

## Coprecipitation of borate-boron with calcium carbonate

YASUSHI KITANO<sup>1</sup>, MINORU OKUMURA<sup>2</sup> and MASATOSHI IDOGAKI<sup>2</sup>

Water Research Institute, Nagoya Univ., Nagoya<sup>1</sup> and  
Faculty of Literature and Science, Shimane Univ., Matsue<sup>2</sup>, Japan

(Received March 20, 1978; accepted in revised form April 19, 1978)

The behavior of borate-boron in a calcium bicarbonate parent solution during the precipitation of calcium carbonate has been studied experimentally.

The amount of borate-boron coprecipitated with calcium carbonate is proportional to the concentration of borate-boron dissolved in a parent solution, and this relationship is affected by the crystal form of calcium carbonate precipitated and the concentration of sodium chloride dissolved in the parent solution. Borate-boron is easily coprecipitated with aragonite rather than with calcite. These experimental results agree with the trend of boron content in carbonate skeletons of marine organisms such as bivalved mollusks. There is a difference in the influence of sodium chloride dissolved in a parent solution on the coprecipitation between calcite and aragonite: The amount of borate-boron coprecipitated with calcite increases with increasing concentration of sodium chloride in a parent solution, whereas the amount of borate-boron coprecipitated with aragonite decreases with increasing concentration of sodium chloride in the parent solution. This fact suggests that the mechanism of the coprecipitation of borate-boron with calcite is different from that with aragonite. Borate-boron dissolved in a parent solution has little influence on the crystal form of precipitated calcium carbonate.

### INTRODUCTION

For the geochemical balance of chemical elements between input to and output from seawater, studies are needed on the geochemical behavior of chemical species at the separation of calcium carbonate. In this sense, the authors have studied the behaviors of bivalent cations such as  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$ ,  $Cd^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $UO_2^{2+}$  and also anions such as  $Cl^-$ ,  $F^-$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$  at the separation of calcite and aragonite in water environments (KITANO and KAWASAKI, 1958; KITANO *et al.*, 1968, 1971, 1975, 1978; KITANO and OOMORI, 1971; KITANO and TERAO, 1972; KITANO and OKUMURA, 1973). Very interesting observations were obtained experimentally for the influence of various anions in a parent solution on the crystal form of forming calcium carbonate and also for the uptake of the anions by forming calcium carbonate. The study on borate-boron, however, has not been made as yet.

Concerning the distribution of borate-boron in *Mytilus edulis* shells, FURST *et al.* (1976)

found that the boron content of aragonite is higher than that of calcite by a factor of 1.5 to 2. WASKOWIAK (1962) also found a similar distribution of boron in mollusk shells.

MUTO (1952) studied on the boron content of travertines from Isobe Mineral Springs (Japan) to conclude that boron is taken by hydrous ferric oxide and also by hydrous magnesium oxide in travertines. ICHIKUNI and KIKUCHI (1972), however, reported that the boron content of travertines is not related to  $Al_2O_3$  or  $Fe_2O_3$  in the samples but is controlled by the Freundlich adsorption isotherm for calcium carbonate, from their study on the boron content of travertines from various hot springs in Japan. And they concluded that boron is mostly incorporated into carbonate portion of travertines through two different types of adsorption: One is caused through the process that monovalent anion  $B(CH_3)_4^-$  electrostatically reacts with positively charged sites on calcium carbonate, and the other through the process, in which hydrogen bond is formed between  $B(OH)_3$  and carbonate of calcium carbonate. But the factors controll-

ing the incorporation of boron into calcium carbonate and the state of boron existing in calcium carbonate have not been clarified exactly.

The primary purposes of this paper are to clarify the correlation between the boron content of calcium carbonate and the boron concentration in a parent solution from which the calcium carbonate has precipitated, the factor controlling the coprecipitation of borate-boron with calcium carbonate and the influence of borate-boron in a parent solution on the crystal form of precipitated calcium carbonate.

