

Incorporation of sodium, chloride and sulfate with calcium carbonate

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Abstract—Calcite and/or aragonite were formed from calcium bicarbonate solutions containing sodium sulfate, sodium chloride and magnesium chloride of various concentrations. Sodium, chloride and sulfate contents of synthetic calcite or aragonite were measured. Sodium and chloride ions are incorporated into aragonitic calcium carbonate more easily than into calcitic calcium carbonate, although sodium and chloride ions in the parent solution favor the formation of calcitic calcium carbonate. On the other hand, sulfate ions are incorporated into calcitic calcium carbonate more easily than into aragonitic calcium carbonate, although sulfate ions in the parent solution favor the formation of aragonitic calcium carbonate. Sodium content of aragonite, which is precipitated from calcium bicarbonate solution containing sodium sulfate, sodium chloride and magnesium chloride, exhibits a maximum value together with sulfate content of aragonite.

INTRODUCTION

The factors that control the distribution of trace and minor metal elements of marine calcareous skeletons have been actively studied through laboratory experiments, as well as through field observations (ODUM, 1951; CHAVE, 1954a, 1954b; LOWENSTAM, 1961; HOLLAND *et al.*, 1963, 1964a, 1964b; DODD, 1964, 1966, CROCKET and WINCHESTER, 1966; TSUSUE and HOLLAND, 1966; KITANO *et al.*, 1968, 1970, 1971; KINSMAN, 1969; KINSMAN and HOLLAND, 1969; KITANO and OOMORI, 1971). However, distributions of such alkaline metals as sodium and of such anions as sulfate, chloride and fluoride in calcium carbonate have been known only partially (KITANO, 1962; GORDON *et al.*, 1970; TOKUYAMA *et al.*, 1972; KITANO and OKUMURA, 1973).

According to TOKUYAMA *et al.* (1972), concentrations of sulfate, chloride and sodium are as follows; SO₄ : 5,700ppm, Cl : 370ppm, Na : 3,300ppm in fresh aragonitic corals and SO₄ : 170ppm, Cl : 30ppm, Na : 120ppm in Riukiu limestones. GORDON *et al.* (1970) found that the sodium content of barnacle shells from Chesapeake Bay varies from 1,600 to 5,000ppm and is proportional to the environmental salinity. Laboratory experiments have not yet been carried out on the incorporation of these ions into calcium carbonate. Mechanisms for the incorporation of sulfate, chloride and sodium ions and their existing states in the skeletal parts are not yet clarified.

The purpose of this paper is to elucidate the behaviors of sulfate, chloride and sodium ions during the precipitation of calcium carbonate and their concentrations in calcium carbonate formed in both inorganic and biological systems.

EXPERIMENTAL

Calcium carbonate has three polymorphic crystal forms (calcite, aragonite and vaterite). In marine biological systems calcites (Mg-poor and Mg-rich) and aragonite are

found, but vaterite is not (KITANO, 1964). Kitano and his co-workers successfully synthesized Mg-poor calcite, Mg-rich calcite and aragonite at low temperatures and pressures from calcium bicarbonate solution containing sodium chloride, magnesium chloride and sodium citrate by changing their concentrations (KITANO and HOOD, 1962; KITANO *et al.*, in press). The incorporation of sulfate, chloride and sodium ions with calcium carbonate has been examined by the release of carbon dioxide gas from calcium bicarbonate solution followed by calcium carbonate precipitation.

Procedure of the experiment: Various amounts of sodium (or potassium) sulfate, sodium chloride and magnesium chloride were placed in one liter reaction vessels containing calcium bicarbonate solution, which had been prepared by bubbling carbon dioxide gas into suspension of calcium carbonate. Then the reaction vessels were stirred with a magnetic stirrer at 25°C until about 90% of calcium was precipitated as calcium carbonate. The carbonate precipitate was filtered off and washed with distilled water until it was free from any trace of the parent solution. A fraction of the dried precipitate was used for the measurement of sulfate, chloride, sodium and potassium contents, and another fraction was used for the identification of crystal forms by X-ray diffraction (KITANO *et al.*, 1968, 1970, 1971; KITANO and OOMORI, 1971; KITANO and OKUMURA, 1973).

