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CONDITIONS CONTROLLING THE CRYSTAL FORM OF CALCIUM CARBONATE MINERALS (I)

(On the Influences of the Temperature and the Presence of Magnesium Ion)

By

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(With 1 Table and 4 Figures)

Contribution from the Department of Geology and Mineralogy,
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Introduction

The conditions controlling the crystal form of calcium carbonate minerals, abundant in hot springs regions, molluscs shells, ore deposits etc. are not only an important subject in crystal chemistry, but also afford important data to geology and mineralogy in thinking of the factors forming strata, etc.

Calcium carbonate is one of the remarkable examples of polymorphism; its crystal forms are vaterite, aragonite, calcite and α-calcite.

Among those four forms α-calcite is stable only above 1000°C[1], whilst vaterite being formed at low temperature, is extremely unstable[2].

Calcite is the stable form of calcium carbonate at the temperatures and pressures encountered near the surface of the earth, while aragonite formed under these same conditions is a metastable form. According to JAMIESON's recent work[3] the transition of aragonite into calcite is thermodynamically possible at ordinary temperatures. This transition has been early reported by ROSE[4] for aragonite precipitate in the laboratory and left in contact with the solution. But another experiment confirmed that no transition occurs even in the case of their contact existence without solution, which suggests that the transition may be very slow in dry state.

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Experiments have been carried out by several investigators to discover the factors which govern the deposition of calcite and aragonite. But the conditions of these experiments5) differ from those accompanying cave or hot spring deposition to such an extent that it seems unsafe to assume that the same factors control cases, with the exception of Murray's work6) only.

The object of this investigation is to discover what are the effective factors controlling the form of calcium carbonate minerals in hot spring deposition.

Apparatus

The apparatus shown in Fig. 1 is made of hard glass. It is designed to make the ammonium carbonate solution and the calcium chloride solution flow very slowly into the reaction vessel at a constant velocity.

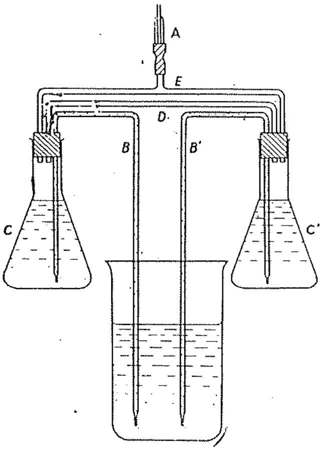


Fig. 1

Apparatus of reaction vessel

A is a capillary tube conditioning respectively the air in B and B' siphons, C and C' 100 cc Elenmeyer's flasks, and D a glass tube balancing up for E.

The reaction vessel is a 500 cc hard glass beaker covered with a watch glass to keep the vapourization loss at the least.

The large glass beaker was filled with 400 cc of distilled water, and a little magnesium chloride was added if necessary, then was set in a thermostat. When a constant temperature had been attained 100 cc of 0.5 N ammonium carbonate solution in C and 100 cc of 0.5 N calcium chloride solution in C' were allowed to flow slowly at the speed of about 20 cc/hr. into the beaker to diffuse with each other and gradually to form crystals of calcium carbonate. All chemicals used were the guaranteed reagents of Katayama Chemical Co..

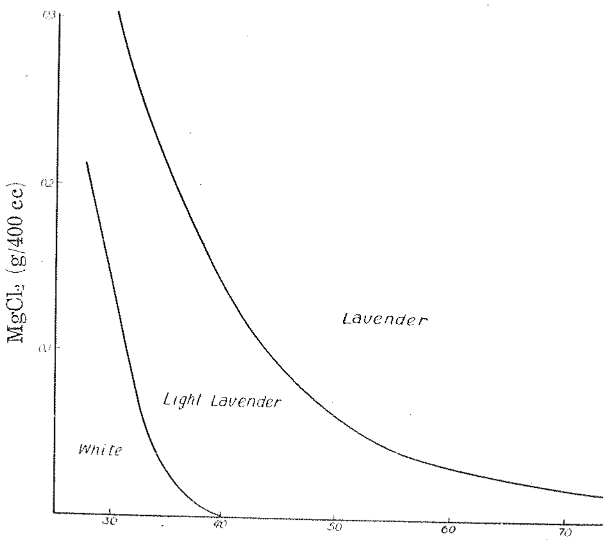
X-ray examinations and MEYGEN's reactions

Every sample of calcium carbonate which was precipitated in the reaction beaker at different temperatures was tested by Meygen's reaction and by Debye-Scherrer's method. The results are shown in Table 1.

