

**Measurements of distribution coefficients of strontium
and barium between carbonate precipitate and solution
– Abnormally high values of distribution coefficients
measured at early stages of carbonate formation**

YASUSHI KITANO, NOBUKO KANAMORI
and TAMOTSU OOMORI

Water Research Laboratory, Faculty of Science,
Nagoya University, Chikusa, Nagoya, Japan

(Received December 7, 1970; in revised form February 23, 1971)

Abstract—The distribution coefficients of Sr and Ba were measured when Mg-poor calcite, Mg-rich calcite or aragonite was precipitated in the calcium bicarbonate solutions containing strontium or barium in trace amounts, MgCl₂, NaCl and/or Na-citrate. The abnormally high values of the distribution coefficients were observed very often at the early stages of carbonate precipitation. The conditions, under which such high values are measured, are investigated. And the use of distribution coefficients measured in the laboratory for interpretation of the trace element contents of marine carbonate skeletons is discussed.

INTRODUCTION

It was reported that the strontium content of calcareous skeletons of marine organisms indicates the chemical composition of sea water in which the skeletons were formed (ODUM, 1951; LOWENSTAM, 1961; KULP *et al.*, 1952; LERMAN, 1965a; TUREKIAN, 1955). Since the result made a great contribution to the geochemistry of the sea, the distribution of trace elements in marine calcareous skeletons has been studied very actively. For this line of research, a clear relation should be known between chemical composition of sea water and trace element content of marine calcareous skeletons.

Two approaches have been used to study the relation: (1) field observations to investigate the relationships between the trace element contents of carbonate skeletons collected and the physicochemical nature of the environment in which the skeletons were formed (BOWEN, 1956; CHAVE, 1954; DODD, 1965, 1967; GRAF, 1960; HALLAM and PRICE, 1968; LERMAN, 1965b; LOWENSTAM, 1963, 1964; ODUM, 1957; PILKEY and HOWER, 1960, 1963; SIEGEL, 1960, 1961; THOMPSON and CHOW, 1955; TUREKIAN, 1957, 1964; TUREKIAN and KULP, 1956; TUREKIAN and ARMSTRONG, 1960). (2) laboratory experiments for measurement of distribution coefficients of trace elements between solution and carbonate precipitated in the solution (HOLLAND *et al.*, 1963, 1964a, 1964b; KINSMAN and HOLLAND, 1969; KINSMAN, 1969; KITANO *et al.*, 1968, 1970;

KITANO and OOMORI, 1971; TSUSUE and HOLLAND, 1966; TSUSUE, 1970). We have studied the trace element contents of carbonate skeletons following the line of the second approach, and discussed the distribution coefficients of zinc and copper measured in various solution systems controlled in the laboratory (KITANO *et al.*, 1968). The ionic radii of zinc and copper are smaller than that of calcium, and their carbonates have only calcite crystal form.

The present paper reports on measurements of the distribution coefficients of strontium and barium between carbonate precipitate and solution. The ionic radii of strontium and barium are larger than that of calcium. Although their carbonates have only aragonite crystal form, the presence of barium ions in a parent solution even in a very small amount is greatly favorable for calcite formation, and the presence of strontium ions has little influence on the crystal form (KITANO, 1962).

Abnormally high values of the distribution coefficients have been measured very often particularly at the early stages of carbonate precipitation (TSUSUE and HOLLAND, 1966; KITANO *et al.*, 1968). The authors have investigated the conditions under which such high values are measured.

The measured values of the distribution coefficients are examined thermodynamically to clarify the factors controlling the strontium and barium contents of carbonates. And the use of the distribution coefficients measured in the laboratory is discussed in relation with the interpretation of the trace element contents of marine calcareous skeletons.

EXPERIMENTAL

Measurement of distribution coefficient

The three carbonates, Mg-poor calcite, Mg-rich calcite and aragonite are observed in the skeletal carbonates of marine organisms (KITANO *et al.*, 1969). Each of the three was synthesized at low temperatures and pressures from the calcium bicarbonate solutions containing sodium chloride, magnesium chloride and/or sodium citrate, by controlling the amounts of magnesium chloride and sodium citrate added to calcium bicarbonate solution (KITANO and HOOD, 1962; KITANO and KANAMORI 1966; KITANO *et al.*, 1968, 1969, 1970; KITANO, 1963). These three salts are found in the body fluids of marine calcareous organisms. The values of the distribution coefficients of strontium and barium were measured in solution systems in which the three carbonate crystals were precipitated.

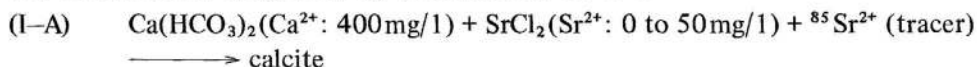
Procedure

Sodium chloride, magnesium chloride and sodium citrate in various proportions were placed in reaction vessels containing calcium bicarbonate solution (Ca^{2+} : 400mg/l) and strontium chloride or barium chloride, where $^{85}\text{Sr}^{2+}$ or $^{140}\text{Ba}^{2+}$ was added into the solution as a tracer. It is noted that trace amounts of strontium and barium are

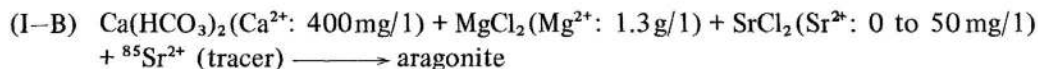
contained in some reagents used here. The solutions in the reaction vessels were stirred very slowly or fairly vigorously with a magnetic stirrer for various length of time at $20 \pm 1^\circ\text{C}$ (KITANO *et al.*, 1968, 1970). The duration of runs ranged from one week to one month. The release of carbon dioxide gas from the parent solution was followed by carbonate precipitation. During the process of carbonate precipitation, portions of a supernatant solution were taken up to determine the change in pH and the decrease in the calcium and strontium (or barium) contents of the solution with the lapse of time. And the values of the distribution coefficient were calculated with the Doerner-Hoskins' equation: $K_{\text{Me}}^{\text{S}} = \log(M_{\text{Me, initial}}^{\text{L}}/M_{\text{Me, final}}^{\text{L}})/\log(M_{\text{Ca, initial}}^{\text{L}}/M_{\text{Ca, final}}^{\text{L}})$, where $M_{\text{Me, initial}}^{\text{L}}$ and $M_{\text{Ca, initial}}^{\text{L}}$ denote the molar concentrations of Me (Sr or Ba) and Ca dissolved in an original parent solution, respectively and $M_{\text{Me, final}}^{\text{L}}$ and $M_{\text{Ca, final}}^{\text{L}}$ denote the molar concentrations of Me and Ca dissolved in a final parent solution, respectively, (KITANO *et al.*, 1968, 1970). Eventually, the formed carbonate precipitates were filtered off and washed with distilled water. After having been dried, a fraction of the precipitates was used for the determination of the chemical composition, while another fraction was used for the identification of the crystal form by an X-ray diffractometer. Calcium in solution was determined volumetrically with EDTA solution, and strontium and barium in solution were determined radio-chemically by a γ -ray spectrometer. Mostly, the measured values of the distribution coefficients of strontium and barium decreased with increasing percentage of calcium precipitated from the parent solution. And a nearly constant value was obtained at the late stages of carbonate precipitation, which was taken as the value of distribution coefficient.

RESULTS

[1] Distribution coefficient of strontium at $20 \pm 1^\circ\text{C}$



Calcite is precipitated with very slow stirring, and the value of the distribution coefficient was measured as shown in Fig.1. The figure shows that the value of K_{Sr}^{C} (distribution coefficient of Sr between calcite and solution) is 0.08 ± 0.02 .



Only aragonite is precipitated with very slow stirring from this solution. The value of K_{Sr}^{A} (distribution coefficient of Sr between aragonite and solution) is shown in Fig.1. The figure shows that the value of K_{Sr}^{A} is 1.1 ± 0.1 . The change in magnesium concentration from 0.5 to 3 g/1 did not have any effect on the value. It is very clear that the value of K_{Sr}^{A} is larger than that of K_{Sr}^{C} . This is easily understood, because SrCO_3 is always of aragonitic lattice configuration. The value measured in this solution is considered to be a thermodynamic value of the distribution coefficient. The thermo-

dynamic distribution coefficient, $K_{Sr}^{T,A}$, is written: $K_{Sr}^{T,A} = S_{CaCO_3(aragonite)}^0 / S_{SrCO_3}^0 \div 1$ where $S_{CaCO_3(aragonite)}^0$ and $S_{SrCO_3}^0$ denote the solubility products of $CaCO_3$ (aragonite) and $SrCO_3$ (aragonite form) in distilled water, respectively (KITANO *et al.*, 1968, 1970). The value of the distribution coefficient measured in this solution almost agrees with the value of the thermodynamic distribution coefficient calculated with the above equation (see Fig.1).