Sulfate content of calcium carbonate was determined colorimetrically with thorium-morin complex (NASU, 1969) after the removal of interfering cations by the use of cation exchange resin, and chloride content was determined colorimetrically with mercury thiocyanate and iron ammonium sulfate (UTSUMI, 1952). Sodium and potassium contents were determined by flame photometry.

An amount of sulfate ions from 0 to 2.7g was added to one liter of calcium bicarbonate parent solution containing various amounts of sodium chloride and/or magnesium chloride. Such an addition of sulfate ions does not cause precipitation of a single mineral phase of calcium sulfate, because the parent solution is in under-saturation with respect to calcium sulfate.

EXPERIMENTAL RESULTS

Incorporation of sodium, chloride and sulfate ions with calcium carbonate at 25°C
 (1) $\text{Ca}(\text{HCO}_3)_2$ (Ca^{2+} : 380mg/l) + Na_2SO_4 or K_2SO_4 (Na_2SO_4 : 0 to 3.99g/l, or K_2SO_4 : 0 to 0.73g/l) + MgCl_2 (MgCl_2 : 0 or 4.98g/l) + NaCl (NaCl : 0 to 26.7g/l) \rightarrow calcite or aragonite

Only calcite was precipitated in calcium bicarbonate solutions without magnesium ions, and only aragonite was precipitated when the concentration of magnesium ions was 1.27g/l. Figure 1 shows the relation between the concentration of sulfate ions in the parent solution and the sulfate content of precipitated carbonate. Figure 2 shows the relation between the concentration of sodium ions in the parent solution and the sodium content of precipitated carbonate. Sulfate and sodium contents of precipitated calcite increase with increasing concentration of sulfate and sodium ions in the parent solution. Sulfate content of calcite is larger than that of aragonite, whereas sodium content of calcite is smaller than that of aragonite. As shown in Fig. 1, sulfate content of calcite from calcium bicarbonate solution containing sodium sulfate (SO_4^{2-} : 0.4g/l) is larger than that from solution containing potassium sulfate (SO_4^{2-} : 0.4g/l), and sulfate content of calcite from solution containing 26.2g/l of sodium chloride (Na^+ : 10.5g/l) is smaller than that from the solution without sodium chloride. The influence of sodium chloride on the incorporation of sulfate is clearly shown in Fig. 3. Sulfate content of precipitated calcite markedly decreases with increasing concentration of sodium ions in the parent solution, whereas that of aragonite remains constant.

Chloride content of calcite precipitated from calcium bicarbonate solution containing 1.5 to 16g/l of chloride ions is within the range of 25 to 50ppm as shown later in Fig. 7,

and is one tenth to one hundredth smaller than sulfate and sodium contents of calcite.

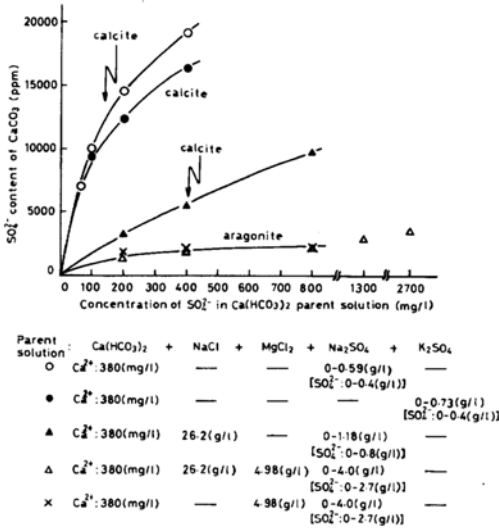


Fig. 1. SO_4^{2-} content of calcite and aragonite, plotted against the concentration of SO_4^{2-} in $Ca(HCO_3)_2$ parent solution at 25°C: $Ca(HCO_3)_2 + NaCl + MgCl_2 + Na_2SO_4$ (or K_2SO_4) → calcite or aragonite.

