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# SOME MINERALO-CHEMICAL PROBLEMS CONCERNING CALCITE AND ARAGONITE, WITH SPECIAL REFERENCE TO THE GENESIS OF ARAGONITE

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## Abstract

Theoretical considerations and experimental work have been described with the purpose of giving a reasonable explanation for the genesis of aragonite. The favourable conditions for the formation of aragonite, and  $\mu$ - $\text{CaCO}_3$  were made clear. The most important factor responsible for the aragonite formation was the diminished solvation effect of water molecules, and the effect of the higher temperatures from  $60^\circ$  to  $100^\circ$  was also ascribed to the same factor. The effect of the reaction velocity, of the diadochic substitution, pH of solution, and the effect of the unbalanced quantities of  $\text{Ca}^+$  and  $\text{CO}_3^-$  also have been examined theoretically and experimentally. It was ascertained that the slow reaction, the higher pH value of solution, and balanced proportion of  $\text{Ca}^+$  in relation to  $\text{CO}_3^-$  are responsible to some extent for the formation of aragonite. The presence of Mg, Sr, and Ba seem to be not favourable for the formation of aragonite.

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## Introduction

Calcium carbonate occurs as two minerals of each different crystal types: calcite and aragonite. Earth scientists are familiar with the minerals because of their common occurrence in nature, and, especially, because of mineralo-chemical interest in this mineral species.

Many interesting problems have appeared in the mineralo-chemistry of this species, and great endeavours have been made to solve these problems by many investigators of geological, mineralogical and chemical fields.

Among these, the problem of genetic circumstances of calcite and aragonite, the problem of the genesis of aragonite in other words, must be considered as of the most important.

It is well known in nature as well as in the laboratory that an unstable modification in a polymorphic species is more likely to occur than other stable modifications under some particular conditions. The pair of calcite and aragonite exhibits a good example of such a case, and has often been adopted as a suitable material for understanding the general rules governing the phenomenon. Probably the abundant occurrence of this species and the great ease of its artifical preparation afford good facilities for such a purpose.

Consequently, a great number of works concerning the problem of genesis of aragonite have been published, and many attempts have been made to explain this interesting problem.

However, in spite of such efforts of previous investigators, the cause and the mechanism of the preferential formation of the unstable modification is yet scarcely known. Moreover, it becomes known today that some of the earlier data on this problem are doubtful in respect to the identification of each modification owing to inadequate methods which had been used at those days.

In the present work, the writer attempts to give a reasonable explanation for the genesis of aragonite. According to this purpose, a hundred and more synthetic experiments were carried out in order to check up earlier data as well as to find some new information about this problem.

It has become evident through the work that the uncertainty as to the genesis of aragonite could not be cleared up without one's possessing more reliable materials about the phenomena of isomorphic replacements in calcite- and aragonite-group minerals. Therefore, experiments were made on this subject too, and no little part of the treatise has been devoted to the explanation of this.

Planning the work, the writer suffered much from the confusion of theoretical considerations upon which various explanations of the aragonite formation, of previous researchers, have been based; some on the basis of the kinetics, some on the energetics, and so on. This situation made it necessary, first of all, to reexamine these theories and to seek some systematic foundation of theory for the present work. In this respect, detailed discussions are given below in CHAPTER (4).

### (1) Historical Review of the Calcite-Aragonite Problem

Early in 1870, CREDNER (1870) found that aragonite rather than calcite formed in the presence of Sr, Ba and Pb. The same observations have been reported by BAUER (1890), JOHNSTON et al. (1916), FAUST (1950), ZELLER and WRAY (1955) and others.

It is apparent that all these ions, and negative  $\text{SO}_4^-$  according to JOHNSTON et al., are easily combined with  $\text{CO}_3^{=}$ , and  $\text{Ca}^{++}$ , to form compounds which have the same structure as aragonite. JOHNSTON et al. concluded on the basis of this fact that the forerunning nucleations of these compounds would provide suitable seed for the nucleation of aragonite.

The preferential formation of aragonite, however, often occurs in

conditions which are lacking in those above ions. It has been thought by many investigators that the effect of  $Mg^{++}$  and/or the effect of "higher temperature" would take the place of the effect of  $Sr^{++}$ ,  $Ba^{++}$  and  $Pb^{++}$  in such cases.