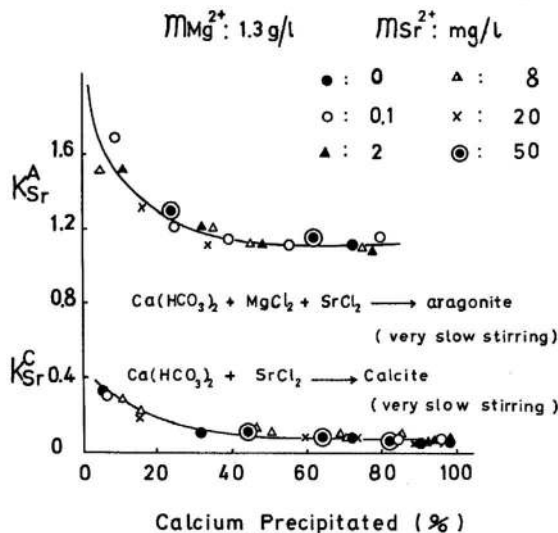
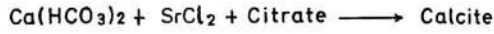


Fig.1. Distribution coefficient, K_{Sr}^C or K_{Sr}^A , plotted against per cent calcium precipitated at 20°C.

(I-C) $Ca(HCO_3)_2$ (Ca^{2+} : 400mg/l) + $SrCl_2$ (Sr^{2+} : 8mg/l) + $^{85}Sr^{2+}$ (tracer) + Na-citrate (citrate: 1.2×10^{-5} to 5.1×10^{-3} mol/l) \longrightarrow calcite

Fig.2 shows the value of K_{Sr}^C measured in this solution system. From Fig.2 it can be seen that the value increases with increasing concentration of citrate added to the calcium bicarbonate parent solution containing 8mg of strontium per liter. The value of K_{Sr}^C is around 0.4 when the concentration of citrate in a parent solution is 10^{-3} mol/l, whereas the value is around 0.1 when it is 10^{-5} mol/l. This trend could be explained partly from the difference in stability constants between Ca and citrate, and Sr and citrate (see Result [II]). And further Fig.2 indicates that the high values of K_{Sr}^C are measured at the early stages of carbonate precipitation and decrease with increasing amount of carbonate precipitated. It is observed that the presence of citrate dissolved in a parent solution does not cause the growth from fine crystals formed at the early stages of carbonate formation to large crystals but the aggregation of the fine crystals. This fact is observed in the cases of (I-D), (II-E), (II-F) and (II-G). They will be discussed in the section of Discussion in this paper.



$M_{\text{Sr}^{2+}} : 8 \text{ mg/l}$

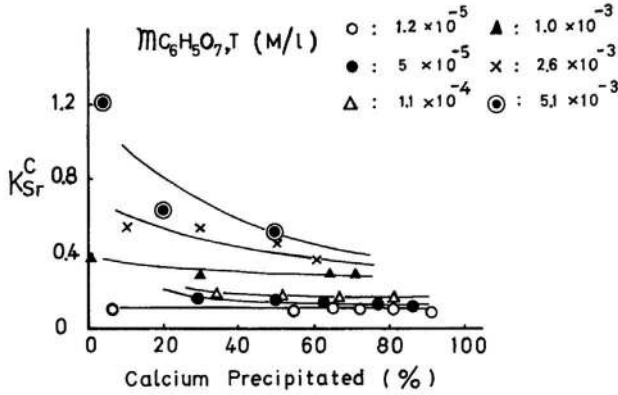
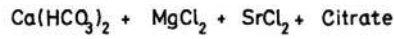


Fig.2. Distribution coefficient, K_{Sr}^{C} , plotted against per cent calcium precipitated at 20°C.



$M_{\text{Mg}^{2+}} : 1.3 \text{ g/l}$ $M_{\text{C}_6\text{H}_5\text{O}_7, \text{T}} \text{ M/l}$
 $M_{\text{Sr}^{2+}} : 8 \text{ mg/l}$

$\bullet : 1.1 \times 10^{-5}$ $\blacktriangle : 1.0 \times 10^{-3}$
 $\circ : 5.1 \times 10^{-5}$ $\times : 2.6 \times 10^{-3}$
 $\triangle : 1.0 \times 10^{-4}$

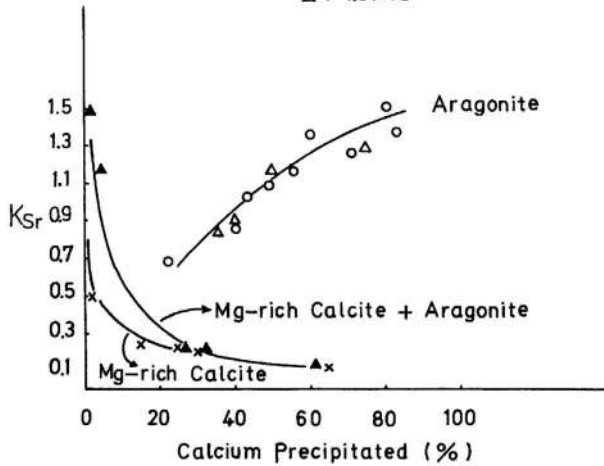
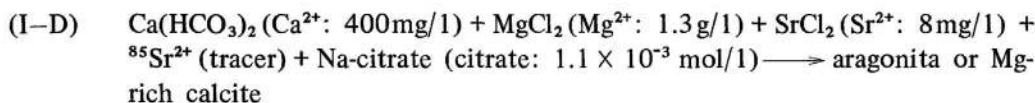


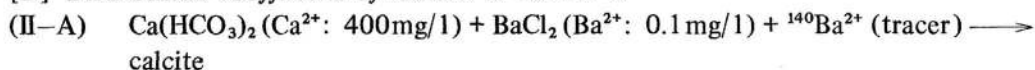
Fig.3. Distribution coefficient, K_{Sr} , plotted against per cent calcium precipitated at 20°C.



The values of $K^{\text{C or A}}$ in this solution system are shown in Fig.3. When the concentration of citrate in a parent solution is higher than 1×10^{-3} mol/l, Mg-rich calcite is precipitated, and the value of K_{Sr}^{C} is around 0.1. When it is less than 1×10^{-4} mol/l, only aragonite is precipitated and the value of K_{Sr}^{A} is larger than 1. Those results are in agreement with those obtained in Fig.1.

The change in the values of K_{Sr}^{A} and K_{Sr}^{C} with increasing carbonate precipitation will be discussed later in the section of Discussion.

[II] *Distribution coefficient of barium at $20 \pm 1^\circ\text{C}$*



The values of K_{Ba}^{C} were measured when calcite is precipitated with slow stirring,

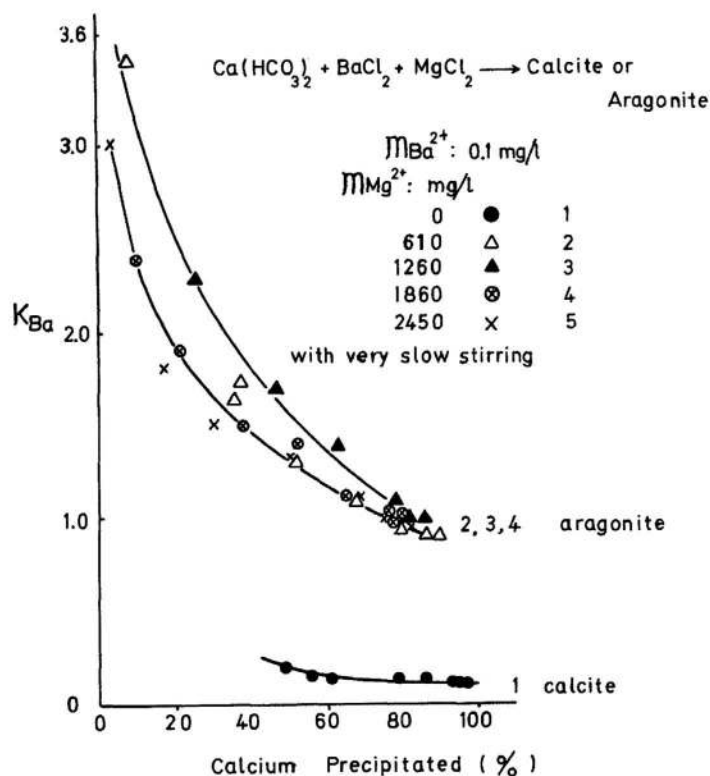


Fig.4. Distribution coefficient, $K_{\text{Ba}}^{\text{C or A}}$, plotted against per cent calcium precipitated at 20°C .

as shown in Fig.4. And also the values were measured when calcite is precipitated with fairly vigorous stirring, as shown in Fig.5. Fig.4 shows that the value of K_{Ba}^C is around 0.1 at slow precipitation. Fig.5 indicates that stirring makes it impossible to give a constant value of K_{Ba}^C throughout the process of carbonate precipitation, and that vigorous stirring makes the values of K_{Ba}^C surprisingly large.