#### EXPERIMENTAL PROCEDURES AND RESULTS

(1) *Coprecipitation of borate-boron with calcium carbonate precipitated from a calcium bicarbonate parent solution at 25°C* Sodium chloride, magnesium chloride and boric acid in various ratios were placed in polyethylene reaction vessels containing calcium bicarbonate solution prepared by bubbling carbon dioxide gas into calcium carbonate-suspended solution. Then the solutions in the reaction vessels were stirred with a magnetic stirrer until about 80% of calcium ions was precipitated as calcium carbonate at 25°C. Calcium carbonate precipitate was filtered off, washed with distilled water and then air-dried at room temperature. A part of the dried precipitate was used to determine the boron content, and the residue to identify the crystal form of calcium carbonate.

Calcium ions and pH value in the parent solution were determined volumetrically with EDTA standard solution and with pH meter, respectively. The borate-boron content of calcium carbonate was determined with a method modified from GRINSTEAD and SNIDER (1967) as follows: Dried calcium carbonate precipitate (0.5 to 1.0g) was dissolved with hydrochloric acid solution and then calcium ions in the solution was separated as calcium sulfate by adding ammonium sulfate to the solution. After the calcium sulfate-suspended solution had been filtered, both curcumin solution and ammonium acetate-acetic acid buffer solution were added to an aliquot of the filtrate to develop color. The boron concentration was determined colorimetrically at 555m $\mu$  of wave length. The crystal form of precipitated calcium carbonate was

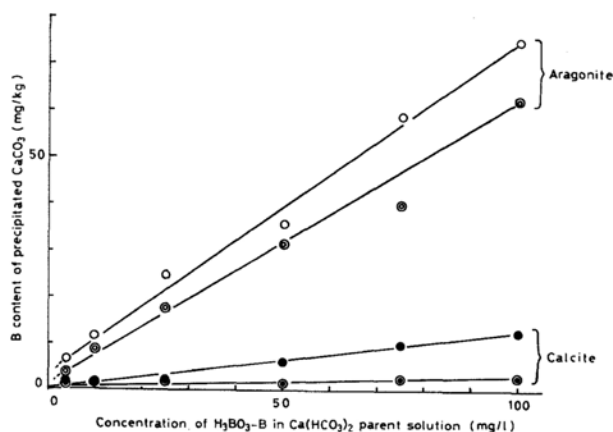


Fig. 1. Boron contents of calcite and aragonite, plotted against the concentration of borate-boron in a parent solution at 25°C.

	Parent solution		Precipitated CaCO <sub>3</sub>
	Na <sup>+</sup> (g/l)	Mg <sup>2+</sup> (g/l)	Crystal form
○	0	1.27	aragonite
⊙	10.5	1.27	aragonite
●	0	0	calcite
●	10.5	0	calcite

identified with an X-ray diffractometer (KITANO *et al.*, 1968, 1970, 1971, 1975, 1978; KITANO and OOMORI, 1971; KITANO and OKUMURA, 1973).

(1-1) Ca(HCO<sub>3</sub>)<sub>2</sub> (Ca<sup>2+</sup>: 360mg/l) + H<sub>3</sub>BO<sub>3</sub> (B: 4 to 100mg/l) + NaCl (Na<sup>+</sup>: 0 to 10.5g) → calcite

Only calcite was precipitated from the parent calcium bicarbonate solution containing only boric acid or both boric acid and sodium chloride. Figure 1 shows the relationship between the concentration of borate-boron in a parent solution and the amount of borate-boron coprecipitated with calcium carbonate. In this figure, the amount of borate-boron coprecipitated with calcite is proportional to the concentration of borate-boron in the parent solution. From the calcium bicarbonate solution containing 10.5g/l of sodium ions as sodium chloride, the boron content of calcite is higher than that from the solution without sodium chloride. The influence of sodium chloride dissolved in the parent solution on the coprecipitation of borate-boron with calcite is seen more clearly from Fig. 2, where the amount of borate-boron coprecipitated with calcite increases with increasing concentration of sodium chloride in the so-