ROSE (1837) stated first that a temperature higher than about  $30^{\circ}$ , of mother solutions, was possible as a principal factor responsible for the preferential formation of aragonite. LINCK (1903), JOHNSTON et al. (1916), KOHLSCHÜTTER and EGG (1925), FAIVRE (1946), ZELLER and WRAY (1955), TOGARI and TOGARI (1955) and others also have observed this effect.

Up to now, no objection has been raised to the certainty of this temperature effect. However, though much attention of previous investigators has been paid to this effect, the essential mechanism of the temperature effect still remains unknown. An attempt, perhaps the only one, to explain this effect was undertaken by SAYLOR (1928), in which he supposed the adsorption effect of water of "high temperature type."

The effect of  $Mg^{++}$  on aragonite formation has been noticed by LEITMEIER (1909), HLAWATSCH (1909), VETTER (1910), PEINE (1915) and TOGARI and TOGARI (1955). LEITMEIER supposed that  $Mg^{++}$  in solutions would change the surface tension of precipitates, so that aragonite formed. According to PEINE,  $Mg^{++}$  increases the solubility of  $CaCO_3$ , and thus is responsible for the formation of aragonite.

It is noteworthy, however, that some investigators, among them JOHNSTON et al. (1916), KOHLSCHÜTTER and EGG (1925), ZELLER and WRAY (1955) and BROOKS et al. (1950), have had negative views on the effect of  $Mg^{++}$ . More detailed examination of this effect is, therefore, very needful.

Though they are not so generally accepted as the three effects above mentioned, there are some different observations and views on this problem. The effect of the reaction velocity, for instance, often has come into question especially among chemists; KEYSER and DUGUELDRE (1950), and KITANO (1955) are among them.

It appears that the authoritative OSTWALD's Stufenregel gives powerful support to the school of reaction velocity. However, it will be seen below that the validity of Stufenregel is doubtful so far as the calcite-aragonite problem is concerned; full discussion in this respect is given in CHAPTER (4).

The effect of pH of mother solution (ZELLER and WRAY, 1955), of organic agencies (MACDONALD, 1956), and the effect of adsorption of some substances (SAYLOR, 1928) also have been considered as being

responsible for the aragonite formation. Recently, an interesting observation on the dependence of the aragonite formation upon the dielectric constant of the mother solution was reported by HARADA and GOTO (1957). The significance of this observation will be discussed in CHAPTER (4) and (5).

## (2) Thermochemical Properties of Calcite and Aragonite

If once formed, aragonite can be kept unchanged for a long period owing to the high energy barrier of the calcite-aragonite transformation. A heating up to about  $450^{\circ}$  is required to cause the transition to begin, that is, the activation energy for the transition\* overcomes the detaining force of the barrier at this temperature, so that the transition becomes able to proceed at a measurable speed. The progress of transition becomes slower with decline of temperature, and at room temperature the transition may be delayed for a long time.

Thus it is evident from the above facts that the transition temperature of  $450^{\circ}$  is merely an apparent one, and the true transition temperature, the very point at that the reversal of the stability relation between calcite and aragonite will occur, is expected to be lower than  $450^{\circ}$ .

Hitherto, many attempts have been made to find the true transition temperature or to define the stability field of both the minerals. Previously, FOOTE (1900), JOHNSTON et al. (1916) and BÄCKSTRÖM (1921) discussed the subject with solubility data of both the minerals. The free energy difference between calcite and aragonite,  $\Delta G$ , can be given by the following equation:

$$\Delta G = R \cdot T \ln(Ka/Kc)$$

where  $Ka$  and  $Kc$  denote the solubility product constant of calcite and aragonite respectively. The values of  $Ka/Kc$  given by FOOTE, BÄCKSTRÖM, and KENDALL (1912) are shown in Table 1.

The  $\Delta G$  values given by BÄCKSTRÖM, for instance, are  $-160$  cal/mol,  $-191.3$  cal/mol, and  $-220$  cal/mol at  $9^{\circ}$ ,  $25^{\circ}$ , and  $35^{\circ}$  respectively. Then the variation of  $\Delta G$  with temperature,  $\Delta G/\Delta T$ , is found to be  $-2$  cal/deg. for the above temperature range.