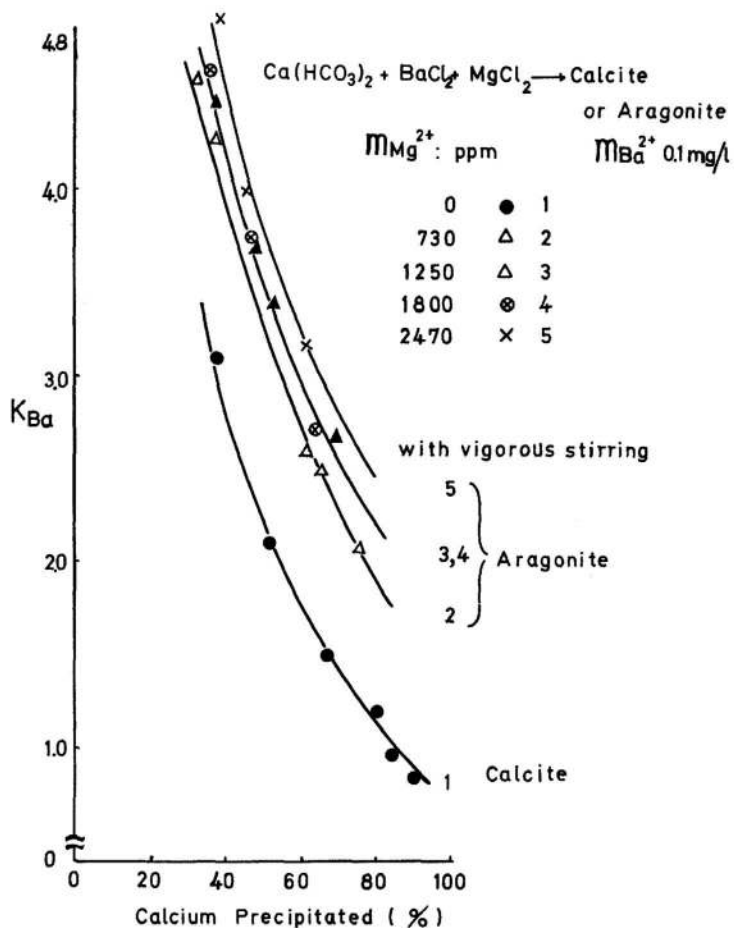
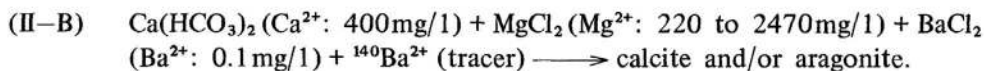


Fig.5. Distribution coefficient, $K_{Ba}^{C \text{ or } A}$, plotted against per cent calcium precipitated at 20°C.



The presence of Mg^{2+} in a parent solution favors aragonite formation, whereas the presence of Ba^{2+} favors calcite formation. The competition occurs between the influ-

ences of Mg^{2+} and Ba^{2+} in a parent solution on the crystal form of carbonate formed from the solution. Figs.4 and 5 show the values of K_{Ba}^C and K_{Ba}^A measured without and with vigorous stirring. With very slow stirring of a parent solution, the value of K_{Ba}^A is around 1 (*cf.* Fig.6), which may be considered as a thermodynamic distribution coefficient, $K_{Ba}^{T,A}$. $K_{Ba}^{T,A}$ is written: $K_{Ba}^{T,A} = S_{CaCO_3(\text{aragonite})}/S_{BaCO_3} \doteq 1$, where $S_{CaCO_3(\text{aragonite})}$ and S_{BaCO_3} denote the solubility products of aragonite and $BaCO_3$ in distilled water, respectively. The thermodynamically calculated value agrees with the experimentally measured value. Vigorous stirring of a parent solution makes it impossible to give a constant value of K_{Ba}^A even at the later stages of carbonate precipitation, and it makes the measured values surprisingly large. The constant value of K_{Ba}^A becomes more difficult to be measured and becomes larger with increasing concentration of Mg^{2+} in a parent solution.

(II-C) $Ca(HCO_3)_2$ (Ca^{2+} : 400mg/l) + $MgCl_2$ (Mg^{2+} : 1.26 g/l) + $BaCl_2$ (Ba^{2+} : 0 to 100 mg/l) + $^{140}Ba^{2+}$ (tracer) \longrightarrow calcite or aragonite

Various amounts of Ba^{2+} are added to the calcium bicarbonate solution containing 1.26g of Mg^{2+} per liter. With very slow stirring, Mg-poor calcite is precipitated from the solutions containing more than 50mg of Ba^{2+} per liter and aragonite is precipitated from solutions containing less than 10mg of Ba^{2+} per liter. The results are shown in Fig.6, from which it can be seen that the value of K_{Ba}^C is around 0.1 and the value of

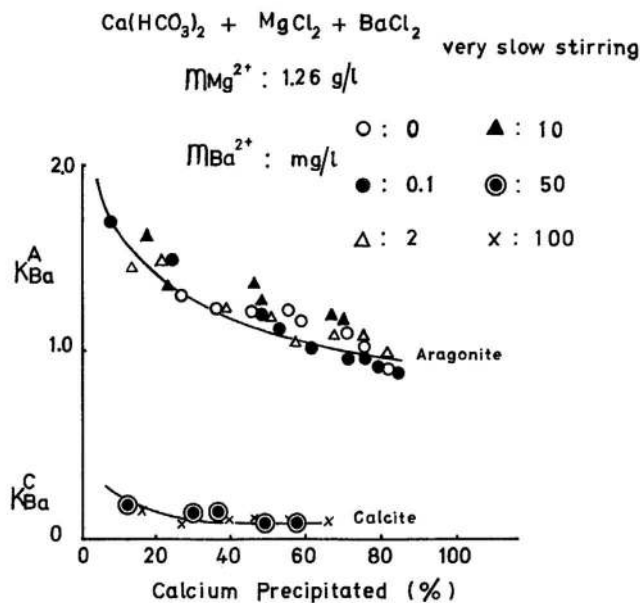
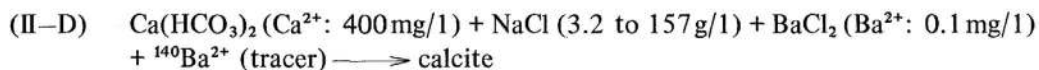


Fig.6. Distribution coefficient, $K_{Ba}^{C \text{ or } A}$, plotted against per cent calcium precipitated at 20°C.

K_{Ba}^A is around 1. These values agree with those given in Figs.4 and 5. Fig.6 shows that very slow stirring gives easily a constant value of the distribution coefficient of Ba in comparison with Figs.4 and 5.



Calcite is precipitated with very slow stirring in this solution system. The measured value of the distribution coefficient is shown in Fig.7. The presence of sodium chloride in a parent solution seems to have a little effect on the value of the distribution coefficient. And the value of K_{Ba}^C in this solution system is around 0.07.

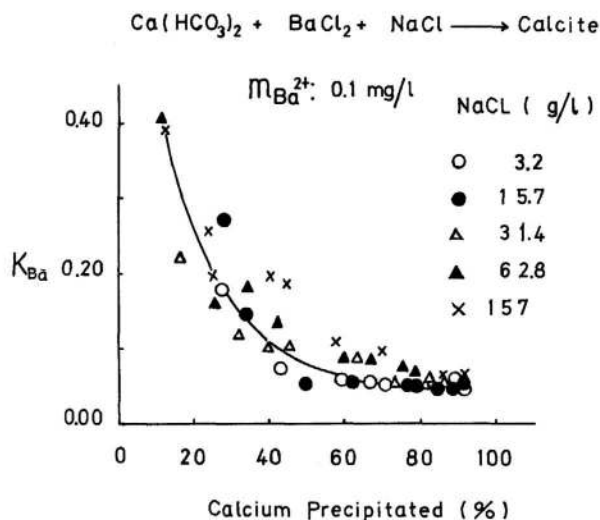
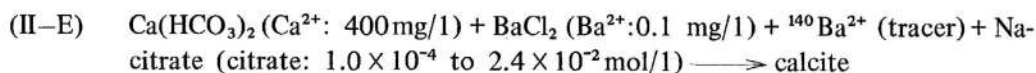


Fig.7. Distribution coefficient, K_{Ba}^C , plotted against per cent calcium precipitated at 20°C.



The values of K_{Ba}^C measured in this solution are shown in Fig.8. Even for calcite, the value of the distribution coefficient K_{Ba}^C is often very large, especially at a high concentration of citrate in a parent solution. The addition of citrate to a parent solution greatly inhibits to give a constant value of K_{Ba}^C and makes the value of K_{Ba}^C very large. The reason for the inhibition remains unexplained. The appearance of an abnormally high value of K_{Ba}^C at the early stages of carbonate precipitation will be discussed in the section of Discussion.

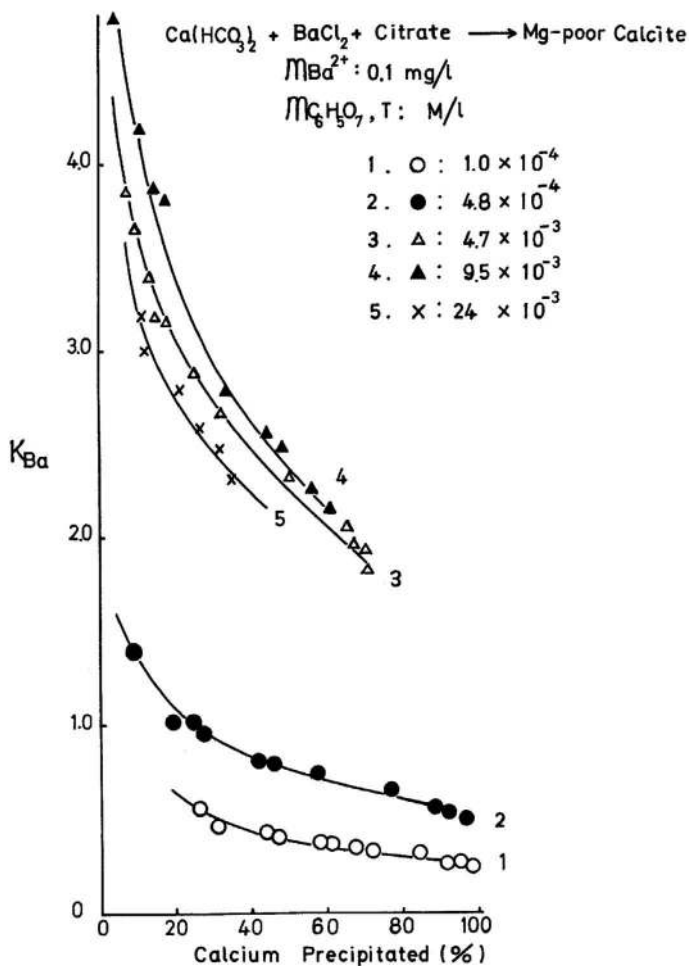


Fig.8. Distribution coefficient, K_{Ba}^{C} , plotted against per cent calcium precipitated at 20°C.

