The State of a Small Amount of Magnesium Contained in Calcareous Shells

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(Received March 23, 1959)

The distribution of magnesium in calcareous parts of marine organisms was studied by K. E. Chave; he listed the factors which controlled distribution of magnesium in the calcareous skeletal formation of marine organisms[1]. He was also the first to succeed in determining the state of magnesium by using X-ray diffraction technique. The magnesium content of the sample in his study was from 2 to 16% $MgCO_3$ in weight. He concluded that magnesium carbonate was present as a solid solution of calcite and dolomite[**,2]. With his own X-ray diffraction technique, however, Chave was not able to determine the state of magnesium, when the content was more than 16% or less than 2% $MgCO_3$. There are a large number of calcareous shells having a magnesium carbonate content less than 2%. One of the authors, Kitano, was the first to devise a new method for determining the state of a small amount of magnesium contained in calcium carbonate deposits from hot springs, as reported in earlier papers[5-7]. This technique was called the "Dissolution Method". In the present paper the same method is applied for calcareous shells. The process greatly simplifies the determination of the state of magnesium in calcareous shells.

Principle of Dissolution Method

As to the state of magnesium*** in calcareous shells or organisms, there are only three possible forms, magnesium carbonate, dolomite and a solid solution of calcite and dolomite. When the authors closely examine the three forms from the crystallographic point of view, magnesium carbonate can not be expected, and consequently there are only two forms, dolomite and a solid solution, to be determined. When carbon dioxide gas is passed into a suspension of calcite mixed with dolomite or a suspension of calcite with a solid solution of calcite and dolomite, the dissolved quantity of magnesium can be expected to differ for each of the two magnesium compounds. Therefore, the state of magnesium present in calcareous shells can be determined by knowing the quantity of magnesium dissolved by carbon dioxide aerated water.

Experimental

Materials. — *Calcite.* — Commercial reagent of extra pure grade is used without further purification.

Aragonite. — The same volume of 1 N $CaCl_2$ solution is added gradually to the boiling solution of 1 N Na_2CO_3; the separated precipitate of aragonite is washed with pure water and allowed to dry.

Magnesium carbonate. — Since it is difficult to prepare magnesium carbonate, basic magnesium carbonate (extra pure grade) is used instead of magnesium carbonate. When $MgCO_3 \cdot nH_2O$ is suspended in water, it changes quickly into basic magnesium carbonate, which proves that $MgCO_3 \cdot nH_2O$ is more unstable in water than basic magnesium carbonate[8]. Consequently for the purpose of this experiment, the authors use basic magnesium carbonate (MgO 44.2%) instead of magnesium carbonate.

TABLE I. CONTENT OF CALCIUM AND MAGNESIUM IN FOUR KINDS OF SEA URCHINS

No.	Ca %	$CaCO_3$ %	Mg %	$MgCO_3$ %
1-a	32.83	82.08	3.49	12.08
2-a	34.82	87.05	3.07	11.62
3-a	33.51	87.78	4.05	14.01
4-a	35.50	88.75	3.50	12.11

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[1] K. E. Chave, *J. Geol.*, **62**, 266 (1954).

** In this connection, the authors can write "present as a solid solution composed of calcite and magnesite". As to these two expressions there appears to be no essential difference[3,4].

[2] K. E. Chave, ibid., **60**, 190 (1952).

[3] R. I. Harkey and O. F. Tuttle, *Am. J. Sci.*, **253**, 209 (1955).

[4] R. I. Harkey and O. F. Tuttle, ibid., **253**, 274 (1955).

[5] Y. Kitano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 211 (1956).

[6] Y. Kitano, ibid., **77**, 215 (1956).

[7] Y. Kitano, ibid., **77**, 218 (1956).

*** It seems better to say "magnesium carbonate" instead of "magnesium".

[8] Y. Hagino, *Bull. Soc. Salt Science* (*Nippon Shio Gakkai-shi*), 8, 121 (1954).

Solid solution of calcite and dolomite.— For this experiment the shells of four kinds of sea urchins are used. The magnesium carbonate in the shells, as found by using X-ray diffraction technique, is contained as a solid solution. The magnesium content of each kind of shell is given in Table I.

Dolomite. — Because it is difficult to prepare this material in a laboratory, the authors use the dolomite found in the Kuzuo Mountain District of Tochigi Prefecture.

(*Anal.*: CaO, 33.80; MgO, 19.37; clay, 0.22%.)