BÄCKSTRÖM concluded on the basis of these values that aragonite barely could find its stability field below a temperature of about  $-43^{\circ}$

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\* According to Chaudron (1954), the activation energies for this transition are as follows: 80 kcal for natural aragonite, 60 kcal for precipitate at  $100^{\circ}$ , and 45 kcal for precipitate at  $60^{\circ}$ .

TABLE 1. The  $K_a/K_c$  Values of Various Authors.

Foote (1900)		Kendall (1912)	Bäckström (1921)
$a^*$	$b^{**}$		
	1.147 ( 8°)	—	1.123 ( 9°, 777 mm CO <sub>2</sub> )
1.35 (25°)	1.130 (25°)	1.0663 (25°)	1.130 (25°, 762 mm CO <sub>2</sub> )
—	1.124 (41°)	—	1.145 (35°, 744 mm CO <sub>2</sub> )
1.365 (50°)	1.115 (48°)	1.0751 (50°)	—
1.24 (59°)	—	—	—
—	—	1.0691 (100°)	—

\* from the relative solubility with calcium oxalate.

\*\* from measurement of the ionic conductance.

under ordinary pressure. FOOTE also supposed that aragonite would be always more unstable than calcite under all temperatures.

Later, BÄCKSTRÖM (1925) presented a more full examination of this subject. In this latter work, the heat of transformation,  $\Delta H$ , was measured to be  $30 \pm 20$  cal/mol by dissolution method, and then the entropy difference,  $\Delta S$ , was found to be 0.74 cal/deg. at 25°. Many existing data of specific heats of both modifications also were employed for the work. The variation of the transition temperature with pressure was calculated from the Clapeyron law. Then he came to the conclusion that the transition temperature must be not so far from absolute zero under ordinary pressure, and that the transition pressure must be in the neighbourhood of 2900 atms. at ordinary temperature.

Many other workers also have tackled this problem. ROTH and CHALL (1928) found the value of  $\Delta H$  to be 60~37 cal/mol. ANDERSON (1934) found  $1.06 \pm 0.70$  cal/deg. for  $\Delta S$ , and BUCHAN (1927) theoretically

TABLE 2. Thermochemical Quantities for Aragonite-Calcite Transition at 25° and 1 atm.

$\Delta S$ cal/deg. mol	$\Delta H$ cal/mol	$\Delta G$ cal/mol	Investigator
0.74	$30 \pm 20$	-191.3	Bäckström (1925)
—	60~37	—	Roth & Chall (1928)
$1.06 \pm 0.7$	—	—	Anderson (1934)
—	—	-273	Anderson & Kelley (1935)
—	—	$-311 \pm 23$	Kobayashi (1951)
1.1	62	-273	Jamieson (1953)
$1.1 \pm 0.2$	$160 \pm 70$	$-160 \pm 70$	MacDonald (1956)

computed  $\Delta G$  to be  $-414$  cal/mol.

Recently, KOBAYASHI (1951), JAMIESON (1953), MACDONALD (1956), and CLARK JR. (1957) respectively have offered reliable data resulting from their excellent work. All these numerical data are in good agreement with each other and also with earlier data such as BÄCKSTRÖM's and ANDERSON's, as shown in Table 2.

In view of all the above results, it is very reasonable to suppose that aragonite is more unstable than calcite under almost all conditions supposed in nature. This supposition must be quite true for the limited conditions under which calcite and aragonite able to crystallize and to exist.

### (3) Structural Aspects of Calcite and Aragonite

The calcium atoms in calcite and those in aragonite are arranged in approximate cubic and hexagonal close packing respectively. In each case, the  $\text{CO}_3$  groups occupy a position between six calcium atoms. The most essential difference in the crystal features of both minerals can be found in their coordinations. In calcite, each oxygen atom of the  $\text{CO}_3$  ion touches two calcium atoms, while in aragonite each oxygen atom touches three calcium atoms. These situations are shown in Fig. 1 somewhat schematically.

Evidently the ratio of the coordination of two atoms, the calcium atom and the oxygen atom, is the reciprocal of the ratio of their chemical subscript. Therefore, the coordination numbers of calcite and aragonite may be written as  $6 : 2$  and  $9 : 3$  respectively.

