our terminology carbonates at the boundary between Ca-dolomite and Q-dolomite) at 50–200 °C reported by Malone et al. (1996). In the seawater-like solution a complete restructuring was not achieved even at 200 °C (a product developed with a maximum of 48.6 mol % MgCO_3). After 336 days some 30 % of the carbonate recrystallized at a temperature of 50 °C to become dolomite.

In addition we note that repeated X-ray analyses of randomly selected samples, stored in a dry place before the analysis, did not show any trace of changes even in samples stored for 18–20 years. It seems that a transport medium (water) is inevitably required to recrystallise unstable CaMg carbonates. If the unstable CaMg carbonate structures remain unchanged in the rocks for a long time (as in the case of Swiss Jurassic limestones), it may be that the original sediments were quickly lithified. As a result water is prevented from migration and various exchange reactions, including restructuring, could not take place.

Conclusions

On the basis of thermodynamical calculation and systematic studies of carbonate formation from various environments a dolomite-like carbonate was prepared. Synthesized dolomite ($\text{Ca}_{50}\text{Mg}_{50}$) does not show superstructural X-ray reflections and hence it was denominated as a Quasi-dolomite (Q-dolomite).

The results obtained at 40 °C indicate that the formation of rhombohedral CaMg carbonates depends on the solid matter/

water ratio (solidus index I_s). The higher the ratio, the more $MgCO_3$ enters into the carbonate structure. The results also confirm a gradual transition of these relationships from calcite, through Mg-calcite, Ca-dolomite and Q-dolomite (Quasi-dolomite) to Mg-dolomite ($Ca_{44}Mg_{56}$). When studying Ca-dolomite in the laboratory it was found to restructure into stable dolomite at 100 °C and into calcite at 180 °C.