No critical data for MEYGEN's reaction could be found in previous records, therefore the writers found it necessary to seek for a suitable condition through some experiments. It is as follows:—

Two cc of 0.1 N $Co(NO_3)_2$ solution are added to 0.2 g of each sample, then are heated to boil and are filtered at once. The color of the residue was examined after being washed with water. It was white in the calcite case but lavender in aragonite case, though in the former case it would become sky-grey when kept boiling over a minute.

The results for the MEYGEN's reaction of samples are shown diagramatically in fig. 2, where the abscissa is the crystallizing temperature in °C and the ordinate is the quantity of magnesium chloride in g. added to the reaction vessel.



Temperature °C

Fig. 2 Diagram of MEYGEN's reaction

The Norelco spectrometer (Cu Kα 1.54 Å) is also applied, determining the former case. The resuls of the data are shown in Fig. 3 and Fig. 4. The last column in figures is each result for natural calcite and aragonite

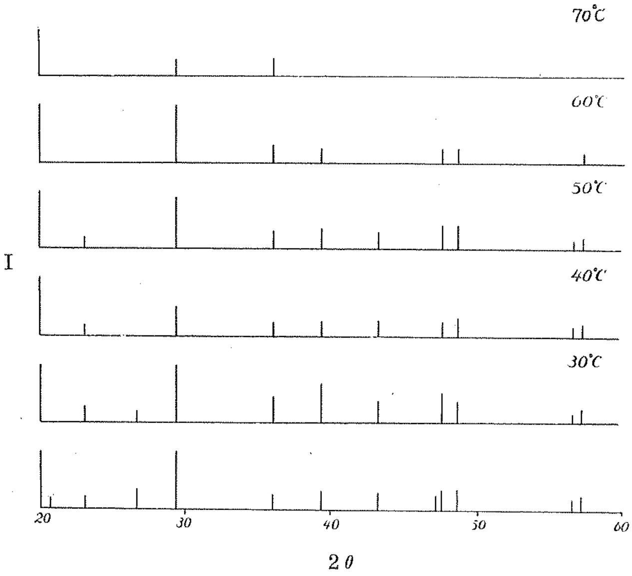


Fig. 3 X-ray diffraction patterns of calcite crystallizing in various temperatures and that of natural calcite.

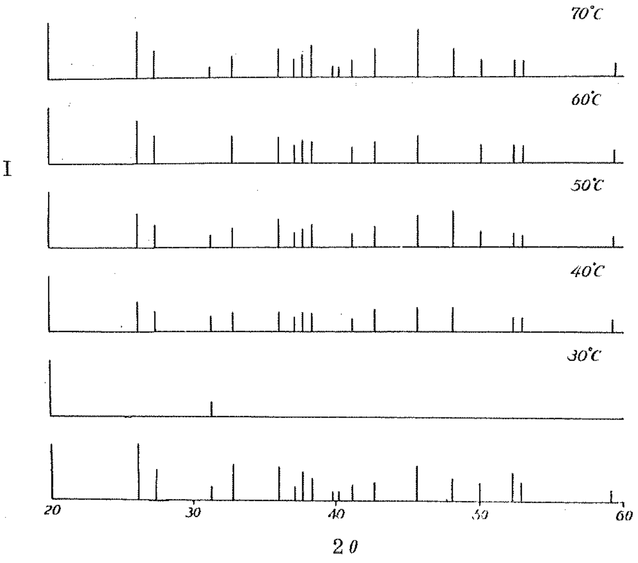


Fig. 4 X-ray diffraction patterns of aragonite crystallizing in various temperatures and that of natural aragonite.

Summary

It is evident from the results shown in Table 1 and Figs. 2–4, that the crystallizing temperature and the co-existing quantity of magnesium ion is concerned with the determination of the crystal forms. When no magnesium ion exists, calcium carbonate is found almost entirely in calcite form under 30°C, and comes to be found more and more in aragonite form as the temperature increases until it is found almost altogether in aragonite form at 70°C.