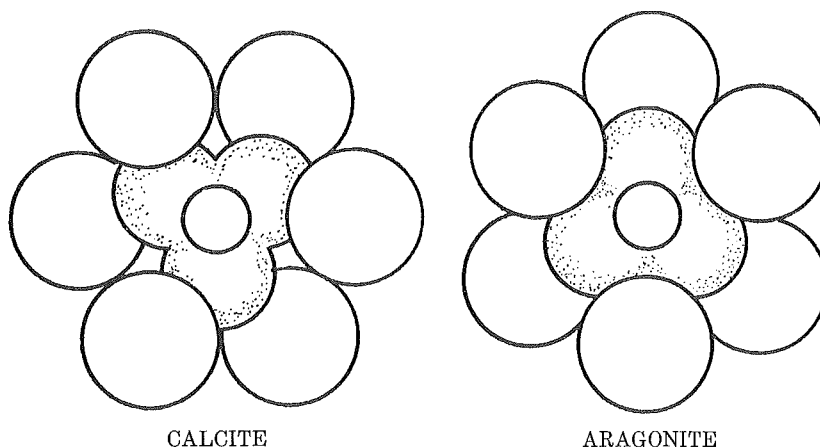


Fig. 1. Environment of  $\text{CO}_3$  ion group.



It is immediately found from this illustration that aragonite is more dense and has more stiff packing than calcite. The space provided for any displacement and any vibration of the constituent atoms may be more open in calcite than in aragonite. Therefore, such atomic movement probably can occur in calcite without so much energy loss as in aragonite. The larger entropy in calcite is well understandable from these structural characteristics.

It should, however, be noticed that each Ca-O bond in calcite is stronger than that in aragonite owing to the difference in the coordination of calcite and aragonite. Consequently, the atomic distance of Ca-O is 2.30(Å) for calcite and 2.5(Å) for aragonite. Thus calcite shows somewhat larger *structural persistency* against hydrostatic pressure than of aragonite.

Now, on the basis of these structural characteristics, possibly one may arrive at a conclusion as follows:

*"Calcite is more adaptable to increasing temperature than aragonite is, but not so much to increasing pressure as aragonite. Therefore, calcite is the modification of high temperature and low pressure type, while aragonite is the modification of high pressure and low temperature."*

#### (4) Theoretical Background of the Calcite-Aragonite Problem

In view of the thermochemical and structural data shown in the foregoing chapters, it is evident that most aragonites have appeared in the stability field of calcite as *unstable formation*. So as to understand the essential meaning of this unstable formation, several different theories have been adopted by different investigators. Some detailed examinations of these theories are given in this chapter.

##### I. Remarks on Ostwald's Stufenregel

Ostwald's Stufenregel has often been employed for the explanation of the unstable formation of some polymorphic substances, including  $\text{CaCO}_3$ . According to this law, the reaction velocity, or the velocity of formation or the velocity of crystallization, is the most essential factor for the unstable formation. Then the law states:

*"A more unstable modification appears with a more rapid reaction, then it transforms step by step, through more stable ones, to the most stable modification."*

For examining this law, let the chemical change be considered through which the Ca ion and the  $\text{CO}_3$  ion in a dispersed phase, such as aqueous solution, come to be combined in calcite. As shown in Fig. 2, there are

some different courses for this chemical change even with ignoring the difference in the grain size of each appearing modification. In a normal course the change goes directly to the final phase, calcite, but in other courses the change goes through transient formations of one or more modifications of unstable. In these latter cases the change is finished when these transient modifications transform, or recrystallize, into the most stable and final modification, calcite.