References

- Babčan J. 1980: Die theoretische und experimentelle Modellierung des Entstehens von Magnesit in Evaporiten des Westkarpaten. *Geol. Zbor. Geol. Carpath.* 31, 65–74.
- Babčan J. 1984: Low temperature synthesis of dolomite. *Abstr. 27-th Internat. Geol. Congress*, Moskva, V, 10.
- Babčan J., Iró S. & Ševc J. 1992: Experimental study of carbonate formation kinetics in a Ca-Mg-CO₃-Cl systems at temperature of 25 °C. *Miner. Slovaca* 24, 1–7.
- Baron G. 1960: Sur la synthèse de la dolomie. Application au phénomène de dolomitisation. *Rev. Inst. Franç. Pétrol. Ann. Combust. Liquides* 15, 3–68.
- Brady P.V., Krumhansl J.L. & Papenguth I.W. 1996: Surface complexation clues to dolomite growth. *Geochim. Cosmochim. Acta* 60, 727–731.
- De Boer R.B. 1977: Stability of Ca-Mg carbonates. *Geochim. Cosmochim. Acta* 41, 265–270.
- Drever J.I. 1982: The geochemistry of natural waters. *Prentice-Hall*, Englewood Cliffs, New Jersey, 1–440.
- Erenburg G.B. 1961: Artificial mixed carbonates in the CaCO₃-MgCO₃ series. *Žurn. Strukt. Chimii* 2, 178–182.
- Folk R.L. & Land L.S. 1975: Mg/Ca ratio and salinity, two controls over crystallization of dolomite. *Bull. Amer. Assoc. Petrol. Geol.* 59, 60–68 (cit. in Hardie 1987).
- Friedman G.M. & Sanders J.E. 1967: Origin and occurrence of dolostones. Carbonate rocks, Part A. *Elsevier*, Amsterdam, 167–348.
- Garrels R.M. & Christ C.L. 1965: Solutions, Minerals, and Equilibria. Harper and Row, New York, 1–450.
- Gažo J. and col. 1974: General and inorganic chemistry. 2-nd Edit., *Alfa Bratislava-SNTL*, Praha, 1–808 (in Slovak).
- Glover E.D. & Sippell R.F. 1967: Synthesis of magnesium calcite. *Geochim. Cosmochim. Acta* 31, 603–613.
- Hardie L.A. 1987: Dolomitization: a critical view of some current views. *J. Sed. Petrology* 57, 166–183.
- Hsü J.K. 1967: Origin of dolomite in sedimentary sequences. *Mineral. Dep.* 2, 133–138.
- Kazanskij Ju.P. 1976: Sedimentology. *Izd. Nauka*, Novosibirsk, 1–272 (in Russian).
- Kukal Z. 1986: Elements of sedimentology. *Academia*, Praha, 1–325 (in Czech).
- Kübler B. 1958: Calcites magnésienne d'eau douce dans le Tertiaire supérieur du Jura neuchâtelois. *Eclogae Geol. Helv.* 51, 676–685 (Suisse).
- Leeder M.R. 1982: Sedimentology, Process and Product. *G. Allen and Univ. London, Boston, Sydney*, 1–439.
- Lippmann F. 1973: Sedimentary Carbonate Minerals. *Springer Verl.*, Berlin-Heidelberg-New York, 1–219.
- Lumsden D.N. 1979: Discrepancy between thin section and X-ray estimates of dolomite in limestones. *J. Sed. Petrology* 49, 429–436.
- Malinin S.D. 1970: An application of theory of strong electrolytes to the solubility of carbonates at high-temperature. *Geochimia* 540–551 (in Russian).
- Malone M.J., Baker B.A. & Burns S.J. 1996: Recrystallization of dolomite — An experimental study from 50–200 degrees. *Geochim. Cosmochim. Acta* 60, 2189–2207.
- Meľnik Ju.P. 1972: Handbook — Thermodynamic constants in the analysis of conditions for iron ores origin. *Naukovaja Dumka*, Kijev, 1–195 (in Russian).
- Naumann C.F. 1850: Lehrbuch der Geognosie, Bd. 1. *Verl. W. Engelmann*, Leipzig, 1–1000.
- Naumov G.B., Ryženko B.N. & Chodakovskij I.L. 1971: Handbook of thermodynamic values. *Atomizdat*, Moskva, 1–195 (in Russian).
- Oppenheimer C.H. & Master I.M. 1965: Transition of silicate and carbonate crystal structure by photosynthesis and metabolism. *Geol. Soc. Amer. Spec. Pap.* 76, 1–125.
- Pokrovsky O.S. 1998: Precipitation of calcium and magnesium carbonates from homogenous supersaturated solutions. *J. Crystal Growth* 186, 233–239.
- Purser B.H., Tucker M.E. & Zenger D.H. 1994: Problems, progress and future research concerning dolomites and dolomitization. Dolomites — A volume in honor of Dolomieu. *Spec. Publ. No-21 of the Intern. Assoc. of sedimentologist. Blackwell Sci. Publ.*, Oxford etc. 3–20.
- Reeder R.J. 1983: Crystallochemistry of trigonal carbonates. In: Reeder R.J. & Ribbe P.H.(Eds.): Carbonates, mineralogy and chemistry. *Min. Soc. Amer. Rev. Mineralogy* 3–61.
- Rodriguervarrio C., Sebastian E. & Rodriguergallego M. 1997: An urban model for dolomite precipitation — authigenic dolomite on weathering. *Sed. Geol.* 109, 1–11.
- Rosen M.R., Miser D.E., Starcher M.A. & Warren K.J. 1989: Formation of dolomite in the Coorong region, South Australia. *Geochim. Cosmochim. Acta* 53, 661–669.
- Tucker M.E., Wright V.P. & Dicson J.A.D. 1990: Carbonate sedimentology. *Blackwell Sci. Publ.*, Oxford etc., 1–482
- Uzdowski E. 1989: Synthesis of dolomite and magnesite at 60 °C in the system Ca-Mg-CO₃-Cl-H₂O. *Naturwissenschaften* 76, 374–375.
- Uzdowski E. 1994: Synthesis of dolomite and geochemical implications. *Spec. Publ. Int. Assoc. Sed.* 21, 345–360.