At the same temperatures calcium carbonate is found and increasingly in aragonite form with increase of the co-existing quantity of magnesium chloride.

The effect of the co-existence of magnesium ion is clearly observable even as the rate of about 0.3 g/l as magnesium chloride at 30°C. Quantitative experiment on the conditions still remains to be performed.

Acknowledgements

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TABLE

Sample Number						21			23			26		
Flow Velocity of Reagents (cc/hr)						20			20			20		
Temperature (°C)						30.0			30.0			30.0		
Concentration of $(NH_4)_2CO_3$						0.5			0.5			0.5		
Concentration of $CaCl_2$						0.5			0.5			0.5		
$MgCl_2$ added in Reaction Vessel						—			0.05			0.15		
Results of Meygen's Reaction									W			lL		
Calcite			Aragonite											
θ	d	*I*	*θ*	d	*I*	*θ*	d	*I*	*θ*	d	*I*	*θ*	d	*I*
10.37	4.29	2				10.26	4.33		10.37	4.29		10.26	4.33	
11.52	3.87	2				11.51	3.87		11.43	3.88		11.51	3.87	
			13.10	3.40	10	13.14	3.39					13.14	3.39	
13.24	3.36	3												
			13.71	3.25	5									
14.72	3.04	10				14.77	3.03		14.77	3.03		14.77	3.03	
			15.70	2.85	2									
			16.46	2.72	7									
18.00	2.49	3				17.79	2.52		17.87	2.51		17.96	2.50	
			18.06	2.49	6									
			18.63	2.42	3									
			18.94	2.38	5									
			19.22	2.34	4	19.43	2.32							
19.73	2.29	3							19.51	2.30		19.59	2.30	
			19.91	2.26	2									
			20.15	2.24	2									
			20.63	2.19	3									
			21.40	2.11	3	21.47	2.11		21.47	2.11		21.47	2.11	
21.61	2.09	3												
			22.85	1.99	7									
23.62	1.93	2				26.59	1.93		23.59	1.93		23.59	1.93	
23.83	1.91	3												
			24.11	1.89	4									
24.33	1.87	3				24.24	1.88		24.24	1.88		24.24	1.88	
			25.00	1.82	3									
			26.16	1.75	5									
			26.47	1.73	3									
28.34	1.63	2				28.30	1.63							
28.71	1.61	2				28.72	1.61		28.60	1.61		28.60	1.61	
			29.62	1.56	2									
30.40	1.52	2				30.19	1.53		30.19	1.53		30.15	1.54	
32.36	1.44	2				32.08	1.45		32.08	1.45		32.16	1.45	
32.82	1.42	2				32.73	1.43		32.73	1.43				

W ··· White lL ··· light Lavender L ··· Lavender

1

24 *			25			20			17			16		
20			20			20			20			20		
30.0			30.0			40.0			40.0			40.0		
0.5			0.5			0.5			0.5			0.5		
0.5			0.5			0.5			0.5			0.5		
0.2			0.3			——			0.05			0.1		
1L			1L			1L			1L			1L		
θ	d	I	θ	d	I	θ	d	I	θ	d	I	θ	d	I
			10.26	4.33		10.28	4.31							
11.52	3.87	2	11.51	3.87					11.34	3.92		11.43	3.88	
									13.06	3.41				
13.24	3.36	1	13.14	3.39		13.30	3.35							
14.72	3.04	10	14.77	3.03		14.77	3.03		14.77	3.03		14.61	3.06	
15.70	2.85	1				15.59	2.87							
18.00	2.49	4	17.96	2.50		12.87	2.51		17.96	2.50		17.87	2.51	
19.73	2.29	6				19.59	2.30					19.67	2.30	
			21.47	2.11		21.47	2.11		21.47	2.11		21.38	2.11	
21.61	2.09	3												
			23.59	1.93		23.59	1.93		23.59	1.93		23.59	1.93	
23.83	1.91	5												
24.33	1.87	3	24.24	1.88		24.24	1.88		24.24	1.88		24.24	1.88	
28.34	1.63	1												
28.71	1.61	2	28.60	1.61		28.60	1.61							
			30.30	1.53		30.30	1.53							
			32.73	1.43										