It should be noticed that the courses shown in Fig. 2 are all equally

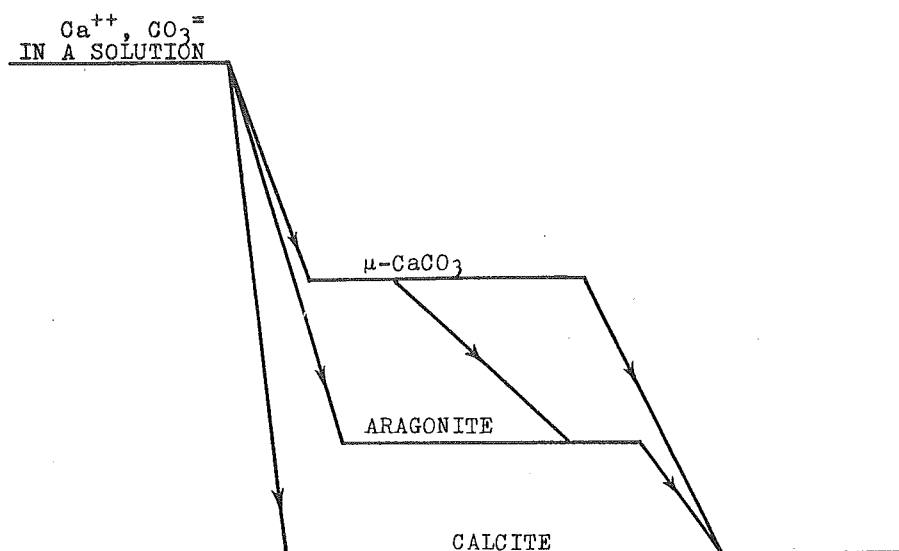


Fig. 2. Various courses of the reaction:  $\text{Ca}^{++} + \text{CO}_3^{--} = \text{calcite}$ .

possible from the thermodynamical standpoint, since none of them in the least conflicts with any thermodynamic law. Thermodynamics is, therefore, incompetent to predict the course of events, and unable to give any material information about the cause and mechanism of these transient or unstable formations. According to thermodynamics, the unstable formation is a phenomenon in the non-equilibrium state in which thermodynamics is unconcerned, and thus it is ascribed wholly to the higher velocity of practical change. The fundamental notion of thermodynamics in this respect is as follows:

*"There can be only one course for any change provided the speed of the change is infinitely slow, and this course must have the minimum potential always throughout the change."*

As one may notice immediately, it is difficult to find any difference in

principle between Stufenregel and the above statement. In fact, Stufenregel only states the hidden meaning of the notion, or it is no more than an empirical confirmation of the notion. Then, as thermodynamics is incompetent to explain any detail of the unstable formation, so naturally stufenregel has no theory with which the unstable formation can be explained even if qualitatively.

Certainly, the existence of any relationship between the unstable formation and the reaction velocity can never be denied, the inquiry into the true feature of such a relationship being required urgently for the present purpose. However, no matter what the relationship is, it is certainly not Stufenregel that will be successful in clarifying the true meaning of the relationship.

## II. An Interpretation of the Effect of Reaction Velocity

Generally speaking, a mineral can be formed at the reaction velocity of very wide range. As to calcite and aragonite, both of them are often formed in nature with very delayed reactions, perhaps agelong, so that they can grow to large and transparent crystals. However, in other cases, they appear as small crystals, powdery precipitates and even as colloidal suspensions with rapid reactions. Probably these facts reveal the absence of any strict distribution of the reaction velocity for each of both minerals. The velocity ranges for the formation of both the minerals evidently overlap for the most part.

Now, it is interesting to consider the *adaptability* of a mineral to the reaction velocity at which the mineral is formed. In reality, no mineral ever has been fixed to a special reaction velocity in its formation. The mineral is *adaptable* to some wide range of the reaction velocity, and the adaptation may be achieved in the following three ways.

### *Changing of grain size*

When the reaction velocity is extremely slow, a mineral is allowed to grow into large and few individual grains, since the very slow increase of the concentration of the reactant is to be managed satisfactorily with the consumption on the growing surface of these few grains.

However, in rapid reactions, to manage the sudden supply of a large amount of the reactant is evidently too difficult for the crystal grains of limited number, since the supply must be received at once by some one of these grains, and then must be settled on the regular position of its growing surface. Therefore, in the case of rapid reaction, the management cannot but rely upon the "division of labor", which necessarily requires a large number of small crystal grains.

### *Changing of the order of crystal lattice*

It is well known that a crystal which had grown at a high speed is inevitably opaque owing to structural defects. In rapid reactions, the work of constructing of the crystal structure must be urged to proceed, keeping pace with the high velocity of the reaction, so some omissions or abbreviations will be necessitated in the progress of the work. In other words, the crystal may adapt its structure to the speed of the reaction by degrading the order of own crystal lattice.