(II-F) $\text{Ca}(\text{HCO}_3)_2$ ($\text{Ca}^{2+} : 400 \text{ mg/l}$) + MgCl_2 ($\text{Mg}^{2+} : 1.26 \text{ g/l}$) + BaCl_2 ($\text{Ba}^{2+} : 0.1 \text{ mg/l}$) + $^{140}\text{Ba}^{2+}$ (tracer) + Na-citrate (citrate : 0.1×10^{-3} to $16 \times 10^{-3} \text{ mol/l}$) \longrightarrow aragonite and aragonite + Mg-rich calcite

Fig.9. shows that in this solution system the constant value of the distribution coefficient can not be obtained. The values are tremendously high, in particular, at the early stages of precipitation. With increasing concentration of citrate in a parent solution, the diffuseness of the X-ray diffraction pattern of precipitates increases owing to the smaller size of the crystallized domain of carbonate precipitates (*cf.* Fig.10 and I-C) and the value of the distribution coefficient becomes abnormally high. The

numbers in Fig.10 correspond to those in Fig.9. Although experimental results have not been examined sufficiently, it seems to be clear that the condition of crystal formation such as aggregation and growth of calcium carbonate crystals has a very significant influence on the coprecipitation of trace elements with calcium carbonate.

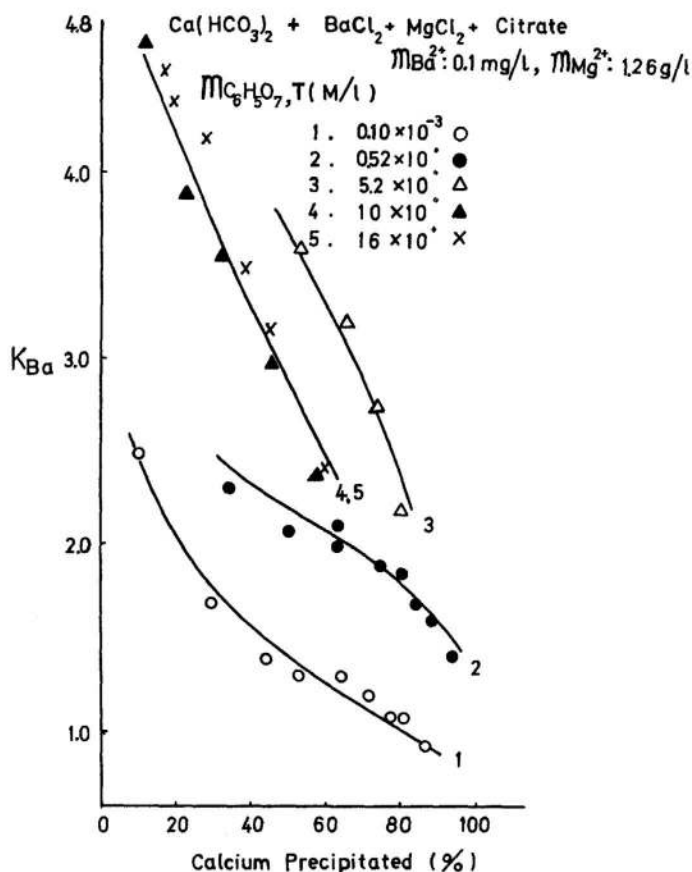


Fig.9. Distribution coefficient, K_{Ba} , plotted against per cent calcium precipitated at 20°C.

(II-G) Ca(HCO₃)₂ (Ca²⁺: 400mg/l) + MgCl₂ (Mg²⁺: 230 to 2560mg/l) + Na-citrate (citrate: 5.2×10^{-3} mol/l) + BaCl₂ (Ba²⁺: 0.1 mg/l) + ¹⁴⁰Ba²⁺ (tracer) → Mg-poor calcite, Mg-poor calcite + Mg-rich calcite, or Mg-rich calcite + aragonite

The results are shown in Fig.11, which indicates following facts: The constant value of K_{Ba}^S can not be obtained. And the value of K_{Ba}^S becomes high with decreasing

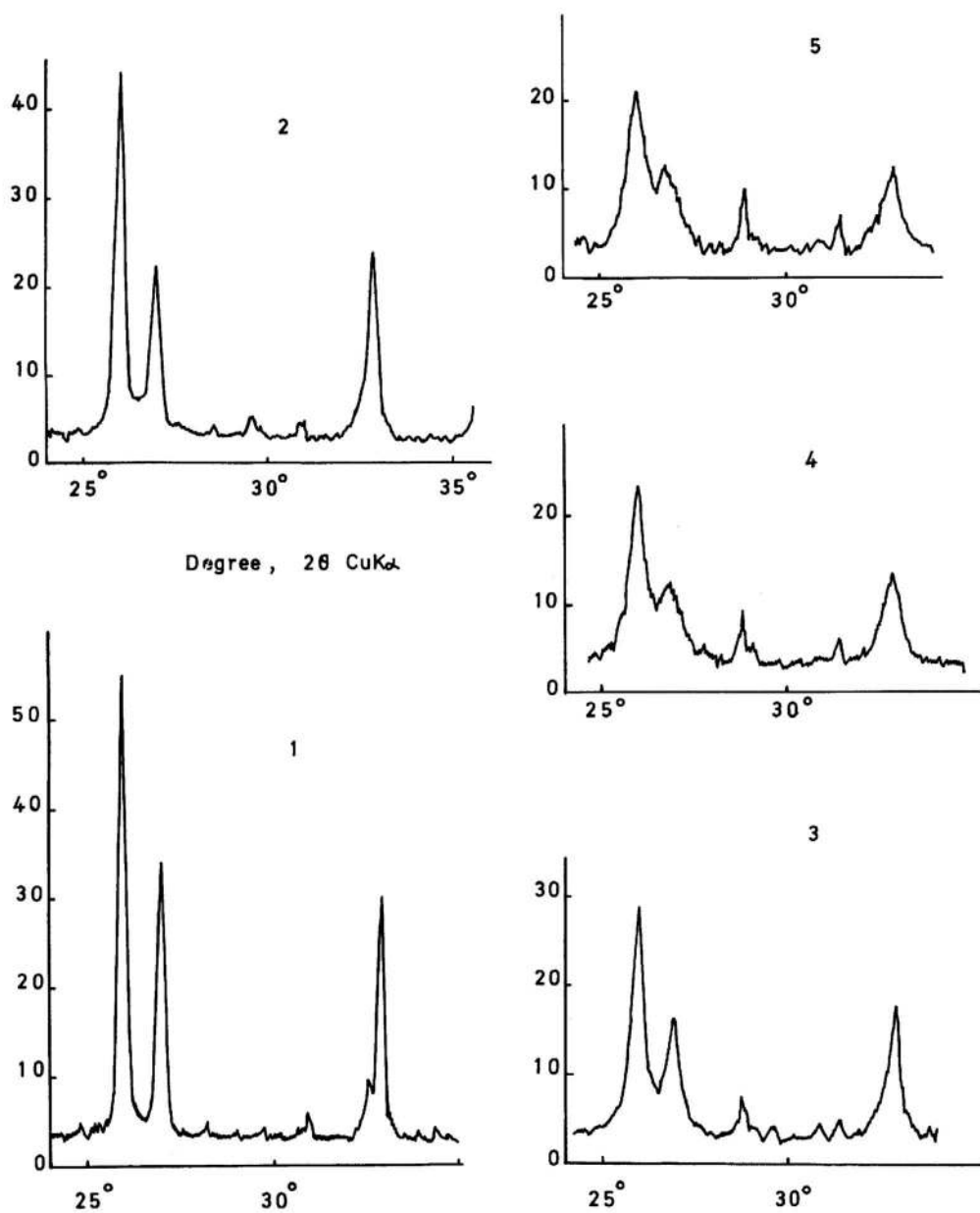


Fig.10. X-ray powder patterns of carbonate precipitates formed from the solution " $\text{Ca}(\text{HCO}_3)_2 + \text{MgCl}_2 + \text{Na} \cdot \text{Citrate} + \text{BaCl}_2$ " at 20°C.