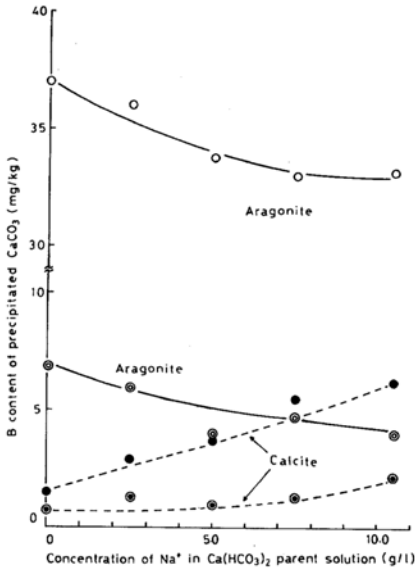


Fig. 2. Influence of Na<sup>+</sup> in a parent solution on the coprecipitation of borate-boron with calcium carbonate.

	Parent solution		Precipitated CaCO <sub>3</sub>
	Borate-B (mg/l)	Mg <sup>2+</sup> (g/l)	Crystal form
○	50	1.27	aragonite
⊙	4	1.27	aragonite
●	50	0	calcite
⊙	4	0	calcite

lution.

(1-2) Ca(HCO<sub>3</sub>)<sub>2</sub> (Ca<sup>2+</sup>: 360mg/l) + H<sub>3</sub>BO<sub>3</sub> (B: 4 to 100mg/l) + NaCl (Na<sup>+</sup>: 0 to 10.5g/l) + MgCl<sub>2</sub> (Mg<sup>2+</sup>: 0 to 1.27g/l) → calcite and/or aragonite

Only aragonite or the mixture of calcite and aragonite was precipitated from the calcium bicarbonate parent solution containing boric acid, sodium chloride and magnesium chloride. Figure 1 includes the relationship between the amount of borate-boron coprecipitated with aragonite and the concentration of borate-boron in the parent solution containing 1.27g/l of magnesium ions and also in the parent solution containing both 1.27g/l of magnesium ions and 10.5g/l of sodium ions. The boron content of aragonite is proportional to the concentration of borate-boron in the solution as is the boron content of calcite, and is very higher than the boron content of calcite as seen from Fig. 1. Contrary to the influence of sodium chloride dissolved in the parent solution on the coprecipitation of borate-boron with calcite, the amount of borate-boron coprecipitated with aragonite decreases with increasing concentration of sodium chloride in the parent solution

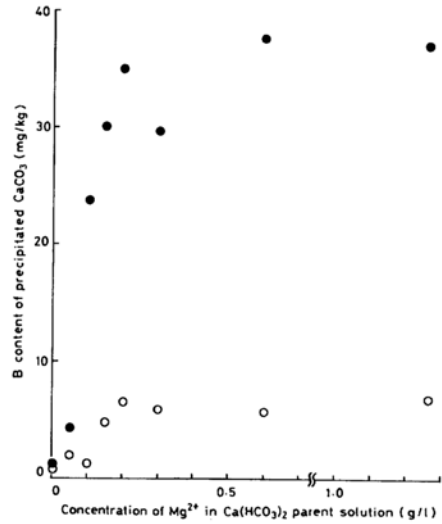


Fig. 3. Influence of Mg<sup>2+</sup> in a parent solution on the coprecipitation of borate-boron with calcium carbonate.

○ Borate-B : 4mg/l  
● Borate-B : 50mg/l

(Figs. 1 and 2).