Now, an important conception can be arrived at, namely that a mineral may be adaptable to the high reaction velocity not necessarily by the revolution of its modification, but also by the conversion of the order of the lattice.

Probably the mineral which has a large capacity for crystal defect is more adaptable to the high reaction velocity than one with a small capacity, since the stability of such a mineral will not be much affected by the degradation of the order of lattice. Fig. 3 illustrates this idea schematically. As seen in this illustration, a slight displacement of each block, which constitutes the structure, from its proper position does not appreciably affect the stability of the whole structure in the case of (a), while the stability of the structure in (b) is supposed to be spoiled by such a displacement. Then, it is certain that the spoiled structure such as supposed in (b) is not anyhow maintainable through the nucleation stage, so it vanishes before it grows into a visible particle.

#### *Changing of the modification*

The preceding speculation leads to an important suggestion about the possible way in which "changing of modification" can be responsible for the adaptation to the reaction velocity. From Fig. 3 it can be found that the *facility of construction* of the structure (a) is being supplemented by another important factor. That is, each block which constitutes structure (a) is more symmetrical than those blocks in (b), and consequently the whole structure (a) is more symmetrical than (b). Thus, in the case of (a), placing the blocks one upon another does not so much suffer from "restriction by symmetry" as in the case of (b). For instance, each block of (a) has a fourfold symmetrical axis whereas each block of (b) has a twofold axis, so that the freedom of placing the block in (a) is twice as great as in (b). Consequently the facility of constructing of structure (a) is also twice as large as of the structure (b), so the former is more adaptable to the high reaction velocity than the latter.

To conclude, the structure of high adaptability to the reaction velocity must be of high symmetry, and must also be of high capacity for structural defect. This means in the thermodynamical sense that the structure of

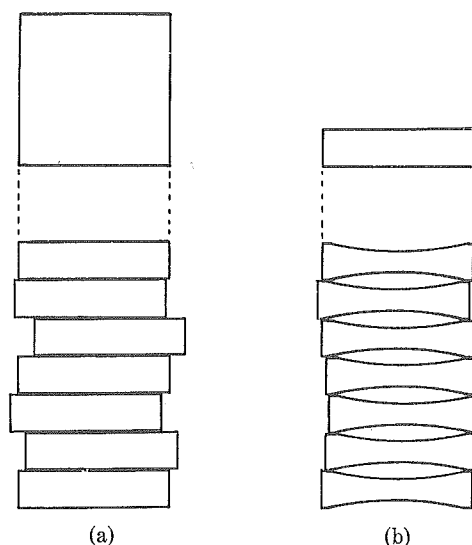


Fig. 3. Schema of the structures of different entropy and different symmetry. (a) Structure of large entropy and high symmetry. (b) Structure of small entropy and low symmetry.

high adaptability must be of large entropy.

Now, on the basis of the above speculation, an amendment of Stufenregel must be possible, and the new expression may be written as: *a higher reaction velocity is apt to cause the formation of a modification of larger entropy.*

A modification of high temperature type always has a more open structure and larger entropy than does one of low temperature type. Therefore, it may be reasonably said that a rapid reaction is more advantageous for the formation of a modification of high temperature type than for of low temperature type.

The larger validity of the new expression than Stufenregel can be seen in the well known example of the unstable formation of  $\text{KNO}_3$ , in comparison with that of  $\text{CaCO}_3$  as shown in the following:

unstable modification	Stable modification	unstable modification
$\alpha\text{KNO}_3$ (high temp. type) (of calcite st.)	$\beta\text{KNO}_3$ (low temp. type) (of aragonite st.)	
	CALCITE (high temp. type)	ARAGONITE (low temp. type)

As has been observed first by Miller (1840), the unstable modification  $\alpha\text{KNO}_3$ , which is high temperature type, appears first from a heavily supersaturated solution with a high velocity of crystallization, then following it, the stable modification of low temperature type  $\beta\text{KNO}_3$  starts to crystallize with a lower velocity, since by this time the degree of the supersaturation has been much lowered by the forerunning crystallization of the  $\alpha\text{KNO}_3$ .