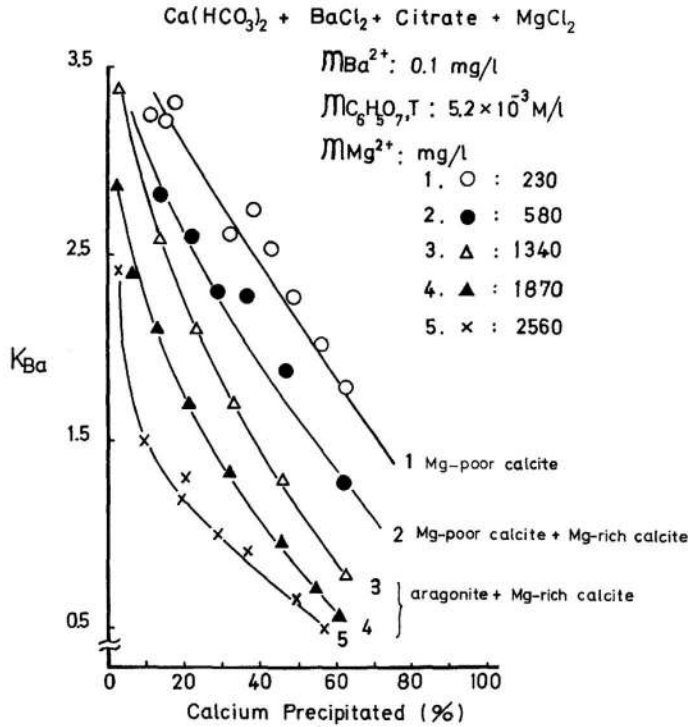


Fig.11. Distribution coefficient, K_{Ba}^C , plotted against per cent calcium precipitated at 20°C.

concentration of Mg²⁺ in a parent solution. And it is noted that the amount of Ba coprecipitated with calcite is larger than that with aragonite in this solution system.

DISCUSSION

[I] *Abnormally high values of distribution coefficient measured at the early stages of precipitation process*

Originally, strontium and barium should be hardly captured in the crystal lattice of a stable calcite, because SrCO₃ and BaCO₃ have only aragonite crystal form. However, coprecipitation of Sr and Ba with calcite is observed particularly at the early stages of carbonate precipitation, as shown in Figs.1 to 11. This might indicate that the properties of fine precipitates of calcite formed at the earlier stages of precipitation should be different from those of large and stable crystals of calcite observed at the later stages of precipitation. The fine calcite precipitates capture strontium and barium probably because of the abnormal nature of the calcite precipitates, but large and stable calcite crystals may not capture them. The activity of calcium carbonate of the fine precipitates should be different from unity (PYTKOWICZ, 1969). A clear X-ray

pattern of calcite was taken for precipitates collected at the end of the precipitation process. Therefore, the fine calcite precipitates formed at the earlier stages seem to have transformed to large and stable calcite crystals after some time, during which the precipitates had been in contact with the parent solution. The values of K_{Sr} and K_{Ba} were calculated by using the Doerner-Hoskins' equation given in EXPERIMENTAL, where M_{Sr}^L (or Ba), initial and M_{Ca}^L , initial denote the molar concentrations of Sr (or Ba) and Ca, respectively, dissolved in the original parent solution and M_{Sr}^L (or Ba), final and M_{Ca}^L , final denote the molar concentrations of Sr (or Ba) and Ca, respectively, dissolved in the solution after some time from the start of the precipitation experiment. The plots in Figs.1 to 11 are the values of distribution coefficient calculated, by using Doerner-Hoskins' equation, from the difference between the calcium and trace element (Sr or Ba) contents of the original solution and those of the solution at each stage of pre-

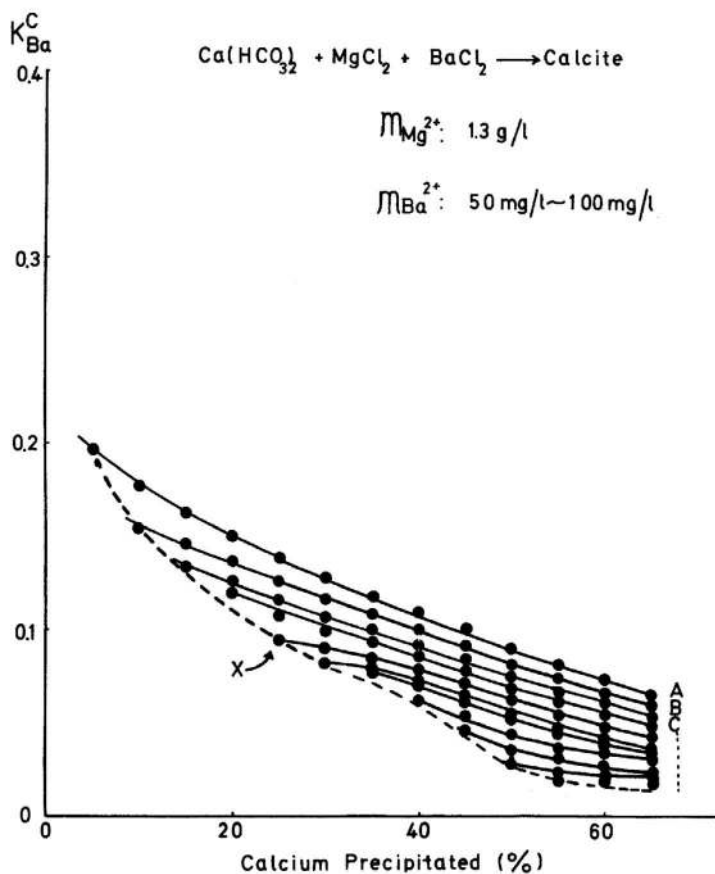


Fig.12. Distribution coefficient, K_{Ba}^C , plotted against per cent calcium precipitated at 20°C.

cipitation.

Now, the values of K_{Ba}^C and K_{Ba}^A are recalculated as shown in Figs.12 and 13, where K_{Ba}^C and K_{Ba}^A are plotted against the amount of calcium precipitated: Curve A shows the values of $K_{Ba}^{C \text{ or } A}$ calculated in the same way as in Figs.1 to 11. The values of $K_{Ba}^{C \text{ or } A}$ in curves B, C and so forth are calculated in the same way as curve A, but assuming the next stage of carbonate precipitation as the original solution. Then, broken line X shows the values of $K_{Ba}^{C \text{ or } A}$ between one stage of carbonate precipitation as the original solution and the next stage as the final solution.

At the late stages of carbonate precipitation, large and stable calcite or aragonite crystals are considered to be precipitated. And therefore, these figures might indicate that barium is hardly captured in the crystal lattice of large and stable calcite, but is easily captured in the crystal lattice of large and stable aragonite. Curve X may indicate that the mechanism of coprecipitation of barium with carbonate precipitates at the early stage is different from that at the late stage of carbonate precipitation. The experimental results show that Ba is captured by calcite precipitates. It should

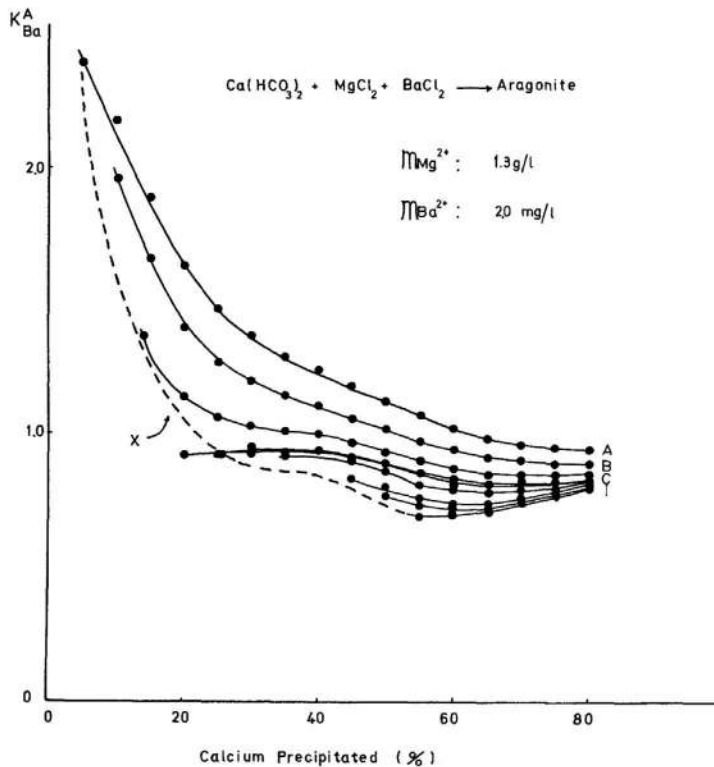


Fig.13. Distribution coefficient, K_{Ba}^C , plotted against per cent calcium precipitated at 20°C.

be considered that coprecipitation of Ba with calcite precipitates is due to an abnormal state and nature of the calcite precipitates formed at the early stages of precipitation such as a nucleation stage. And these figures further indicate that the captured barium is not released from the precipitates but remains even through the process of transformation or growth from the fine precipitates to large and stable crystals.

Figs.1 to 11 show that carbonate precipitates formed at a nucleation stage are never pure calcium carbonate but contain barium carbonate in large amounts. This fact should be of much importance for discussion on nucleation phenomena and on the mechanism underlying the effects of metal ions in a parent solution on the crystal form of calcium carbonate. It will be reported in detail elsewhere.