An organic substance, a protein, is always present with minerals in shells, and its presence makes the minerals stable. Therefore, when inorganically prepared minerals are suspended in water, they are less stable than minerals containing an organic material. In this experiment the authors would prefer to use minerals which contain an organic material, but since those can not be obtained, inorganic compounds have to be used. Judging from results given in detail later, however, the use of inorganic minerals, calcite and dolomite, is found to be suitable.

Procedure. — The best procedure for the determination of the magnesium state is as follows: Two and a half gram of powdered sample, (<325 mesh), are suspended in 200 ml. of pure water. Carbon dioxide gas, washed by passing through water, is passed into the suspension for 25 min., and is allowed to stand for 10 min. After filtering the suspension with No. 6 Toyo filter paper, the magnesium content in the filtrate is determined. By comparing the dissolved quantities of magnesium in shells with those in mixed samples of calcite and possible magnesium compounds in shells, the state of magnesium in calcareous shells can be determined.

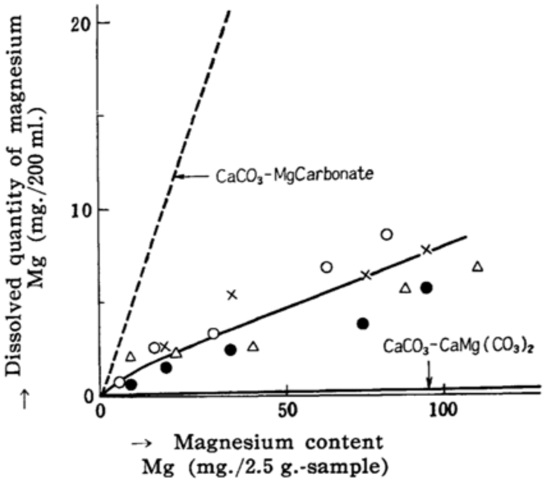

Fig. 1. Relationships between magnesium content and quantity of magnesium dissolved by CO$_2$-aerated water, for possible magnesium compounds in calcareous shells.

× 1-a—e ○ 2-a—e

△ 3-a—e ● 4-a—e

TABLE II. DISSOLVED AMOUNTS OF CALCIUM AND MAGNESIUM IN CO$_2$-AERATED WATER, CALCITE-SHELL OF THE SEA URCHIN, AT ROOM TEMPERATURE

	Sample							Dissolved quantity		Ratio in dissolution*	
	Shell g.	CaCO$_3$ g.	Ca %	Mg %	MgCO$_3$ %	Ca mg.	Mg mg.	Ca mg./200 ml.	Mg mg./200 ml.	Ca, %	Mg, %
1-a	2.5	0.0	32.83	3.49	12.08	821	87	85	7.6	10	8.7
1-b	2.0	0.5	34.26	2.78	9.62	857	70	82	6.4	9.6	9.1
1-c	1.0	1.5	36.80	1.39	4.71	928	35	76	5.4	8.1	15
1-d	0.5	2.0	38.58	0.70	2.42	964	17	74	2.6	7.7	15
1-e	0.2	2.3	39.43	0.28	0.97	986	7.0	71	0.9	7.2	13
2-a	2.5	0.0	34.82	3.07	11.62	871	77	82	8.5	9.4	11
2-b	2.0	0.5	35.86	2.46	8.51	896	61	80	6.7	8.9	11
2-c	1.0	1.5	37.93	1.23	4.26	948	31	70	3.1	7.4	10
2-d	0.5	2.0	38.96	0.61	2.11	974	15	70	2.0	7.2	13
2-e	0.2	2.3	39.59	0.25	0.85	990	6.1	72	0.8	7.3	13
3-a	2.5	0.0	33.51	4.05	14.01	838	101	76	6.8	9.0	6.6
3-b	2.0	0.5	34.81	3.24	11.21	870	81	71	5.7	8.2	7.0
3-c	1.0	1.5	37.40	1.62	5.61	935	41	68	2.6	7.3	6.3
3-d	0.5	2.0	38.70	0.81	2.80	968	20	67	2.3	6.9	12
3-e	0.2	2.3	39.48	0.32	1.11	987	8.1	68	2.3	6.9	29
4-a	2.5	0.0	35.50	3.50	12.11	888	88	82	5.6	9.2	6.4
4-b	2.0	0.5	36.40	2.80	9.69	910	70	78	3.9	8.6	5.6
4-c	1.0	1.5	38.20	1.40	4.84	955	35	70	2.4	7.4	6.9
4-d	0.5	2.0	39.10	0.70	2.42	977	18	65	1.5	6.6	8.7
4-e	0.2	2.3	39.64	0.28	0.97	991	7.0	68	0.6	6.9	8.1