In the case of  $\text{CaCO}_3$ , on the contrary, hitherto no experimental confirmation has ever been reported about the positive effect of the high reaction velocity on the formation of the unstable modification, aragonite. In fact, the formation of aragonite seems to be rather hindered by rapid reactions as shown later; the situation probably tends to confirm the new expression rather than Stufenregel.

It may be said, then, that the new expression can satisfactorily explain the above noted examples of both  $\text{CaCO}_3$  and  $\text{KNO}_3$ , while Stufenregel is in merely formal agreement with only the case of  $\text{KNO}_3$ .

### III. Considerations from Standpoint of Energetics

The preceding interpretation on the effect of the reaction velocity was carried out somewhat on the kinetic basis. In that connection, however, the writer began to think that the essential agency of the velocity factor was probably in influencing the *stability* of the modification through changing the order of lattice and/or changing the grain size of the modification. Also it was then thought that the increasing reaction velocity was unlikely to cause the preferential formation of aragonite. Consequently it is now needful to seek for the cause of the formation of aragonite in factors other than the reaction velocity. Some considerations from the standpoint of energetics, instead of kinetics, will be necessitated for this purpose.

#### a) Metastable Nature of Aragonite

The phrase "metastable formation" has been used rather carelessly by some authors in the explanation of aragonite formation. As customary, an unstable modification is called "metastable" when the modification is able to be kept for a long time without transforming to a stable modification, so all aragonite is sure to be in the metastable state in this sense.

The physical meaning of the metastable state has been well settled as shown already in CHAPTER (2). It should be noticed, however, that the theory on the metastable state is quite useless to prove the significance, if any, of the phrase "metastable formation." Surely aragonite, if once formed, can be kept unchanged for a long period, but aragonite is never formed by reason of its metastable nature.

It may be readily supposed that the metastable nature of aragonite

is not maintainable under wet conditions especially in the aqueous solution. The solubilities of calcite and aragonite in a solution are principally the function of their lattice energies, and high or lowness of the energy barrier of aragonite is unconcerned in the solubility of aragonite. Hence, it should be kept in mind, aragonite has always higher solubility than calcite *even in the solution in which aragonite can form much more predominantly than calcite*. Then, if a macrocrystal of calcite and that of aragonite are together put in this solution, evidently the macrocrystal of aragonite is more dissolved than that of calcite, so the macrocrystal of calcite is to grow through the dissolution of the other. Here, however, it should be recognized that the new formation of calcite nucleus is much more difficult of occurrence than that of aragonite in this same solution, since the solution is, as noted above, much more favorable to the formation of aragonite than to that of calcite.

Thus, one can not but conclude that the condition which is favorable to the maintenance and the growth of a macrocrystal is probably not always favorable to the nucleation of the same crystal.

b) Stability of Calcite and Aragonite in Nuclear State

The above speculation possibly leads to the supposition that the stability relation between calcite and aragonite may be different in the macrostate and in the nuclear state. In an adequate solution the nucleus of aragonite may be more stable than the nucleus of calcite, then a large number of nuclei of aragonite together with less nuclei of calcite may form in this solution, since the number of nuclei of a modification is probably a rough function of the stability of the nucleus. When they grow to macrocrystal, however, aragonite becomes no more stable than calcite, and thus it will transform to calcite through the dissolution soon or late after the reaction has ceased.

As is well known, the properties of the surface layer of the ionic crystal are largely different from those of the inner part of the crystal. The electric charge of the ions in the surface layer is not neutralized owing to the asymmetrical situation of those ions. Thus, as LENNARD JONES and DENT (1928) have pointed out, an appreciable structural contraction takes place in the surface layer, and this contraction LENNARD JONES and DENT estimated for an ionic crystal to be 5% of the ordinary atomic distance.

Another characteristic nature of the surface layer is a tendency to adsorb foreign substances of various kinds. In general, the interaction between the unsaturated surface ion and the adsorbed substance is due to electrostatic force, and thus the atomic bond in the surface layer must

be loosened by adsorption of this kind. Then it is obvious that the degree of the structural contraction in the surface layer is largely variable dependent upon the degree of the affinity between the surface ion and the adsorbed substance.