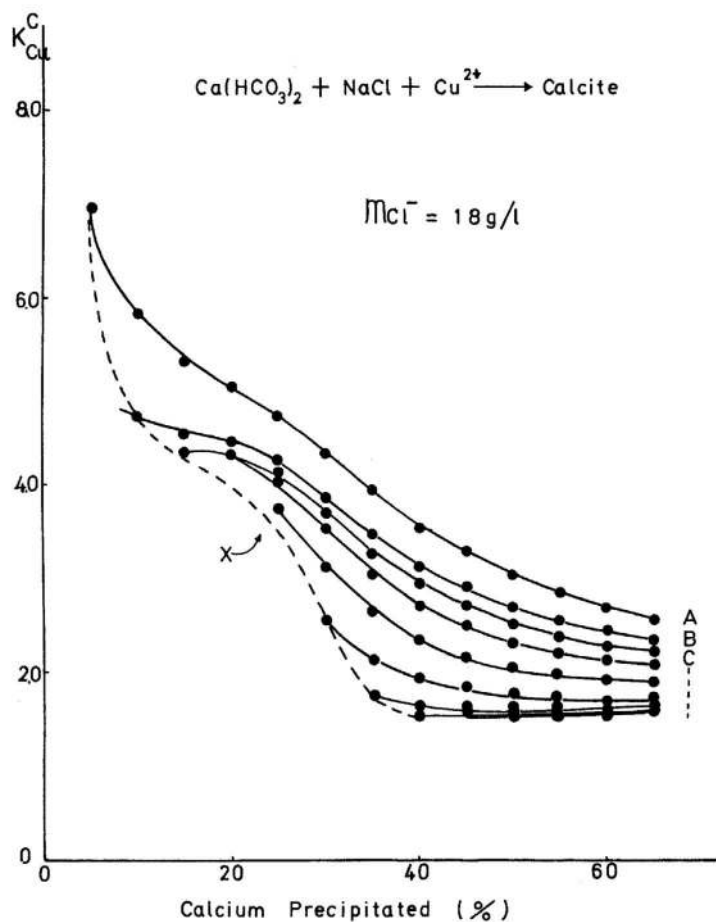


Fig.14. Distribution coefficient, K_{Cu}^{C} , plotted against per cent calcium precipitated at 20°C.

The same results, discussion and conclusions were obtained in the case of Sr as in the case of Ba.

We reported on measurements of the distribution coefficients of zinc and copper (KITANO *et al.*, 1968). Zinc and copper carbonates have only calcite crystal form. According to the experimental results, a large amount of copper is captured by aragonite precipitates formed at the early stages of precipitation as well as by calcite precipitates. The same recalculation is made for K_{Cu}^C and K_{Cu}^A as for K_{Ba}^C and K_{Ba}^A . Figs.14 and 15 show the recalculated results for Cu, where the same marks as those in Figs.12 and 13 are used. And the results make it possible to conclude the following: Copper is coprecipitated with stable calcite- $CaCO_3$ but not with stable aragonite- $CaCO_3$. The same conclusion as for Cu is reached for Zn. And it is known that copper and zinc are captured by aragonite precipitates formed at early stages, and that they are not released to solution even through the process of transformation from fine and

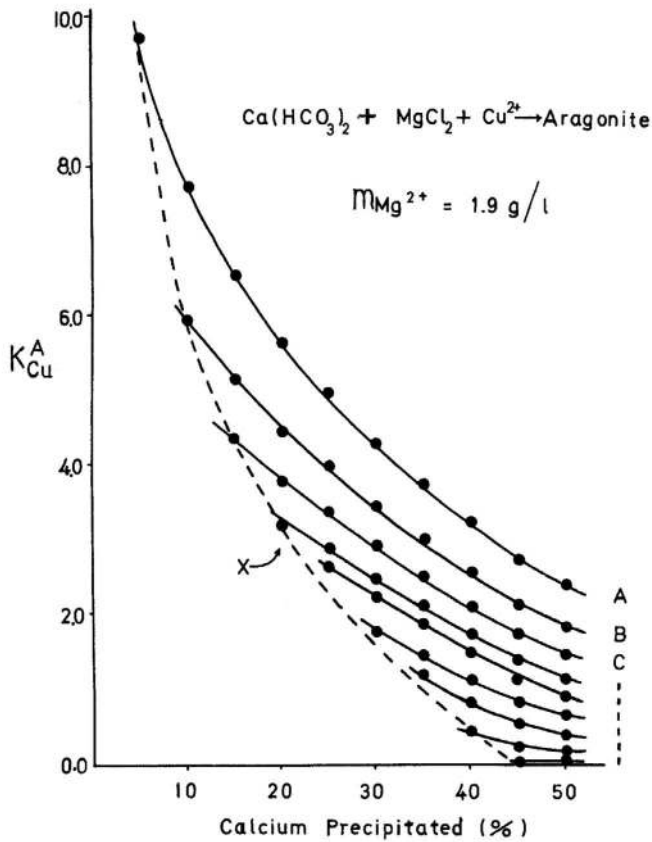


Fig.15. Distribution coefficient, K_{Cu}^A , plotted against per cent calcium precipitated at 20°C.

unstable aragonite precipitates to large and stable aragonite crystals.

Those experimental results indicate that the value of the distribution coefficient depends on appearance of the abnormal precipitates formed at the early stages of precipitation. It is not known whether such abnormal precipitates are formed during the process of marine skeletal carbonate formation.

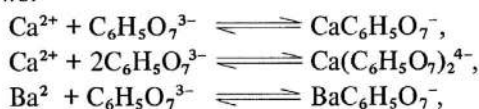
The mechanism for appearance of the abnormally high values at the early stages has not yet been clarified (TSUSUE *et al.*, 1966; TSUSUE, 1970).

[II] Reasonable change in the value of distribution coefficient with increasing amount of precipitated carbonate

The value of the distribution coefficient of Ba in the following solution system is discussed:

$\text{Ca}(\text{HCO}_3)_2 + \text{Na-citrate} + \text{BaCl}_2 + {}^{140}\text{Ba}^{2+} \longrightarrow \text{calcite}$ (see RESULTS, II-E).

Citrate ions form complexes with calcium and barium ions, and the stability constants are as follows:



$$\frac{M_{\text{CaC}_6\text{H}_5\text{O}_7^{-}}^{\text{L}}}{M_{\text{Ca}^{2+}}^{\text{L}} \cdot M_{\text{C}_6\text{H}_5\text{O}_7^{3-}}^{\text{L}}} = 10^{3.22}, \quad \frac{M_{\text{Ca}(\text{C}_6\text{H}_5\text{O}_7)_2^{4-}}^{\text{L}}}{M_{\text{Ca}^{2+}}^{\text{L}} \cdot (M_{\text{C}_6\text{H}_5\text{O}_7^{3-}}^{\text{L}})^2} = 10^{8.02}, \quad \frac{M_{\text{BaC}_6\text{H}_5\text{O}_7^{-}}^{\text{L}}}{M_{\text{Ba}^{2+}}^{\text{L}} \cdot M_{\text{C}_6\text{H}_5\text{O}_7^{3-}}^{\text{L}}} = 10^{2.84} \quad (1)$$

where $M_{\text{Ca}^{2+}}^{\text{L}}$, $M_{\text{C}_6\text{H}_5\text{O}_7^{3-}}^{\text{L}}$, $M_{\text{CaC}_6\text{H}_5\text{O}_7^{-}}^{\text{L}}$, $M_{\text{Ca}(\text{C}_6\text{H}_5\text{O}_7)_2^{4-}}^{\text{L}}$, $M_{\text{Ba}^{2+}}^{\text{L}}$ and $M_{\text{BaC}_6\text{H}_5\text{O}_7^{-}}^{\text{L}}$ denote the molar concentrations of Ca^{2+} , $\text{C}_6\text{H}_5\text{O}_7^{3-}$, $\text{CaC}_6\text{H}_5\text{O}_7^{-}$, $\text{Ca}(\text{C}_6\text{H}_5\text{O}_7)_2^{4-}$, Ba^{2+} and $\text{BaC}_6\text{H}_5\text{O}_7^{-}$, respectively. The total concentrations of calcium ($M_{\text{Ca},\text{T}}^{\text{L}}$) and barium ($M_{\text{Ba},\text{T}}^{\text{L}}$) dissolved in solution are written:

$$M_{\text{Ca},\text{T}}^{\text{L}} = M_{\text{Ca}^{2+}}^{\text{L}} + M_{\text{CaC}_6\text{H}_5\text{O}_7^{-}}^{\text{L}} + M_{\text{Ca}(\text{C}_6\text{H}_5\text{O}_7)_2^{4-}}^{\text{L}} = M_{\text{Ca}^{2+}}^{\text{L}} \cdot (1 + \beta), \quad (2)$$

where

$$\beta = M_{\text{C}_6\text{H}_5\text{O}_7^{3-}}^{\text{L}} \times 10^{3.22} + (M_{\text{C}_6\text{H}_5\text{O}_7^{3-}}^{\text{L}})^2 \times 10^{8.02} \quad (3)$$

$$M_{\text{Ba},\text{T}}^{\text{L}} = M_{\text{Ba}^{2+}}^{\text{L}} + M_{\text{BaC}_6\text{H}_5\text{O}_7^{-}}^{\text{L}} = M_{\text{Ba}^{2+}}^{\text{L}} \cdot (1 + \alpha), \quad (4)$$

where

$$\alpha = M_{\text{C}_6\text{H}_5\text{O}_7^{3-}}^{\text{L}} \times 10^{2.84}. \quad (5)$$

The pH values of solutions changed from 7.8 to 8.5 during the process of carbonate precipitation in the experiment.

