Synthesis of magnesian calcite at low temperatures and pressures

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Abstract—As one of the steps that lead to an understanding of the secretion of magnesian calcite in skeletal parts of marine organisms, the laboratory synthesis of the mineral from aqueous solutions was carried out at low temperatures and pressures. The conditions of the laboratory synthesis of magnesian calcites are shown in this paper. Magnesian calcites are precipitated from calcium bicarbonate solutions containing magnesium ions and certain organic materials such as organic acids, which are found in the body fluids of carbonate-secreting organisms, in various concentrations.

Most sedimentary carbonates are derived from the skeletal parts of calcareous marine organisms. These skeletons are composed of the minerals, calcite (magnesium-poor calcite), aragonite (always low in magnesium carbonate), and magnesian calcite (magnesium-rich calcite) (CHAVE, 1954; LOWENSTAM, 1954; KITANO, 1964). Magnesium carbonate in skeletal calcites is present as a solid solution between calcite and dolomite or magnesite (CHAVE, 1952; KITANO *et al.* 1959). And magnesian calcites and aragonite are unstable, relative to calcite, at low temperatures and pressures (CHAVE *et al.*, 1962; JANSEN and KITANO, 1963).

Considerable number of studies have been carried out in order to determine the physico-chemical factors controlling the formation of calcite* and aragonite from aqueous solutions (LIPPMANN, 1960; KITANO, 1962 a, b; KITANO and HOOD, 1962; SIMKISS, 1964), and the formation of calcites** and aragonite in skeletal materials (LOWENSTAM, 1954; CHAVE, 1954, 1962; WATABE and WILBUR, 1960; WILBUR, 1960; WILBUR and WATABE, 1963); however very little has been done on the mechanisms of the formation of magnesian calcites.

The distribution of magnesian calcites in the skeletal materials of calcareous marine organisms was described (CHAVE, 1954; PILKEY and HOWER, 1960; PILKEY and GOODELL, 1963; LOWENSTAM, 1961, 1963). Laboratory synthesis of this spectrum of minerals was accomplished only at high temperatures and pressures (HARKER and TUTTLE, 1955; GRAF and GOLDSMITH, 1955; GOLDSMITH, 1959; GOLDSMITH and HEARD, 1961).

* Magnesium-poor calcite.

** Magnesium-poor and -rich calcites.

One of the steps that lead to an understanding of the secretion of magnesium-rich calcite in skeletal parts of marine organisms is the laboratory synthesis of the mineral from aqueous solutions at low temperatures and pressures. This paper describes the conditions of the laboratory synthesis of magnesian calcites. Magnesian calcites are precipitated from calcium bicarbonate solutions containing magnesium ions and certain organic materials such as organic acids, which are found in the body fluids of carbonate-secreting organisms, in various concentrations.

EXPERIMENTAL

A calcium bicarbonate solution ($0.35\text{--}0.37\text{ g/l Ca}^{+2}$) was prepared by bubbling carbon dioxide gas for one day in calcium carbonate suspended distilled water. This was allowed to stand for thirty minutes, filtered, and bubbled with carbon dioxide gas for additional 2 hr.

A magnesium chloride solution (24 g/l Mg^{+2}) was prepared from reagent grade $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and distilled water.

Solutions of sodium or acid salts of citric, malic, pyruvic, succinic and chondroitin sulfuric acids, at a pH of 7.0 and with a concentration of 13.5 g/l , were prepared in distilled water.

The three solutions were mixed in various proportions, as shown in Tab. 1 and 2, put in Erlenmeyer flasks, plugged with cotton, and allowed to stand at a constant temperature for 2 to 8 weeks. Over this period of time the carbon dioxide gas gradually escaped and carbonate crystals precipitated. The pH of the solutions was measured at the beginning and the end of each experiment. At the end of each experiment the calcium concentration in the filtered solution was determined by adding hydrochloric acid and then boiling to remove carbon dioxide, and titration at a pH of 9.5–10.0 with EGTA standard solution using Zincon* as an indicator.

The mineralogy of the precipitated carbonate was determined by X-ray diffraction. Calcium in the carbonate was determined by EGTA titration and magnesium was determined by the color intensity measurement of the complex between magnesium ions and Thymolphthalein Complexone at a pH 9.5–10 (KANAMORI and KITANO, in press).

RESULTS AND DISCUSSION

A mother solution must contain magnesium ions for the precipitation of magnesian calcite, which is of calcitic lattice configuration.