Figure 3 shows the influence of magnesium chloride dissolved in the parent solution on the coprecipitation of borate-boron with calcium carbonate. The influence of magnesium chloride is clearly different from that of sodium chloride. The amount of borate-boron coprecipitated with calcium carbonate remarkably increases with increasing concentration of magnesium ions in the parent solution within the range of 0 to 0.2g/l of magnesium ions in the solution. And the concentration of magnesium ions is kept almost constant in the solutions containing more than 0.2g/l of magnesium ions. The proportion of aragonite in the precipitated calcium carbonate increases with increasing concentration of magnesium ions in the parent solution within the magnesium concentration of 0 to 0.3g/l (see Fig. 4). And almost pure aragonite is precipitated from the solution containing more than 0.4g/l of magnesium ions (Fig. 4). This result indicates that the crystal form of precipitated calcium carbonate influences the amount of borate-boron coprecipitated with calcium carbonate.

(2) Influence of borate-boron in a parent solution on the crystal form of precipitated calcium carbonate Sodium chloride, magnesium chloride and boric acid in various ratios were

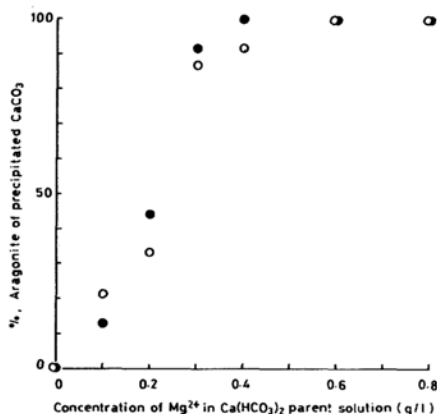


Fig. 4. Influence of borate-boron in a parent solution on the crystal form of precipitated calcium carbonate.

- Borate-B : 0mg/l
- Borate-B : 50mg/l

placed in reaction vessels containing calcium bicarbonate solution. The solutions in the reaction vessels were kept to stand with occasional agitation at 25°C, until about 50% of calcium ions in the parent solution was precipitated as calcium carbonate. The crystal form of precipitated calcium carbonate was identified with an X-ray diffractometer.

Figure 4 shows the influence of borate-boron dissolved in the calcium bicarbonate parent solution containing 0 to 0.8g/l of magnesium ions on the crystal form of precipitated calcium carbonate. The aragonite proportion in precipitated calcium carbonate increases with increasing concentration of magnesium ions, because magnesium ions in a parent solution favor aragonite formation and inhibit calcite formation (KITANO, 1962; KITANO and HOOD, 1962; KITANO *et al.*, 1962, 1969, 1972). In the calcium bicarbonate solution containing 50 mg/l of borate-boron, the trend of increase in the aragonite proportion in precipitated calcium carbonate with increasing concentration of magnesium ions is almost similar to that in the solution without borate-boron. That is, the presence of borate-boron in the parent solution has no significant influence on the crystal form of precipitated calcium carbonate.

#### DISCUSSION

(1) *Effect of magnesium ions in a parent solution on coprecipitation of borate-boron with calcium carbonate* It was reported that mag-

nesium ions in a parent solution effectively influence the crystal form of calcium carbonate precipitated from the solution, that is, the aragonite proportion in precipitated calcium carbonate increases with increasing concentration of magnesium ions and also with increasing ratio of  $[Mg^{2+}]/[Ca^{2+}]$  in a parent solution (KITANO, 1962; KITANO and HOOD, 1962; KITANO *et al.*, 1962, 1969, 1972).

The present experiment also shows that the aragonite proportion in precipitated calcium carbonate increases with increasing concentration of magnesium ions in the calcium bicarbonate solution containing magnesium ions of 0 to 0.4g/l, and in the solution containing more than 0.4g/l of magnesium ions almost pure aragonite is precipitated.