* (dissolved quantity/content in sample) × 100

TABLE III. DISSOLVED AMOUNTS OF CALCIUM AND MAGNESIUM IN CO_2-AERATED WATER, VARIOUS KINDS OF CALCAREOUS SHELLS, AT ROOM TEMPERATURE

Sample Number	Genus	Sample					Dissolved quantity		Ratio in dissolution	
		Ca %	Mg %	$MgCO_3$ %	Ca mg./2.5 g.	Mg mg./2.5 g.	Ca mg./200 ml.	Mg mg./200 ml.	Ca %	Mg %
1	Protothaca jedoesis (Lischke)	37.89	0.81	2.80	947	20	77	4.0	8.1	20
2	Venerupis Amggdala japonica (Deshdyes)	36.71	0.65	2.25	918	16	87	0.3	9.4	1.8
3	Meretrix lusorid (Roding)	36.45	0.66	2.28	911	17	80	0.2	8.8	1.5
4	Paphia euglypta (philippi)	37.01	1.23	4.26	925	31	68	2.1	7.3	6.8
5	Ostrea (Carssoslraea) gigas Thunberg	34.60	1.79	6.19	865	45	75	2.6	8.6	5.7
6	Chlamgs mpponensis Kuroda	36.71	0.85	2.94	918	21	85	1.0	9.3	4.5
7	〃 (Niotha) levescens	35.70	1.21	4.19	893	30	85	1.0	9.4	3.2
8	Neverita (glass aulax) didyma	37.70	0.92	3.18	943	23	78	0.9	8.2	3.8
9	Babyloma japonica (Reeve)	35.00	0.42	1.45	875	11	55	0.3	6.3	2.8
10	Tonna luteostomo (Kuster)	36.50	0.61	3.11	913	15	74	1.7	8.2	11
11	Rapana thomasiana Crosse	38.88	0.29	1.00	972	7.3	77	1.3	7.9	18
12	Mytilus crassitesta Lischke	36.19	0.49	1.70	905	12	68	1.8	7.5	15
13	Atrina japonica (Reeve)	36.01	0.17	0.59	900	4.3	61	2.6	6.8	61
14	Ostrea denselamellosa Lischke	38.79	0.00	0.00	970	0.0	61	0.0	6.2	0.0
15	Saxidomus purpuratus (Sowerby)	35.73	1.90	6.57	893	48	79	1.6	8.9	3.4
16	Anadara suncrenata (Lischke)	40.68	0.00	0.00	1017	0.0	77	0.0	7.6	0.0
17	Pinctada Martensi (Dunker)	35.18	0.80	2.77	880	20	69	3.9	7.9	15
18	Hyriopsis schlegele (Martens)	37.07	0.08	0.28	926	2.0	77	1.6	8.3	82
19	Mya japonica Jay	37.84	1.08	3.74	946	27	73	0.6	7.8	2.1
20	Polynices didyma (Röding)	38.06	0.85	2.94	952	21	79	1.2	8.4	5.8
21	Dosinaia japonica (Reeve)	37.27	1.56	5.40	932	39	71	1.2	7.6	3.1
22	Babylonia japonica (Reeve)	38.58	1.29	4.46	965	32	78	2.7	8.1	8.4
23	?	38.31	0.59	2.04	958	15	81	0.0	8.5	0.0
24	Rapana thomasiana Crasse	37.78	1.23	4.26	945	31	70	2.6	7.4	8.4
25	Ostrea sp.	36.90	1.71	5.92	923	43	60	3.1	6.5	7.4
26	Serpulorlis ? sp.	34.29	2.90	10.03	857	73	74	1.5	8.6	2.1
27	?	37.03	1.47	5.09	926	37	78	2.6	8.4	7.1
28	coral-reef	37.81	0.43	1.49	945	6.5	75	1.5	6.4	23
29	coral-reef	36.06	1.53	5.29	902	23	71	3.2	7.9	14
30	Astriclypeus manni Verrill	33.93	3.69	12.77	848	92	74	7.9	8.8	8.5
31	?	38.51	0.29	1.00	963	7.3	78	0.96	8.1	13
32	Callista sinensis (Sowerby)	38.18	0.37	1.28	955	9.3	67	0.19	7.0	1.3
33	Ciree scripta stutzeri (Donvan)	38.00	0.65	2.25	950	16.2	65	0.09	6.8	0.5