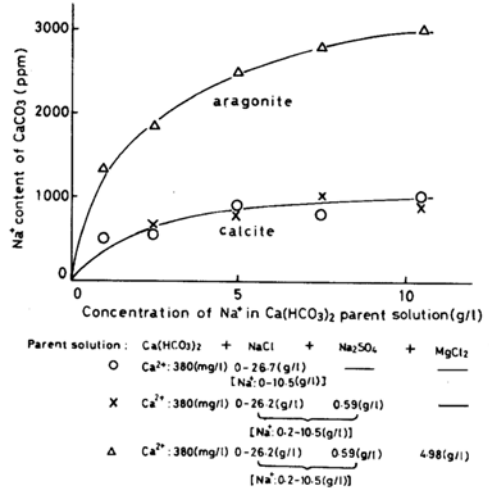


Fig. 2. Na^+ content of calcite or aragonite, plotted against the concentration of Na^+ in $Ca(HCO_3)_2$ parent solution at 25°C: $Ca(HCO_3)_2 + NaCl + Na_2SO_4 + MgCl_2$ → calcite or aragonite.

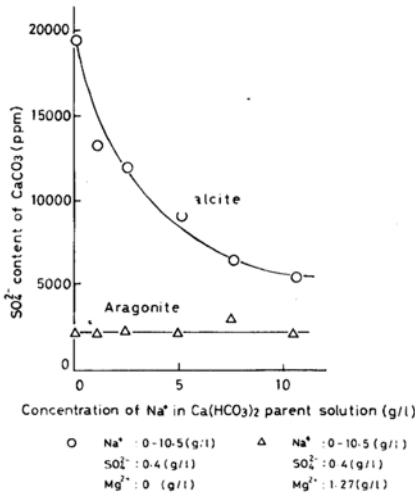


Fig. 3. Influence of Na^+ in $Ca(HCO_3)_2$ parent solution on the SO_4^{2-} content of calcium carbonate precipitated at 25°C: $Ca(HCO_3)_2 + Na_2SO_4 + MgCl_2 + NaCl$ → calcite or aragonite.

(2) $Ca(HCO_3)_2$ (Ca²⁺: 380mg/l) + Na₂SO₄ or K₂SO₄ (Na₂SO₄: 0 to 3.99g/l or K₂SO₄: 0 to 0.73g/l) + MgCl₂ (MgCl₂: 0 to 4.98g/l) + NaCl (NaCl: 0 to 26.7g/l) → aragonite and/or calcite.

It has been known that the fraction of aragonite in carbonate increases with increase in the concentration of magnesium ions and also with the Mg/Ca ratio in the parent solution (KITANO, 1962; KITANO and HOOD, 1962; KITANO *et al.*, 1962, 1969, 1972). Such a trend was observed also in the present experiment, as given in Fig. 4.

Sulfate, chloride and sodium contents of carbonates with various proportions of

aragonite were measured. Figures 5, 6 and 7 show the relationship between sulfate content, sodium content, chloride content and aragonite proportion of the precipitated carbonate.

Figure 5 shows: (a) With increasing aragonite proportion, sulfate content decreases markedly in the carbonate formed from the parent solution containing not a large amount of sodium chloride, but it does not decrease in the carbonate from the parent solution which contains a large amount of sodium chloride. As mentioned earlier, sodium ions in the parent solution reduce sulfate content of calcite formed, whereas they do not exert any significant influence on the sulfate content of formed aragonite. (b) Aragonite contains about 2,000 to 3,000ppm of sulfate, while calcite exhibits higher sulfate contents of 5,000 to 20,000ppm, depending on the sodium concentration in the parent solution (see Fig. 3).

In Fig. 6, the following facts are seen: (a) With increasing aragonite proportion, sodium content of precipitated carbonate increases. (b) Calcite contains about 1,000ppm of sodium, and aragonite contains 2,600 to 3,000ppm of sodium.

Figure 7 gives following information: (a) With increasing aragonite proportion, chloride content of precipitated carbonate increases. (b) Calcite contains 25 to 50ppm of chloride, and aragonite contains 150 to 200ppm of chloride.

From these figures it is concluded that sulfate and sodium contents of precipitated carbonate are much larger than the chloride content.