Figure 5 indicates that the amount of borate-boron coprecipitated with calcium carbonate increases with increasing aragonite proportion in the calcium carbonate, that is, with increasing concentration of magnesium ions in the parent solution. These experimental results indicate that the crystal form of precipitated calcium carbonate is the important factor controlling the coprecipitation of borate-boron and that borate-boron is more easily coprecipitated with aragonite than with calcite. Such a phenomenon was observed for the coprecipitation of fluoride, chloride and phosphate ions with calcium car-

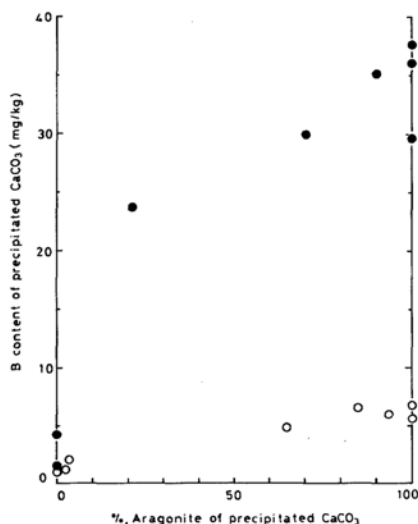


Fig. 5. Influence of the crystal form of precipitated calcium carbonate on the coprecipitation of borate-boron with calcium carbonate.

- Borate-B : 4mg/l
- Borate-B : 50mg/l

bonate (KITANO and OKUMURA, 1973; KITANO *et al.*, 1975, 1978).

(2) *Influence of sodium chloride in a parent solution on coprecipitation of borate-boron with calcium carbonate* The amounts of borate-boron coprecipitated with calcite and with aragonite respectively increase and decrease with increasing concentration of sodium chloride in a parent solution. The formation of stable complexes in a solution between sodium ions and borate ions is not known.

Borate ions in the solution form partly polymers such as  $B_3O_3(OH)_4^-$  beside monomers at the high concentrations. But at the concentrations lower than 0.025M, borate-boron in the solution exists essentially only as monomers such as  $B(OH)_3$  and  $B(OH)_4^-$  (COTTON and WILKINSON, 1966). And the ratio of  $[B(OH)_4^-]/[B(OH)_3]$  increases with increasing pH value and also with increasing concentration of salts co-existing in the solution (OWEN and KING, 1943; EDMOND and GIESKES, 1970). In the present experiment, the concentration of borate-boron in the solution is lower than 0.025M and pH value changes within the range of 7.5 to 8.2 during the process of calcium carbonate precipitation. Borate-boron in the solution of the present experiment is dissolved dominantly as the undissociated form of  $B(OH)_3$  rather than monovalent anion  $B(OH)_4^-$ .

The activity of borate ions in a solution is important for the discussion on the coprecipitation of borate-boron with calcium carbonate. The activity coefficient of undissociated  $B(OH)_3$  (slightly larger than unity) increases and that of monovalent anion  $B(OH)_4^-$  (smaller than unity) decreases with increasing concentration of dissolved chemical species (HARNED and OWEN, 1959; GARRELS and CHRIST, 1965). Then it is supposed that the change in the amount of borate-boron coprecipitated with calcium carbonate, according to the change in the sodium chloride concentration in a parent solution, is dependent on the dissolved state of borate-boron in the parent solution,  $B(OH)_3$  or  $B(OH)_4^-$ . The surface of aragonite in a solution is more basic than that of calcite. If the coprecipitation of  $B(OH)_4^-$  is dominant for aragonite and that of  $B(OH)_3$  for calcite, the trend of the coprecipitation of borate-boron with varying concentration of sodium chloride seen from Fig. 2 seems to be understood qualitatively. But there is a difficulty in explaining the big difference in the amount of the coprecipitation of borate-

boron between calcite and aragonite only from the idea. The following has been microscopically ascertained: The particle size of aragonite formed from the calcium bicarbonate solution containing sodium chloride is generally larger than those formed from the parent solution without sodium chloride. The particle size of calcite formed from the calcium bicarbonate solution containing sodium chloride is almost similar independently of the sodium chloride concentration. The adsorption mechanism proposed by ICHIKUNI and KIKUCHI (1972) may partly explain the difference in the coprecipitation of borate-boron between calcite and aragonite. The exact mechanism for the difference, however, remains unsolved to be studied.