Results

Fig. 1 shows the relationship between the amount of magnesium dissolved by carbon dioxide aerated water and the magnesium content in mixed samples of calcite**** and dolomite[5]. In Table II and Fig. 1 the relationship is given for mixed samples[9] of calcite and four kinds of sea urchin shells. When magnesium is contained as dolomite, it is difficult to find any dissolved quantity of magnesium, as is seen from Fig. 1. It may be expected that dolomite becomes more stable and no dissolved quantity of magnesium can be found when it is present with an organic material in calcareous shells. Therefore, it is quite suitable to use in this experiment native dolomite mineral having no organic material.

Determination of the State of Magnesium Contained in Calcareous Shells

The above procedure is applied to various kinds of calcareous shells and the results are given in Table III and Fig. 2. Fig. 2 includes the result obtained for mixed samples of calcite and dolomite as well as for mixed samples of calcite and a solid solution of calcite and dolomite. From the results given in Fig. 2, it is inferred that a dissolved quantity of magnesium in calcareous shells comes from a solid solution[10]. Therefore, it can be concluded that magnesium carbonate, having a content less than 2% in weight, is contained in calcareous shells as a solid solution. Meanwhile K. E. Chave reported that magnesium carbonate, having a content from 2 to 16% $MgCO_3$, was present in calcareous shells as a solid solution. Kitano reported previously that magnesium in limestone was always present as dolomite[7]. It is known that limestone in nature comes from calcareous shells. Consequently, it may be expected that the natural state of magnesium changes from a solid solution into dolomite during the process of limestone formation from calcareous shells. This finding is important and useful for an understanding of the formation of limestone in nature.

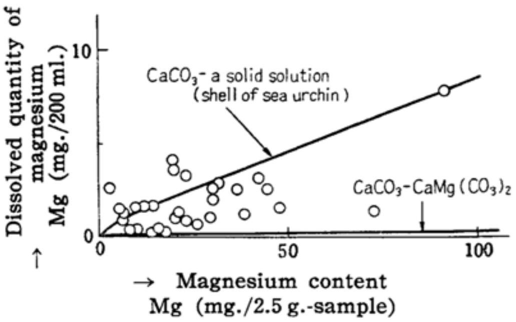

Fig. 2. Relationships between magnesium content and quantity of magnesium dissolved by CO_2-aerated water, for various kinds of calcareous shells.

Summary

An original method (Dissolution Method) for determining small amounts of magnesium contained in calcareous shells has been devised, and the state of magnesium has been determined by this method. As a result, it can be verified that small amounts of magnesium in calcareous shells are always contained as a solid solution of calcite and dolomite.

The authors express their sincere thanks to Mr. Sakae Ichihashi of Osaka City University for his advice given throughout this work.

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**** Two kinds of calcium carbonate, viz. calcite and aragonite, are used, and no difference between the dissolved quantities of magnesium for these two calcium carbonates can be found. Almost the same amount of calcium carbonate in shells, coexisting with an organic material, as the amount of inorganically prepared calcium carbonate can be dissolved by carbon dioxide aerated water. Hence, the use of inorganically prepared calcite instead of calcium carbonate coexisting with an organic material, is justified.

[9] Fig. 1 also shows the relationship in mixed samples of calcium carbonate and magnesium carbonate[5]. It can be expected that the dissolved quantity of magnesium in the solid solution will be higher than that in magnesium carbonate. However, as seen in Fig 1, the latter is in reality higher than the former. That the solid solution used in this experiment is made stable by a coexisting organic material may be responsible for this discrepancy between the presumed and actual results. (The presence of magnesium carbonate can not be expected in calcareous shells, as mentioned earlier).

[10] From Fig. 2, it is clear that the dissolved quantity of magnesium in some calcareous shells is less than that in mixed samples of calcium carbonate and shell of four kinds of sea urchins. This can be understood by the following findings: 1) By mixing calcium carbonate with a sea urchin's shell in which 16% $MgCO_3$ is contained as a solid solution, the authors prepare semples containing a small amount of magnesium as a solid solution. It can be expected that the dissolved quantity in the mixed sample will be higher than that in natural shell samples, because a solid solution is less stable with an increase of magnesium content. 2) Since some calcareous shells are not fresh, it appears possible that a part of the solid solution changes to a stable dolomite.