TABLE 1

Sample Number						18*			19			15		
Flow Velocity of Reagents (cc/hr)						20			20			20		
Temperature °C						40.0			40.0			50.0		
Concentration of $(NH_4)_2CO_3$						0.5			0.5			0.5		
Concentration of $CaCl_2$						0.5			0.5			0.5		
$MgCl_2$ added in Reaction Vessel						0.2			0.3			0.05		
Results of Meygen's Reaction						L			L			L		
Calcite			Aragonite											
θ	d	I	θ	d	I	θ	d	I	θ	d	I	θ	d	I
10.37	4.29	2							10.28	4.31				
11.52	3.87	2				11.52	3.87	3	11.51	3.87		11.59	3.85	
			13.10	3.40	10	13.10	3.40	7	13.06	3.41		13.06	3.41	
13.24	3.36	3												
			13.71	3.25	5	13.71	3.25	5						
14.72	3.04	10				14.72	3.04	10	14.77	3.03		14.77	3.03	
			15.70	2.85	2	15.70	2.85	4				15.67	2.86	
			16.46	2.72	7	16.46	2.72	5				16.99	2.71	
18.00	2.49	3				18.00	2.49	5	17.96	2.50				
			18.06	2.49	6	18.06	2.49	5				18.04	2.49	
			18.63	2.42	3	18.63	2.42	3						
			18.94	2.38	5	18.94	2 38	4						
			19.22	2.34	4	19.22	2.34	4						
19.73	2.29	3				19.73	2.29	5	19.67	2.30		19.76	2.28	
			19.91	2.26	2									
			20.15	2.24	2									
			20.63	2.19	3	20.63	2.19	3						
			21.40	2.11	3	21.40	2.11	5	21.47	2.11				
21.61	2.09	3				21.61	2.09	5				21.63	2.09	
			22.85	1.99	7	22.85	1.99	6				23.02	1.97	
23.62	1.93	2							23.59	1.93				
23.83	1.91	3				23.83	1.91	4				23.80	1.91	
			24.11	1.89	4	24.11	1.89	6						
24.33	1.87	3				24.33	1.87	6	24.24	1.88				
			25.00	1.82	3	25.00	1.82	3						
			26.16	1.75	5	26.16	1.75	3						
			26.47	1.73	3	26.47	1.73	3						
28.34	1.63	2				28.34	1.63	3						
28.71	1.61	2				28.71	1.61	4						
			29.62	1.56	2	29.62	1.56	2						
30.40	1.52	2												
32.36	1.44	2												
32.82	1.42	2												

(continued)

13			12 *			14			30			31		
20			20			20			20			20		
50.0			50.0			50.0			60.0			60.0		
0.5			0.5			0.5			0.5			0.5		
0.5			0.5			0.5			0.5			0.5		
0.1			0.2			0.3			——			0.05		
L			L			L			lL			L		
θ	d	*I*	*θ*	d	*I*	*θ*	d	*I*	*θ*	d	*I*	*θ*	d	*I*
11.59	3.85		11.52	3.87	2	11.59	3.85		11.51	3.87		11.51	3.87	
13.14	3.39		13.10	3.40	4	13.14	3.39		12.98	3.43		12.98	3.43	
			13.71	3.25	3									
14.77	3.03		14.72	3.04	10	14.77	3.03		14.69	3.04		14.77	3.03	
			15.70	2.85	1									
16.99	2.71		16.46	2.72	2	16.99	2.71		16.57	2.71		16.57	2.71	
			18.00	2.49	3				17.96	2.50				
18.04	2.49		18.06	2.49	3	18.04	2.49					18.04	2.49	
			18.63	2.42	2									
			18.94	2.38	2									
			19.22	2.34	3									
			19.73	2.29	4	19.76	2.28		19.76	2.28		19.76	2.28	
			20.63	2.19	2									
			21.40	2.11	2				21.47	2.11				
21.63	2.09		21.61	2.09	3	21.63	2.09					21.55	2.10	
23.02	1.97		22.85	1.99	4				22.86	1.99		22.86	1.99	
			23.62	1.93	2				23.59	1.93		23.59	1.93	
23.91	1.90		23.83	1.91	5	23.83	1.91							
			24.11	1.89	5									
			24.33	1.87	5				24.24	1.88		24.24	1.88	
			25.00	1.82	2									
			26.16	1.75	2									
			26.47	1.73	2									
			28.34	1.63	2									
			28.71	1.61	2									
			29.62	1.56	1									