(3) *The boron content of marine calcareous skeletons* MILLIMAN (1974) compiled the data on the concentrations of various elements in marine calcareous skeletons. The boron content of pelecypods is higher in nacreous layers the range of some ppm to some tens ppm. According to WASKOWIAK (1962), the boron content of pelecypods is higher in nacreous layers (aragonite) than in prismatic layers (calcite). Concerning the distribution of boron in recent mollusk shells, FURST *et al.* (1976) observed the following facts: (a) Boron is concentrated in calcium carbonate inorganic parts rather than in shell organic matrix parts, and is enriched more greatly in aragonite portion than in calcite portion by a factor of 1.5 to 2. (b) There is a good correlation between the boron content of aragonite portion and the salinity of seawater in which the shell has grown.

From the extrapolation of the relationship shown in Fig. 4, the borate-boron content of calcium carbonate precipitated from the calcium bicarbonate solution containing 4mg/l of borate-boron with 0.7 of ionic strength is about 5ppm in aragonite and about 3.5ppm in calcite. These results roughly agree with WASKOWIAK (1962) and FURST *et al.* (1976) for mollusk shells.

The present experiment shows a good correlation between the concentration of borate-boron in a parent solution and the boron content of calcium carbonate precipitated from the solution (Fig. 1). Considering that the constant ratio of borate-boron concentration to salinity is kept in seawater (CULKIN, 1965), we presume that this good correlation suggests that the boron content of calcareous shell fossils possibly indicates paleosalinity, as FURST *et al.* (1976) pointed out.

(4) *Influence of borate-boron dissolved in a parent solution on the crystal form of precipitated calcium carbonate* Concerning the coprecipitation of anions with calcium carbonate, the present authors have reported the following facts: Fluoride, chloride and phosphate ions are more easily coprecipitated with aragonite than with calcite, although the presence of these anions in a parent solution favors the formation of calcite and inhibits that of aragonite (KITANO, 1962; KITANO and OKUMURA, 1973; KITANO *et al.*, 1975, 1978). Sulfate ions are more easily coprecipitated with calcite than with aragonite, although the presence of sulfate ions in a parent solution favors the formation of aragonite and inhibits that of calcite (KITANO, 1962; KITANO *et al.*, 1975).

It may be expected from these facts that borate-boron in a solution favors the formation of calcitic calcium carbonate rather than aragonitic calcium carbonate, because borate-boron is more easily coprecipitated with aragonite than with calcite. However, as seen from Fig. 4, the presence of borate-boron dissolved in a parent solution does not give any significant influence on the crystal form of precipitated calcium carbonate. This may be attributed to the dissolved state of borate-boron in the solution, which is presumed to be mostly undissociated form of  $B(OH)_3$ .