DISCUSSION

Decrease in sulfate content of calcite with increase in sodium chloride concentration in the parent solution Sulfate ions are more easily incorporated into calcite than into aragonite, and with increasing concentration of sodium chloride in the parent solution, sulfate content of precipitated calcite decreases markedly (Figs. 1, 3, 5, Tables 1 and 2). However, sulfate content of aragonite is low and does not change even with the change in the sodium chloride concentration in the parent solution. In seawater, 40 ~ 50% of sulfate is dissolved as free anions and the remaining portion as ion pairs with sodium and magnesium (GARRELS and THOMPSON, 1962; KESTER and PYTKOWICZ, 1968, 1969). PYTKOWICZ and KESTER (1969) reported that the apparent formation constant (K^*) of NaSO_4^- is controlled by the ionic strength (I), in a manner of the following form:

$$K^* = \frac{[\text{NaSO}_4^-]}{[\text{Na}^+]_F \cdot [\text{SO}_4^{2-}]_F} = 2.73 - 2.58 \cdot I + 2.28 \cdot I^2 \quad (1),$$

where brackets denote molal concentration and subscript F indicates free ions.

The increase in the sodium chloride concentration in the parent solution causes the increase in ionic strength, which results in the decrease in the activity of sulfate ions in the parent solution. The activity of sulfate ($a_{\text{SO}_4^{2-}}$) is calculated from the following equation:

$$a_{\text{SO}_4^{2-}} = f_{\text{SO}_4^{2-}} \cdot [\text{SO}_4^{2-}]'_F = f_{\text{SO}_4^{2-}} \cdot \left\{ [\text{SO}_4^{2-}]_T - [\text{MeSO}_4^{n-2}] \right\} \quad (2),$$

where f_X denotes the activity coefficient of X chemical species, the subscript T indicates the total molality of sulfate dissolved in solution and $[\text{MeSO}_4^{n-2}]$ represents the concentration of ion pairs of sulfate with metal ions (Me^{n+}).

In the calcium bicarbonate solution containing sodium chloride and sodium sulfate, from which only calcite precipitates, only sodium-sulfate ion pair (NaSO_4^-) is formed significantly. The concentration of sodium ions was calculated from equation (1) and

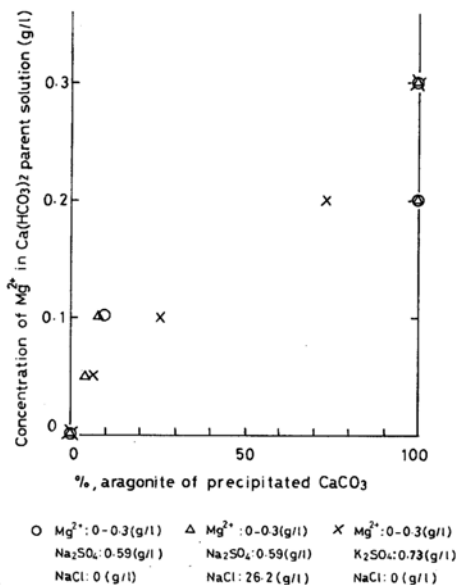


Fig. 4. Influence of Mg^{2+} in $Ca(HCO_3)_2$ parent solution on the crystal form of calcium carbonate precipitated.

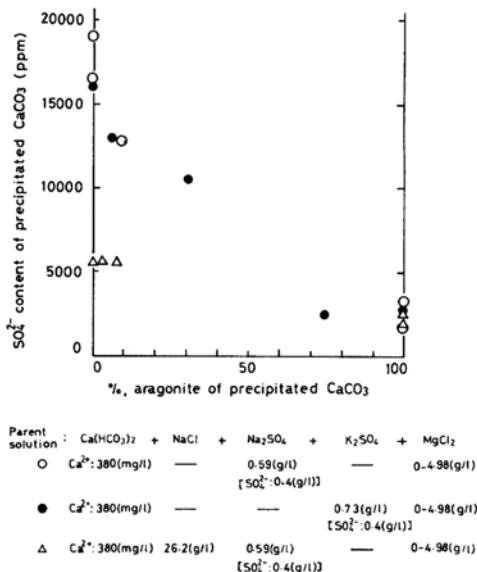


Fig. 5. SO_4^{2-} content of precipitated $CaCO_3$, plotted against aragonite proportion of precipitated $CaCO_3$.