The dissociation constants of citric acid are as follows: $K_1 = 8.7 \times 10^{-4}$, $K_2 = 1.8 \times 10^{-5}$ and $K_3 = 4.0 \times 10^{-6}$. Therefore, the total concentration of citrate dissolved in solution ($M_{\text{C}_6\text{H}_5\text{O}_7,\text{T}}^{\text{L}}$) is written:

$$M_{\text{C}_6\text{H}_5\text{O}_7,\text{T}}^{\text{L}} = M_{\text{C}_6\text{H}_5\text{O}_7^{3-}}^{\text{L}} + M_{\text{CaC}_6\text{H}_5\text{O}_7^{-}}^{\text{L}} + 2M_{\text{Ca}(\text{C}_6\text{H}_5\text{O}_7)_2^{4-}}^{\text{L}} + M_{\text{BaC}_6\text{H}_5\text{O}_7^{-}}^{\text{L}} \quad (6)$$

The apparent distribution coefficient K_{Ba}^{C} is written:

$$K_{\text{Ba}}^{\text{C}} = \frac{1 + \beta}{1 + \alpha} \cdot K_{\text{Ba}}^{\text{O,C}} = \frac{1 + \beta}{1 + \alpha} \cdot \frac{S_{\text{CaCO}_3}^{\text{O}}}{S_{\text{BaCO}_3}^{\text{O}}} \cdot \frac{\lambda_{\text{CaCO}_3}^{\text{s}}}{\lambda_{\text{BaCO}_3}^{\text{s}}} \cdot \frac{\gamma_{\text{Ba}^{2+}}^{\text{L}}}{\gamma_{\text{Ca}^{2+}}^{\text{L}}} \quad (7)$$

where $K_{Ba}^{O,C}$ is the distribution coefficient in a complex free solution. $\lambda_{CaCO_3}^s, \lambda_{BaCO_3}^s, \gamma_{Ba^{2+}}^L$ and $\gamma_{Ca^{2+}}^L$ denote the activity coefficients of $CaCO_3$ (aragonite), $BaCO_3$ in crystalline phase, barium ions and calcium ions in solution, respectively. By using equations (1) to (6), the values of α and β can be calculated when $M_{Ca,T}^L, M_{Ba,T}^L$ and $M_{C_6H_5O_7,T}^L$ are given. $M_{Ba,T}^L$ is small as compared with $M_{Ca,T}^L$. Fig.16 shows the calculated values of $(1+\beta)/(1+\alpha)$ against the concentrations of $M_{C_6H_5O_7,T}^L$. With increasing carbonate precipitation, $M_{Ca,T}^L$ decreases though $M_{C_6H_5O_7,T}^L$ does not change. Fig.16 indicates that $(1+\beta)/(1+\alpha)$ tends to increase with decreasing concentration of $M_{Ca,T}^L$ at a definite concentration of $M_{C_6H_5O_7,T}^L$. Equation (7) indicates that the value of $K_{Ba}^{O,C}$ may change with changing value of $(1+\beta)/(1+\alpha)$. The value of $K_{Ba}^{O,C}$ may change with increasing carbonate precipitation, because $(S_{CaCO_3}^O/S_{BaCO_3}^O) \cdot (\lambda_{CaCO_3}^s/\lambda_{BaCO_3}^s)$ should change in this solution system. It can be said that with increasing amount of precipitated carbonate the value of K_{Ba}^C may change.

In the solution system, $Ca(HCO_3)_2 + Na\text{-citrate} + SrCl_2 \longrightarrow$ calcite, the same treatment was made as in the system of barium discussed above and the same result was obtained.

In the cases of zinc and copper also the same calculation of $(1+\beta)/(1+\alpha)$ was made. The result for zinc is shown in Fig.17, which indicates that $(1+\beta)/(1+\alpha)$ changes with decreasing concentration of calcium dissolved in a parent solution. $ZnCO_3$ and $CuCO_3$ have a calcite crystal form. The values of $K_{Zn}^{O,C}$ and $K_{Cu}^{O,C}$ are constant (KITANO *et al.*, 1968). Therefore, the values of their distribution coefficients should

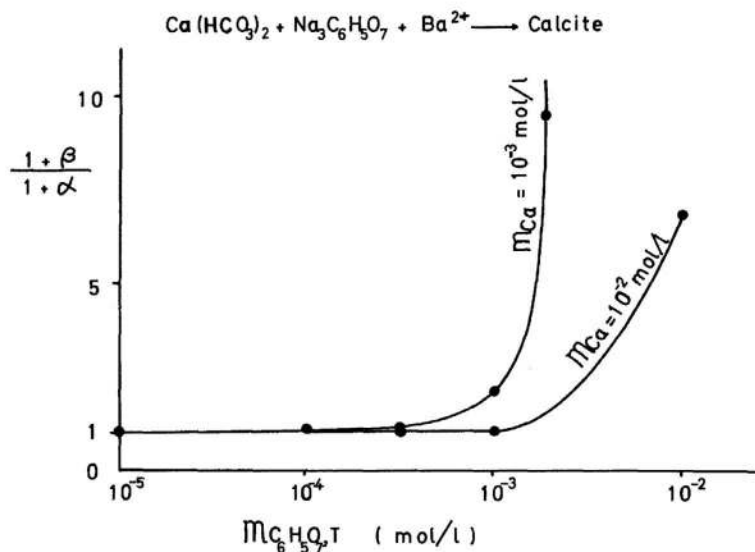


Fig.16. $(1+\beta)/(1+\alpha)$ plotted against citrate concentration in a parent solution.

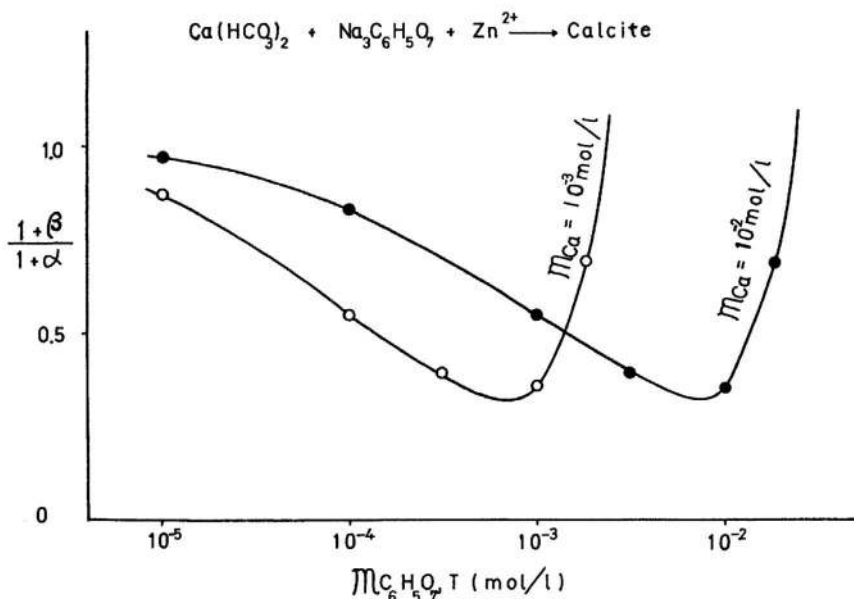


Fig.17. $(1+\beta)/(1+\alpha)$ plotted against citrate concentration in a parent solution.

change theoretically with increasing amount of precipitated carbonate, when the coprecipitation takes place in a state of equilibrium. In the cases of zinc and copper, the thermodynamically expected trend is observed in the experimental results.

[III] Values of distribution coefficients of Sr and Ba and conditions of appearance of abnormally high values of their distribution coefficients

When the values were measured without vigorous stirring of parent solutions, the thermodynamic values of Sr and Ba for aragonite were measured to be around 1, whereas the values for calcite in a complex free solution were around 0.1. When the coprecipitation of Sr and Ba with calcium carbonate is carried out in a state of equilibrium, the values of distribution coefficients of Sr and Ba naturally depend on the crystal form of calcium carbonate as mentioned in RESULTS [I–B]. The crystal form is influenced greatly by the presence of Mg^{2+} and organic material in a parent solution, but a little by the presence of NaCl (KITANO *et al.*, 1969). The concentration of Mg^{2+} in a body fluid of a certain marine organism seems a little different from those of other organisms. The most important factor affecting the crystal form is the kind and concentration of organic material in a parent solution. And, on the other hand, the value of distribution coefficient depends on the chemical composition of a parent solution which controls the activities of calcium and trace elements dissolved in a parent solution. Organic material forms complexes with both calcium and trace element ions in solution. Then, the presence of organic material in a parent medium

has a very important influence on the value of distribution coefficient because of its great influence on both crystal form and the activities of calcium and trace elements in solution.

Very often the abnormally high values of distribution coefficients of Ba and Sr are measured experimentally (see Figs.1 to 11). We have studied the condition for appearance of the abnormally high values. The abnormally high values of the distribution coefficient for Ba appear much more easily than for Sr. The influence of Ba^{2+} in a parent solution on the crystal form of a major component $CaCO_3$ is much greater than that of Sr^{2+} . That is, the presence of Ba^{2+} even in a very small amount greatly favors calcite formation, whereas the presence of Sr^{2+} has only a little influence on the crystal form, although the carbonates of Sr and Ba have aragonite crystal form (KITANO, 1962).