**Acknowledgement**—This study was supported by a grant from the Ministry of Education.

#### REFERENCES

- COTTON, F. A. and WILKINSON, G. (1966) *Advanced inorganic chemistry*, 2nd ed. Interscience. New York.
- CULKIN, F. (1965) The major constituents of seawater. in *Chemical oceanography*, Vol. 1. ed. J. P. RILEY and G. SKIRROW, Academic Press, 121–161. London.
- EDMOND, J. M. and GIESKES, J. M. T. M. (1970) On the calculation of the degree of saturation of seawater with respect to calcium carbonate under *in situ* conditions. *Geochim. Cosmochim. Acta* **34**, 1261–1291.
- FURST, M., LOWENSTAM, H. A. and BURNETT, D. S. (1976) Radiographic study of the distribution of boron in recent mollusc shells. *Geochim. Cosmochim. Acta* **40**, 1381–1386.
- GARRELS, R. M. and CHRIST, C. L. (1965) *Solutions, minerals, and equilibria*. Harper and Row. New York.
- GRINSTEAD, R. R. and SNIDER, S. (1967) Modification of the curcumin method for low level boron determination. *Analyst* **92**, 532–533.
- HARNED, H. S. and OWEN, B. B. (1958) *The physical chemistry of electrolytic solutions*, 3rd ed. Reinhold. New York.
- ICHIKUNI, M. and KIKUCHI, K. (1972) Retention of boron by travertines. *Chem. Geol.* **9**, 13–21.
- KITANO, Y. (1962) The behavior of various inorganic ions in the separation of calcium carbonate from a bicarbonate solution. *Bull. Chem. Soc. Japan* **35**, 1973–1980.
- KITANO, Y. and KAWASAKI, N. (1958) Behavior of strontium ion in the process of calcium carbonate separation from bicarbonate solution. *J. Earth Sci. Nagoya Univ.* **6**, 63–74.
- KITANO, Y., PARK, K. and HOOD, D. W. (1962) Pure aragonite synthesis. *J. Geophys. Res.* **67**, 4873–4874.
- KITANO, Y. and HOOD, D. W. (1962) Calcium carbonate crystal formed from sea water by inorganic processes. *J. Oceanogr. Soc. Japan* **18**, 208–219.
- KITANO, Y., TOKUYAMA, A. and KANAMORI, N. (1968) Measurement of the distribution coefficient of zinc and copper between carbonate precipitate and solution. *J. Earth Sci. Nagoya Univ.* **16**, 1–102.
- KITANO, Y., KANAMORI, N. and TOKUYAMA, A. (1969) Effect of organic matter on solubilities and crystal form of carbonates. *Am. Zoologist* **9**, 681–688.
- KITANO, Y., KANAMORI, N. and TOKUYAMA, A. (1970) Influence of organic matter on inorganic precipitation, in *Organic matter in natural waters*, ed. D. W. HOOD, Inst. of Marine Sci. Univ. of Alaska, 413–447.
- KITANO, Y., KANAMORI, N. and OOMORI, T. (1971) Measurements of distribution coefficients of strontium and barium between carbonate and solution - Abnormally high values of distribution coefficients measured at early stages of carbonate formation. *Geochem. J.* **4**, 183–206.
- KITANO, Y. and OOMORI, T. (1971) The coprecipitation of uranium with calcium carbonate. *J. Oceanogr. Soc. Japan* **27**, 34–42.
- KITANO, Y. and TERAOKA, H. (1972) Measurement of the distribution coefficient of minor elements between carbonate precipitate and solution - Strontium-barium coexistent system. *Kaseki* **23/24**, 26–32 (in Japanese).
- KITANO, Y., YOSHIOKA, S. and KANAMORI, N. (1972) The mineral composition of calcium carbonate formed in the processes of separation from bicarbonate solution. *Kaseki* **23/24**, 3–14 (in Japanese).
- KITANO, Y. and OKUMURA, M. (1973) Coprecipitation of fluoride with calcium carbonate. *Geochem. J.* **7**, 37–49.
- KITANO, Y., OKUMURA, M. and IDOGAKI, M. (1975) Incorporation of sodium, chloride and sulfate with calcium carbonate. *Geochem. J.* **9**, 75–84.
- KITANO, Y., OKUMURA, M. and IDOGAKI, M. (1978)

- Uptake of phosphate ions by calcium carbonate.  
*Geochem. J.* **12**, 29–37.
- MILLIMAN, J. D. (1974) *Marine carbonates*. Springer-Verlag.
- MUTO, S. (1952) Geochemistry of boron, II. Boron in travertines from Isobe Mineral Spring. *Nippon Kagaku Zasshi* **73**, 110–112 (in Japanese).
- OWEN, B. B. and KING, E. J. (1943) The effect of sodium chloride upon the ionisation of boric acid at various temperatures. *J. Am. Chem. Soc.* **65**, 1612–1620.
- WASKOWIAK, R. (1962) Geochemische Untersuchungen an rezenten Molluskenschalen mariner Herkunft. *Freiberger Forschungsh.* **136**, 1–155.