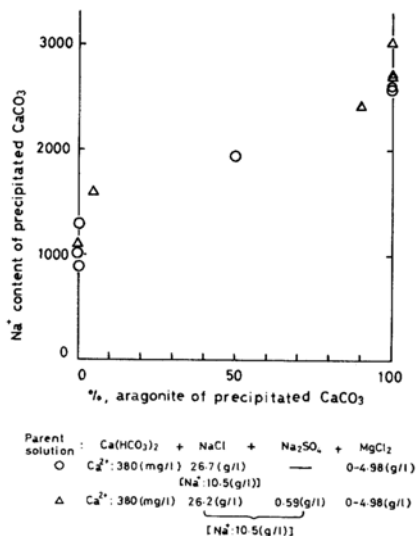


Fig. 6. Na^+ content of precipitated $CaCO_3$, plotted against aragonite proportion of precipitated $CaCO_3$.

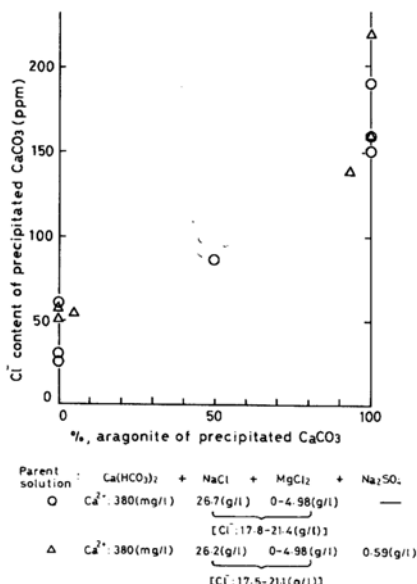


Fig. 7. Cl^- content of precipitated $CaCO_3$, plotted against aragonite proportion of precipitated $CaCO_3$.

the amount of sodium ions added to the parent solution. The activity of $NaSO_4^-$ was calculated from equation (1) by using the value of $f_{HCO_3^-}$ as that of $f_{NaSO_4^-}$ (GARRELS *et al.*, 1961; GARRELS and THOMPSON 1962). Figure 8 shows the relation between the

sulfate content of precipitated calcite and the activity of sulfate ions calculated from equations (1) and (2) with the aid of the value of $f_{\text{SO}_4^{2-}}$ obtained by the mean salt method (GARRELS and CHRIST, 1965).

The sulfate content of precipitated calcite increases with increasing activity of sulfate ions in the parent solution (Fig. 8). There is, however, no conspicuous relationship between the sulfate content of precipitated calcite and the activity of sodium-sulfate ion pair in the parent solution (Fig. 8). This fact suggests that the sulfate content of precipitated calcite depends on the activity of sulfate ions in the parent solution and sulfate is incorporated into calcite as free ions rather than ion pair such as NaSO_4^- .

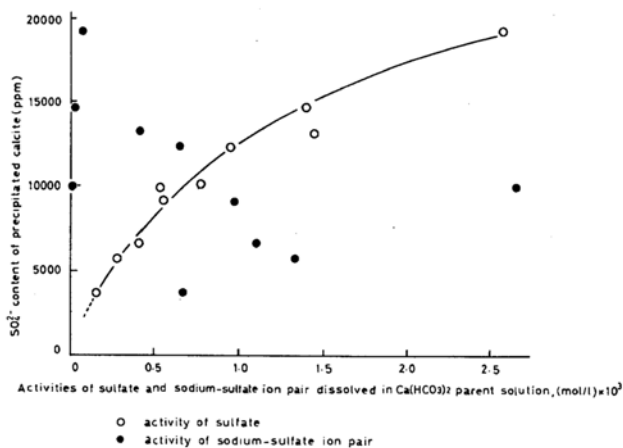


Fig. 8. SO_4^{2-} content of precipitated calcite, plotted against the activities of sulfate and sodium-sulfate ion pair in $\text{Ca}(\text{HCO}_3)_2$ parent solution at 25°C : $\text{Ca}(\text{HCO}_3)_2 + \text{Na}_2\text{SO}_4 + \text{NaCl} \rightarrow \text{calcite}$.

Incorporation of sodium with aragonitic calcium carbonate

Figure 9 shows that the high sodium content of the formed aragonite increases to reach 4,000ppm at the sulfate concentration of 1g/l in the parent solution containing a large amount of sodium chloride, say 25g/l, but the low sodium content of the formed calcite remains virtually constant.