Previous experiments, KITANO *et al.* (1962), showed that, in the absence of organic compounds, magnesium ions favor the precipitation of aragonite, which contains little magnesium in the lattice, from supersaturated calcium bicarbonate

* Zincon (2-carboxy-2'-hydroxy-5-sulphoformazyl benzene). Solution was prepared by dissolving 0.2 g in 5 ml of 0.1 N sodium hydroxide solution and diluted with distilled water to 100 ml.

solutions. Preliminary results, reported by KITANO and HOOD (1965), suggested that organic materials influenced this precipitation, and in some cases favored the formation of calcite, even in the presence of magnesium ions. This could accomplish the precipitation of magnesian calcite at low temperatures and pressures. The experimental results are shown in Tables 1 and 2, and in Fig. 2, 3, 4 and 5 based on the tables.

The values for the differences in spacing of (0114) reflection between the pure calcite and precipitated calcites were plotted against magnesium carbonate content as chemically determined in Fig. 1 on the basis of Table 1. The linear relationship between these variables indicates that magnesium carbonate is contained as a form of magnesian calcite.

The present experiments indicate (see Table 1) that sodium citrate and sodium malate favor the formation of magnesian calcite, probably by complexing calcium ions, reducing the precipitation rate of carbonate, giving a stable calcitic lattice configuration and causing a capture of magnesium in the calcitic lattice.

Fig. 1. The relation between magnesium carbonate content and interplanar spacing.

Further, an increase in concentration of both magnesium ions and these organic materials causes formation of a magnesium-rich calcite (see Fig. 2 and 3).

Table 2 shows that an increase in temperature causes an increase in the magnesium content of the calcite when sodium citrate, sodium pyruvate and sodium malate are added (see Fig. 4 and 5). Chondroitin sulfate and sodium succinate, at all studied temperatures and concentrations, allow primary aragonite precipitation

Fig. 2. MgCO₃ content of magnesian calcite formed from the Ca(HCO₃)₂ solution containing MgCl₂ and sodium citrate. 20±1°C.

Fig. 3. MgCO₃ content of magnesian calcite formed from the Ca(HCO₃)₂ solution containing MgCl₂ and sodium malate. 20±1°C.

Fig. 4. MgCO_3 content of magnesian calcite formed from the calcium bicarbonate mother solution (500 ml) containing MgCl_2 (Mg^{2+} , 400 mg/500 ml) and sodium citrate (citrate ions, 50–200 mg/500 ml).

Fig. 5. MgCO_3 content of magnesian calcite formed from the calcium bicarbonate mother solution (500 ml) containing MgCl_2 (Mg^{2+} , 400 mg/500 ml) and sodium malate (malate ions, 250–1000 mg/500 ml).

in the presence of magnesium ions, probably by having a little influence on the precipitation rate and the precipitation of polymorphic crystals of calcium carbonate (KITANO *et al.*, 1965).

While the magnesium carbonate content of magnesian calcites increases with increasing temperature and concentrations of magnesium ions and the organic compound in a mother solution, it differs with the kind of organic compound.

The immediate interpretations and the real mechanisms, which fit the present results, have not been determined as yet. However, it can be said that the organic molecules, favoring the formation of magnesian calcite, complex calcium ions, gradually release the ions* and reduce the precipitation rate of carbonate. At this point, it is noted that the amounts of organic molecules such as citrate, malate and pyruvate are very small as compared with the amounts of calcium and magnesium ions as seen from Tables 1 and 2.

It was reported that the magnesium carbonate concentration in skeletal magnesian calcites of marine organisms increases with increasing temperature and salinity of sea water, and varies with the phylogenetic level of the organism (CHAVE, 1954; PILKEY *et al.*, 1960, 1963; LOWENSTAM, 1961, 1963).

If we can consider that the increase in salinity means an increase in the concentration of magnesium ions, and that a biological group or species can be charac-

* No microorganisms occurred in the solutions.

terized by a metabolic cycle involving organic compounds, in other words, by the composition and concentration of organic materials in a body fluid, the present laboratory results seem to have some analogy to the observational facts of natural calcareous marine organisms concerning the conditions of magnesian calcite formation.