According to the experimental results of measurements of the distribution coefficients of zinc and copper (KITANO *et al.*, 1968), the abnormally high values of the distribution coefficient for Cu appear much more easily than for Zn. It was known that the presence of zinc and copper in a parent solution favors aragonite formation even though the carbonates of Zn and Cu have calcite crystal form and that the influence of copper ions on aragonite formation is much greater than that of zinc (KITANO *et al.*, 1969).

It seems to be clear that there is a correlation in mechanism between appearance of the abnormally high values of distribution coefficient and intensity in the influence of trace element in a parent solution on the crystal form of precipitated carbonate.

Barium and strontium carbonates have aragonite crystal form. The abnormally high values of the distribution coefficients of barium and strontium were measured more easily at the early stages of Mg-rich or Mg-poor calcite precipitation than at aragonite precipitation. Copper and zinc carbonates have calcite crystal form. The abnormally high values of copper and zinc were measured more easily at the early stages of aragonite or Mg-rich calcite precipitation than at Mg-poor calcite precipitation. It is noted that the precipitation of Mg-poor calcite, Mg-rich calcite or aragonite depends on the chemical composition of a parent solution, that is, the concentrations of magnesium chloride and sodium citrate dissolved in a parent solution.

The presence of citrate dissolved in a parent solution easily produces the abnormally high values of distribution coefficient, probably because the presence of citrate inhibits the growth from fine and unstable crystals to large and stable crystals.

Agitation of a parent solution makes it impossible to give a constant value of the distribution coefficient of metal ions having a great influence on the crystal form of calcium carbonate. And agitation has a great influence on the values of the distribution coefficient. Agitation does not cause the growth from fine and unstable crystals to large and stable crystals but the aggregation of the fine and unstable crystals. And in many cases agitation has a great influence on the crystal form of calcium

carbonate precipitated (KITANO, *et al.*, to be published elsewhere). It must be known whether agitation occurs in a parent medium of marine skeletal carbonates.

The appearance of the abnormally high values of distribution coefficient is due to the formation of abnormal precipitates at the early stages of precipitation which are different from large and stable crystals in physicochemical properties.

There seems to be a correlation between the value of distribution coefficient and the state of precipitated carbonate, which will be reported in detail elsewhere (KITANO *et al.*, to be published elsewhere).

Without the exact knowledge on the controlling factors in the value of distribution coefficient shown in this paper and also on the conditions for the formation of marine skeletal carbonates, the exact and appropriate use of the values of the distribution coefficients of trace metals measured in the laboratory would not be made for interpretation of trace element contents of marine skeletal carbonates.

REFERENCES

- BOWEN, H. H. M. (1956) Strontium and barium in sea water and marine organisms. *J. Mar. Biol. Ass. U. K.* **35**, 451–460.
- CHAVE, K. E. (1954) Aspects of the biogeochemistry of magnesium, 1. Calcareous marine organisms. *J. Geol.* **62**, 266–283.
- DODD, J. R. (1965) Environmental control of strontium and magnesium in *Mytilus*. *Geochim. Cosmochim. Acta* **29**, 385–398.
- DODD, J. R. (1967) Magnesium and strontium in calcareous skeletons: A review. *J. Paleontology* **41**, 1313–1329.
- GRAF, D. L. (1960) Geochemistry of carbonate sediments and sedimentary rocks (Part III). Illinois State Geol. Survey Circ. No. **309**, 1–71.
- HALLAM, A. and PRICE, N. B. (1968) Environmental and biochemical control of strontium in shells of *Cardium edule*. *Geochim. Cosmochim. Acta* **32**, 319–328.
- HOLLAND, H. D., BORCSIK, M., MUNOZ, J. L. and OXBURGH, U. M. (1963) The coprecipitation of Sr^{++} with aragonite and of Ca^{++} with strontianite between 90 and 100°C. *ibid.* **27**, 957–977.
- HOLLAND, H. D., HOLLAND, H. J. and MUNOZ, J. L. (1964a) The coprecipitation of cations with CaCO_3 —II. The coprecipitation of Sr^{++} with calcite between 90 and 100°C. *ibid.* **28**, 1287–1302.
- HOLLAND, H. D., KIRSIPU, T. V., HUEBVER, J. S. and OXBURGH, U. M. (1964b) On some aspects of the chemical evolution of cave waters. *J. Geol.* **72**, 36–67.
- KINSMAN, D. J. J. (1969) Interpretation of Sr^{2+} concentration in carbonate minerals and rocks. *J. Sediment. Petrol.* **39**, 486–508.
- KINSMAN, D. J. J. and HOLLAND, H. D. (1969) The coprecipitation of cations with CaCO_3 —IV. The coprecipitation of Sr^{2+} with aragonite between 16 and 96°C. *Geochim. Cosmochim. Acta* **33**, 1–17.
- 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. (1963) Geochemistry of calcareous deposits found in hot springs. *J. Earth Sciences, Nagoya Univ.* **11**, 68–100.

- 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. and KANAMORI, N. (1966) Synthesis of magnesian calcite at low temperatures and pressures. *Geochem. J.* **1**, 1–10.
- KITANO, Y., TOKUYAMA, A. and KANAMORI, N. (1968) Measurement of the distribution coefficient of zinc and copper between carbonate precipitate and solution. *J. Earth Sciences, Nagoya Univ.* **16**, 1–102.
- KITANO, Y., KANAMORI, N. and TOKUYAMA, A. (1969) Effects 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*, edited by D. W. HOOD, Institute of Marine Science, Univ. of Alaska, 413–447.
- KITANO, Y. and OOMORI, T. (1971) The coprecipitation of uranium with calcium carbonate. *J. Oceanogr. Soc. Japan* **27**, 34–42.
- KULP, J. L., TUREKIAN, K. K. and BOYD, D. W. (1952) Strontium content in limestones and fossils. *Bull. Geol. Soc. Am.* **63**, 701–716.
- LERMAN, A. (1965a) Paleocological problems of Mg and Sr in biogenic calcites in light of recent thermodynamic data. *Geochim. Cosmochim. Acta* **29**, 977–1002.
- LERMAN, A. (1965b) Strontium and magnesium in water and in *Crassostrea* calcite. *Science* **150**, 745–751.
- LOWENSTAM, H. A. (1961) Mineralogy, $^{18}\text{O}/^{16}\text{O}$ ratios and strontium and magnesium contents of recent and fossil brachiopods and their bearing on the history of the oceans. *J. Geol.* **69**, 241–260.
- LOWENSTAM, H. A. (1963) Sr/Ca ratio of skeletal aragonites from the recent marine biota at Palau and from fossil gastropods. *Isotopic and cosmic chemistry*, edited by Craig, Miller, and Wasserburg, North Holland Pub. Co., Amsterdam. 114–132.
- LOWENSTAM, H. A. (1964) Coexisting calcites and aragonites from skeletal carbonates of marine organisms and their strontium and magnesium contents. *Recent researches in the fields of hydrosphere, atmosphere and nuclear geochemistry*. Maruzen, 373–404.
- ODUM, H. T. (1951) The stability of the world strontium cycle. *Science* **114**, 407–411.
- ODUM, H. T. (1957) Biogeochemical deposition of strontium. *Inst. Marine Sci., Univ. Texas* **4**, 39–114.
- PILKEY, O. H. and HOWER, J. (1960) The effect of environment on the concentration of skeletal magnesium and strontium in *Dendraster*. *J. Geol.* **68**, 203–216.
- PYTKOWICZ, R. M. (1969) Chemical solution of calcium carbonate in sea water. *Am. Zoologist* **9**, 673–679.
- SIEGEL, F. R. (1960) The effect of strontium on the aragonite-calcite ratios of Pleistocene corals. *J. Sed. Petrology* **30**, 297–304.
- SIEGEL, F. R. (1961) Variation of Sr/Ca ratio and Mg contents in recent carbonate sediments of the northern Florida Keys area. *ibid.* **31**, 336–342.
- THOMPSON, T. G. and CHOW, T. J. (1955) The strontium-calcium atom ratio in carbonate-secreting marine organisms. *Deep Sea Res. Supp.* **3**, 20–39.
- TSUSUE, A. (1970) The coprecipitation of calcium with rhodochrosite at elevated temperatures. *Volcanism and ore genesis*, edited by TATSUMI, Univ. Tokyo Press, Tokyo.
- TSUSUE, A. and HOLLAND, H. D. (1966) The coprecipitation of cations with CaCO_3 . III. The coprecipitation of Zn^{++} with calcite between 50 and 250°C. *Geochim. Cosmochim. Acta* **30**, 439–453.

- TUREKIAN, K. K. (1955) Paleocological significance of the strontium ratio in fossils and sediments. *Bull. Geol. Soc. Am.* **66**, 155–158.
- TUREKIAN, K. K. (1957) The significance of variations in the strontium content of deep sea cores. *Lim. Oceanogr.* **4**, 309–314.
- TUREKIAN, K. K. (1964) The marine geochemistry of strontium. *Geochim. Cosmochim. Acta* **28**, 1479–1496.
- TUREKIAN, K. K. and KULP, J. L. (1956) The geochemistry of strontium. *ibid.* **10**, 245–296.
- TUREKIAN, K. K. and ARMSTRONG, R. L. (1960) Magnesium, strontium, and barium concentrations and calcite-aragonite ratios of some recent molluscan shell. *J. Marine Res.* **18**, 133–151.