Aragonite was precipitated from calcium bicarbonate solution containing 0 to 2.7g/l of sulfate ions (as Na_2SO_4), 0 to 10.5g/l of sodium ions (as Na_2SO_4 and/or NaCl) and 0.2 to 2.5g/l of magnesium ions (as MgCl_2).

Figure 10 shows the relation between sodium and sulfate contents of precipitated aragonite. In the case of aragonite formed from solution containing sodium sulfate and magnesium chloride without sodium chloride, a nearly positive linear relationship is seen. The linear relationship indicates that sodium and sulfate are incorporated into aragonite in a form of sodium sulfate (see solid circles in Fig. 10). The sulfate content of aragonite precipitated from calcium bicarbonate solution containing 0.4g/l of sulfate ions (as Na_2SO_4), 1.0 to 10.5g/l of sodium ions (as NaCl) and 1.27g/l of magnesium ions (as MgCl_2) is almost constant, say, about 40meq/kg, independent of the sodium content of precipitated aragonite (see open triangles in Fig. 10). Table 2 gives sodium, chloride and sulfate contents of aragonite formed in the above systems. Table 2 and Fig. 10 show that sodium content of precipitated aragonite increases with increasing sulfate content to reach a maximum value at about 50meq/kg of sulfate content and then decreases with further increase in the sulfate content (see open circles in Fig. 10). The chloride content of aragonite is quite low as compared with sodium and sulfate contents,

Table 1 gives sodium, chloride and sulfate contents of calcite precipitated from calcium bicarbonate solution containing sodium chloride and sodium sulfate. This table suggests following facts: The chloride content of calcite is negligibly small as compared with sodium and sulfate contents. And sulfate is incorporated into calcite mainly in the forms of calcium and sodium sulfates. The case of aragonite will be discussed in the next section.

and the sodium content is higher than the sulfate content. On the basis of these facts, it is inferred that a part of the sodium is incorporated with sulfate and another significant part of the sodium not with chloride but with carbonate into aragonite precipitated from the parent solution containing only a significant amount of sodium chloride. Figures 2 and 6 suggest that sodium content of aragonite is higher than that of calcite. Then, it is inferred that the larger amount of sodium is incorporated into aragonitic calcium carbonate in the form of sodium carbonate than into calcitic calcium carbonate.

Table 1. Sodium, chloride and sulfate contents of calcite

Composition of parent solution				Contents of calcite		
SO ₄ ²⁻	Na ⁺	Cl ⁻	Mg ²⁺	SO ₄ ²⁻	Na ⁺	Cl ⁻
(g/l)	(g/l)	(g/l)	(g/l)	(meq/kg)	(meq/kg)	(meq/kg)
0.80	10.5	15.6	0	230	43	1.2
0.40	10.5	15.9	0	120	36	1.0
0.40	7.5	11.3	0	140	40	0.7
0.40	5.0	7.4	0	190	31	0.7
0.40	2.5	3.6	0	—	27	—

Table 2. Sodium, chloride and sulfate contents of aragonite

Composition of parent solution				Contents of aragonite		
SO ₄ ²⁻	Na ⁺	Cl ⁻	Mg ²⁺	SO ₄ ²⁻	Na ⁺	Cl ⁻
(g/l)	(g/l)	(g/l)	(g/l)	(meq/kg)	(meq/kg)	(meq/kg)
2.70	10.5	18.1	1.27	69	160	4.6
1.30	10.5	19.0	1.27	66	170	4.7
0.80	10.5	19.3	1.27	44	170	4.3
0.40	10.5	19.6	1.27	37	130	4.4
0.20	10.5	19.8	1.27	24	110	4.6
0.40	7.5	15.0	1.27	50	120	4.1
0.40	5.0	11.1	1.27	40	110	3.8
0.40	2.5	7.3	1.27	42	80	3.0
0.40	1.0	4.9	1.27	38	59	2.6
0.40	10.5	23.2	2.50	32	140	6.1
0.40	10.5	17.6	0.60	40	120	4.2
0.40	10.5	16.8	0.30	42	120	4.6

TAKANO and WATANUKI (1974) reported that in calcitic travertine from Yunomata hot springs, the value of D_{Sr} (distribution coefficient of strontium between hot spring water and travertine) increases to have a maximum value in relation to MnO content of the travertine, and that sulfate content also exhibits a maximum value at 4~5% of the MnO content.