Table 1. Formation of magnesian calcite in

Composition of mother solution								
at the start								
Ca(HCO ₃) ₂		MgCl ₂		Organic material		org. radicle	distilled	pH
ml	Ca ²⁺ mg	ml	Mg ²⁺ mg	material	ml	mg	water ml	
500	189	3.3	200	Na-Citrate	0.4	50	22	6.19
"	"	"	"	"	0.8	100	21	6.18
"	"	"	"	"	1.6	200	20	6.19
"	"	"	"	"	2.4	300	19	6.18
"	"	"	"	"	4	500	18	6.18
"	"	"	"	"	8	1000	14	6.17
"	"	"	"	"	12	1500	10	6.17
"	"	6.6	400	"	2.4	300	16	6.20
"	"	"	"	"	4	500	14	6.19
"	"	"	"	"	8	1000	10	6.19
"	"	"	"	"	12	1500	6	6.18
"	"	10	600	"	0.4	50	15	6.19
"	"	"	"	"	0.8	100	14	6.17
"	"	"	"	"	1.6	200	13	6.15
"	"	"	"	"	2.4	300	12	6.15
"	"	"	"	"	4	500	11	6.10
"	"	"	"	"	8	1000	7	6.10
"	"	"	"	"	12	1500	3	6.10
"	"	13.2	800	"	0.8	100	11	6.02
"	"	"	"	"	2.4	300	9	6.02
"	"	"	"	"	4	500	8	6.02
"	"	"	"	"	8	1000	4	6.02
"	"	"	"	"	12	1500	0	6.02
500	189	3.3	200	Na-malate	0.8	100	21	6.10
"	"	"	"	"	2.4	300	19	6.17
"	"	"	"	"	4	500	18	6.10
"	"	"	"	"	8	1000	14	6.10
"	"	"	"	"	12	1500	10	6.12
"	"	6.6	400	"	0.8	100	18	6.00
"	"	"	"	"	2.4	300	15	6.02
"	"	"	"	"	4	500	14	6.00
"	"	"	"	"	8	1000	10	6.00
"	"	"	"	"	12	1500	6	6.00
"	"	10	600	"	0.8	100	14	6.15
"	"	"	"	"	2.4	300	12	6.10
"	"	"	"	"	4	500	11	6.05
"	"	"	"	"	8	1000	7	6.13
"	"	"	"	"	12	1500	3	6.10
"	"	13.2	800	"	0.8	100	11	6.10
"	"	"	"	"	2.4	300	9	6.05
"	"	"	"	"	4	500	8	6.05
"	"	"	"	"	8	1000	4	6.01
"	"	"	"	"	12	1500	0	6.00

The data which the authors present should stimulate further work, which may lead eventually to a greater understanding of the biological system.

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$\text{Ca}(\text{HCO}_3)_2$ - MgCl_2 -organic material system at $20 \pm 1^\circ\text{C}$

Carbonate formed during a 52-day period							
at the end (on the 52th day)	crystal form		MgCO ₃ content determined chemically $\frac{\text{MgCO}_3 \times 100}{\text{CaCO}_3 + \text{MgCO}_3}$ % by weight		angle of diffraction $^\circ\theta$	lattice distance $d(\text{\AA})$	$\frac{\Delta d}{d(\text{calcite})}$ (3.037) $-\frac{\Delta d(\text{sample})}{\text{\AA}}$
pH	Ca ²⁺ mg	calcite %	aragonite %				
8.65	61	100	0	3.8	14.779	3.022	0.015
8.61	72	"	"	3.8	14.776	3.023	0.014
8.64	79	"	"	4.7	14.786	3.021	0.016
8.69	79	"	"	4.8	14.790	3.020	0.017
8.70	83	"	"	4.8	14.805	3.017	0.020
8.75	97	"	"	4.8	14.812	3.016	0.021
8.88	113	"	"	5.3	14.812	3.016	0.021
8.65	82	"	"	6.7	14.819	3.014	0.023
8.68	92	"	"	7.3	14.841	3.010	0.027
8.72	100	"	"	8.2	14.879	3.002	0.035
8.80	115	"	"	9.2	14.890	3.000	0.037
8.62	76	"	"	8.4	14.862	3.005	0.032
8.62	81	"	"	8.2	14.867	3.044	0.033
8.60	86	"	"	9.0	14.880	3.002	0.035
8.62	94	"	"	9.2	14.884	3.001	0.036
8.66	101	"	"	9.0	14.889	3.001	0.036
8.70	117	"	"	10.8	14.937	2.990	0.047
8.84	135	"	"	11.5	14.950	2.988	0.049
8.58	80	"	"	9.3	14.891	3.000	0.037
8.56	93	"	"	10.5	14.915	2.995	0.042
8.62	108	"	"	10.3	14.937	2.990	0.047
8.68	131	"	"	12.5	14.977	2.983	0.054
8.75	149	"	"	12.0	14.959	2.987	0.050
8.60	48	100	0	3.4	14.802	3.017	0.020
8.65	48	"	"	4.4	14.800	3.018	0.019
8.67	52	"	"	4.3	14.791	3.020	0.017
8.61	68	"	"	4.8	14.837	3.010	0.027
8.55	89	"	"	5.6	14.821	3.014	0.023
8.58	59	"	"	5.0	14.851	3.008	0.029
8.59	64	"	"	5.0	14.850	3.008	0.029
8.50	72	"	"	6.6	14.850	3.008	0.029
8.68	78	"	"	7.2	14.864	3.006	0.031
8.70	78	"	"	8.1	14.864	3.003	0.031
8.59	65	"	"	7.2	14.856	3.008	0.029
8.50	73	"	"	8.1	14.867	3.004	0.030
8.54	75	"	"	8.7	14.879	3.002	0.035
8.70	82	"	"	9.0	14.912	2.993	0.041
8.72	100	"	"	9.7	14.936	2.990	0.047
8.40	42	43	57	8.3 (in calcite portion)	14.889	3.001	0.036
8.50	68	88	12	9.3 (")	14.894	3.000	0.037
8.60	69	90	10	9.5 (")	14.912	2.996	0.041
8.68	74	89	11	10.0 (")	14.939	2.990	0.047
8.72	70	95	5	10.3 (")	14.937	2.990	0.047