TABLE 1

Sample Number						27			28 *			32		
Flow Velocity of Reagents (cc/hr)						20			20			25		
Temperature (°C)						60.0			60.0			70.0		
Concentration of $(NH_4)_2CO_3$						0.5			0.5			0.5		
Concentration of $CaCl_2$						0.5			0.5			0.5		
$MgCl_2$ added in Reaction Vessel						0.1			0.2			——		
Results of Meygen's Reaction						L			L			L		
Calcite			Aragonite											
θ	d	*I*	θ	d	*I*	θ	d	*I*	θ	d	*I*	θ	d	*I*
10.37	4.29	2												
11.52	3.87	2				11.51	3.87							
			13.10	3.40	10	13.14	3.39		13.10	3.40	3	12.98	3.43	
13.24	3.36	3										13.47	3.31	
			13.71	3.25	5				13.71	3.25	2			
14.72	3.04	10				14.77	3.03		14.72	3.04	10	14.53	3.07	
			15.70	2.85	2									
			16.46	2.72	7				16.46	2.72	2	16.41	2.73	
18.00	2.49	3				17.96	2.50		18.00	2.49	2	17.96	2.50	
			18.06	2.49	6				18.06	2.49	2			
			18.63	2.42	3				18.63	2.42	1			
			18.94	2.38	5				18.94	2.38	2.5	18.97	2.37	
			19.22	2.34	4				19.22	2.34	2.5			
19.73	2.29	3				19.67	2.30		19.73	2.29	1			
			19.91	2.26	2									
			20.15	2.24	2									
			20.63	2.19	3				20.63	2.19	1	20.49	2.20	
			21.40	2.11	3	21.47	2.11		21.40	2.11	1	21.38	2.11	
21.61	2.09	3												
			22.85	1.99	7				22.85	1.99	2	22.77	1.99	
23.62	1.93	2				23.59	1.93							
23.83	1.91	3							23.83	1.91	1			
			24.11	1.89	4				24.11	1.89	1	24.00	1.90	
24.33	1.87	3				24.24	1.88		24.33	1.87	1			
			25.00	1.82	3				25.00	1.82	1			
			26.16	1.75	5				26.16	1.75	1			
			26.47	1.73	3				26.47	1.73	1			
28.34	1.63	2												
28.71	1.61	2							28.71	1.61	1			
			29.62	1.56	2				29.62	1.56	1			
30.40	1.52	2												
32.36	1.44	2												
32.82	1.42	2												

(continued)

33			37			34 ※			38			35		
25			25			25			25			25		
70.0			70.0			70.0			70.0			70.0		
0.5			0.5			0.5			0.5			0.5		
0.5			0.5			0.5			0.5			0.5		
0.1			0.15			0.2			0.25			0.3		
L			L			L			L			L		
θ	d	*I*	θ	d	*I*	θ	d	*I*	θ	d	*I*	θ	d	*I*
12.98	3.43		12.98	3.43		13.10	3.40	10	12.98	3.43		12.98	3.43	
13.47	3.31													
			13.55	3.29		13.71	3.25	6	13.55	3.29		13.55	3.29	
14.53	3.07		14.69	3.04		14.72	3.04	5	14.69	3.04		14.69	3.04	
15.51						15.70	2.85	2						
16.41	2.73		16.45	2.72		16.46	2.72	5	16.45	2.72		16.45	2.72	
12.87	2.51		18.04	2.49		18.00	2.49	5	18.01	2.49		17.96	2.50	
						18.06	2.49	5						
						18.63	2.42	3						
18.97	2.37					18.94	2.38	4						
			19.18	2.34		19.22	2.34	6	19.18	2.34		19.18	2.34	
						19.91	2.26	2						
						20.15	2.24	2						
20.49	2.20		20.49	2.20		20.63	2.19	3	20.49	2.20		20.55	2.20	
21.38	2.11		21.30	2.12		21.40	2.11	5	21.30	2.12		21.47	2.11	
22.80	1.99		22.86	1.99		22.85	1.99	10	22.86	1.99		22.86	1.99	
24.00	1.90		24.20	1.88		24.11	1.89	6						
									24.24	1.88		24.24	1.88	
						25.00	1.82	3						
						26.16	1.75	3						
						26.47	1.73	3						
						29.62	1.56	2						