The fact found for D_{Sr} and the enrichment factor of sulfate in the natural calcitic travertine-water system seems to be analogous to the observed fact on the relationship between sulfate content and sodium content of calcite in this study, though the mechanisms may not completely be the same.

Relationship between crystal form and sulfate, chloride and sodium contents of calcium carbonate

Figures 1, 3 and 5 show that sulfate ions are incorporated into calcite more easily than into aragonite. Figures 2, 5 and 6 show that chloride and sodium are incorporated into aragonite more easily than into calcite.

KITANO (1962) reported that sulfate dissolved in the parent solution favors aragonite formation, and chloride and sodium favor calcite formation.

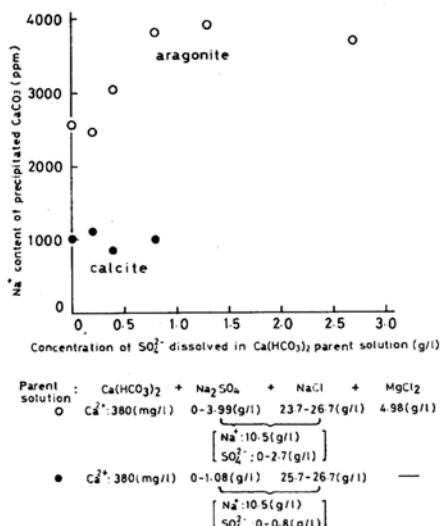


Fig. 9. Na⁺ content of precipitated CaCO₃, plotted against the concentration of SO₄²⁻ dissolved in Ca(HCO₃)₂ parent solution at 25°C: Ca(HCO₃)₂ + Na₂SO₄ + NaCl + MgCl₂ → calcite or aragonite.

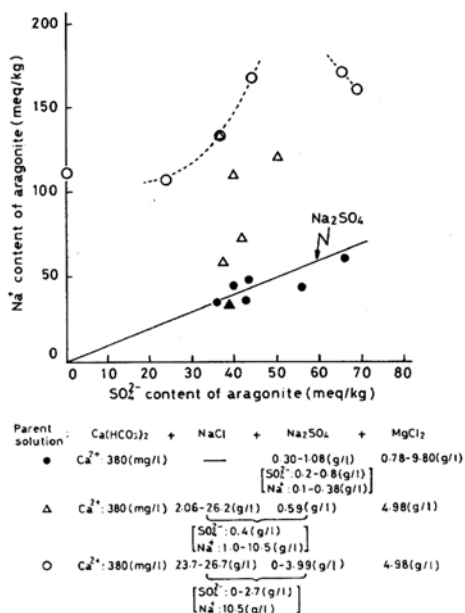


Fig. 10. Na⁺ content of aragonite, plotted against the SO₄²⁻ content of aragonite.

KITANO and OKUMURA (1973) reported that fluoride dissolved in the parent solution, even of a very small amount, favors calcite formation, although fluoride is coprecipitated more easily with aragonite than with calcite.

KITANO (1962) and KITANO *et al.* (1969) pointed out that magnesium and copper, which have smaller ionic radii than does calcium, are captured very easily in the lattice of calcitic calcium carbonate to form solid solution, (Ca,Mg)CO₃ and (Ca,Cu)CO₃, respectively, but hardly in the lattice of aragonitic calcium carbonate. It was observed, however, that magnesium and copper dissolved in the parent solution favor the formation of aragonitic calcium carbonate very strongly (KITANO, 1962; KITANO *et al.*, 1969). Barium, which has larger ionic radius than does calcium, is captured very easily in the lattice of aragonitic calcium carbonate. However, barium ions in the parent solution, even of a very small amount, strongly favor the formation of calcitic calcium carbonate (KITANO, 1962; KITANO *et al.*, 1971).

These peculiar, interesting observational facts seem to show that chemical behaviors of Mg²⁺, Cu²⁺, Ba²⁺, Na⁺, F⁻, Cl⁻, and SO₄²⁻ are common in the process of the selective formation of calcitic or aragonitic calcium carbonate. The mechanisms that govern the chemical behaviors of these ions remain to be solved.

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