Table 2. Formation of magnesian calcite in $\text{Ca}(\text{HCO}_3)_2$ - MgCl_2 -organic material system at various temperatures

Temp. °C	Composition of mother solution						Formed carbonate				
	at the start					at the end*			crystal form		MgCO ₃ content determined chemically MgCO ₃ × 100 (CaCO ₃ + MgCO ₃) % by weight
	Ca(HCO ₃) ₂	MgCl ₂	material	Organic material		pH	pH	Ca ²⁺ mg			
	ml	Ca ²⁺ mg		Mg ²⁺ mg	radicle of organic material mg						
5	500	198	400	Na-citrate	50	6.09	8.18	83	100	0	4.3
5	"	"	"	"	100	6.10	8.25	89	100	0	5.0
5	"	"	"	"	200	6.10	8.25	96	100	0	6.4
20	"	"	"	"	50	6.10	8.10	68	100	0	6.0
20	"	"	"	"	100	6.10	8.06	75	100	0	7.1
20	"	"	"	"	200	6.10	8.74	81	100	0	7.8
30	"	"	"	"	50	6.10	8.85	108	100	0	6.7
30	"	"	"	"	100	6.10	8.90	99	100	0	7.2
30	"	"	"	"	200	6.10	8.97	118	100	0	8.5
5	"	"	"	Na-pyruvate	100	6.10	8.10	78	100	0	4.5
5	"	"	"	"	250	6.10	8.20	83	100	0	6.0
5	"	"	"	"	500	6.10	8.25	94	100	0	6.1
20	"	"	"	"	100	6.10	8.35	43	40	60	5.0
20	"	"	"	"	250	6.10	8.00	61	100	0	6.9
20	"	"	"	"	500	6.10	8.00	69	100	0	6.8
30	"	"	"	"	100	6.10	8.60	101	15	85	5.0 in calcite part
30	"	"	"	"	250	6.10	8.64	87	60	40	8.2
30	"	"	"	"	500	6.10	8.82	93	100	0	8.2
5	"	"	"	Na-malate	250	6.10	8.25	83	100	0	5.7
5	"	"	"	"	500	6.10	8.25	91	100	0	5.7
5	"	"	"	"	1000	6.10	8.32	92	100	0	7.6
20	"	"	"	"	250	6.10	8.08	64	99	1	7.7
20	"	"	"	"	500	6.10	7.95	64	98	2	10.0
20	"	"	"	"	1000	6.10	8.10	64	98	2	9.6
30	"	"	"	"	250	6.10	8.70	101	90	10	8.5
30	"	"	"	"	500	6.10	8.84	90	99	1	10.0
30	"	"	"	"	1000	6.10	8.93	172	99	1	9.8
5	"	"	"	chondroitin	500	6.10	7.98	45	0	100	0.75
5	"	"	"	sulfate	800	6.14	8.02	43	0	100	1.1
5	"	"	"	"	1200	6.13	7.97	46	5	95	0.62
20	"	"	"	"	500	6.10	8.35	41	0	100	0.58
20	"	"	"	"	800	6.15	8.25	43	0	100	0.47
20	"	"	"	"	1200	6.14	8.45	77	0	100	0.74
30	"	"	"	"	500	6.10	8.52	89	0	100	0.35
30	"	"	"	"	800	6.15	8.50	80	0	100	0.40
30	"	"	"	"	1200	6.15	8.00	63	0	100	0.77
5	"	"	"	Na-succinate	500	6.10	7.95	40	0	100	0.35
5	"	"	"	"	800	6.15	8.00	38	0	100	0.60
5	"	"	"	"	1200	6.13	8.00	41	0	100	0.42
20	"	"	"	"	500	6.10	8.30	38	0	100	0.45
20	"	"	"	"	800	6.15	8.25	38	0	100	0.40
20	"	"	"	"	1200	6.15	8.30	42	0	100	0.40
30	"	"	"	"	500	6.10	8.35	77	0	100	0.80
30	"	"	"	"	800	6.15	8.30	73	0	100	0.50
30	"	"	"	"	1200	6.14	8.01	58	0	100	0.90

* Carbonate samples were precipitated at 5°C during a 71-day period, at 20°C during a 44-day period, and at 30°C during a 16-day period.

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