The surface layer is thought to be of three or four atomic layers deep for ordinary ionic crystals. Therefore, in a large crystal the proportion of the surface layer to the remainder is negligibly small. However, the surface layer comes to occupy a large proportion in a small crystal, and then in the nucleus and in the embryo all the ions certainly have the characteristic features of those in the surface layer. Namely, in the case of a macro-crystal, the influence of the absorbed substance reaches into only few atomic layers deep from the surface, but in the case of a nucleus or an embryo the effect may be influential throughout the nucleus or the embryo.

On the basis of the above speculation, it may be reasonably supposed that the adsorption effect is capable of changing or modifying the structure of the nucleus thoroughly, and that a nucleus in the condition which is entirely lacking in the absorbed substance must be much more contracted than if it is influenced by the adsorbing substances.

As already shown, calcite has a more open structure than aragonite, and the Ca-O bond in calcite is stronger than that in aragonite. Thus it seems very probable that the calcite nucleus of open structure is more stable than the aragonite nucleus of compact one under the influence of strong adsorption effect, while in the absence of the adsorption effect, the structure of the nuclei of both calcite and aragonite being contracted tightly, the nucleus of high pressure type, of aragonite, is more stable than the nucleus of low pressure type, of calcite.

The conception on this peculiarity of the stability of nuclear state particles was proposed first by HARADA and GOTO (1955), and experimental confirmations of it were shown later by the same authors (1957). Full discussion on this matter will be given in the following chapter.

#### c) Chemical Factors in the Stability Change

The respective chemical compositions of calcite and aragonite, especially of the former, are not exactly fixed. For instance in calcite, the Ca ion is replaceable wholly with Mn ion, and partially with Fe, Mg, Zn and other ions.

In reality, natural minerals inevitably contain more or less quantities of some foreign elements as a result of diadochic substitutions of camouflage, capturing and admission types. Then, as to calcite and aragonite, the high entropy structure of calcite may be more capable of containing such diadochic atoms than the low entropy structure of aragonite. In



other words, the lattice energy of calcite must not so much affected as that of aragonite by these diadochic substitutions.

During the crystal growth process, which is of course one of non-equilibrium, those substitutions may occur owing to kinetic necessity rather than to the requirement of energetics, and so these may occur in aragonite as well as in calcite provided the concentrations of the absorbable atoms are large. Thus it is very probable that the stabilities of both calcite and aragonite may vary with the chemical environment of formation of the minerals, and that the stability of aragonite in concentrated absorbable atoms may be more severely affected than that of calcite in most cases.

Some investigators have thought that absorption of some atoms such as Mg and Sr into aragonite would cause to stabilize the aragonite, so that it can form more dominantly than calcite. This explanation, however, is incompatible with the above speculation. It seems to the writer that this explanation implies the possibility of existence of the aragonite which is more stable than calcite. Detailed discussions on this point will be offered below in CHAPTERS (6) and (7) with experimental data.

### (5) Solvation Effect of Water on Aragonite Formation

The water molecule possesses a large dipole moment. In the immediate neighbourhood of an ion, therefore, the polar molecules of water tend to become oriented to the ion. This orientation of the water molecules may occur not only around an isolated ion in aqueous solutions, but also upon an ion which is bound on the crystal surface immersed in any aqueous medium. The probable features of these two cases are illustrated in Fig. 4.

These connections between the water molecules and the ions, isolated and bound, are made at the expense of the electric potentials of these ions. Thus if an ionic crystal is put into an aqueous medium, the electric potentials of the ions in the surface layer will largely be consumed by the orientation of water molecules, so that the crystal begins to dissolve at the surface.

The potential energy,  $P$ , which is to be lost by the interaction between one ion and one water molecule may be given by the following formula (GOTO and MATSUDA, 1957) :

$$P(z, r) = ze \cdot \mu / (r + L)^2$$

where  $ze$ ,  $r$  and  $\mu$  denote the charge of the ion, the radius of the ion and the dipole moment of the water molecule respectively, and the value of the symbol  $L$  is approximately equal to the radius of the water molecule.

As seen in this formula, the potential energy is the reciprocal of the

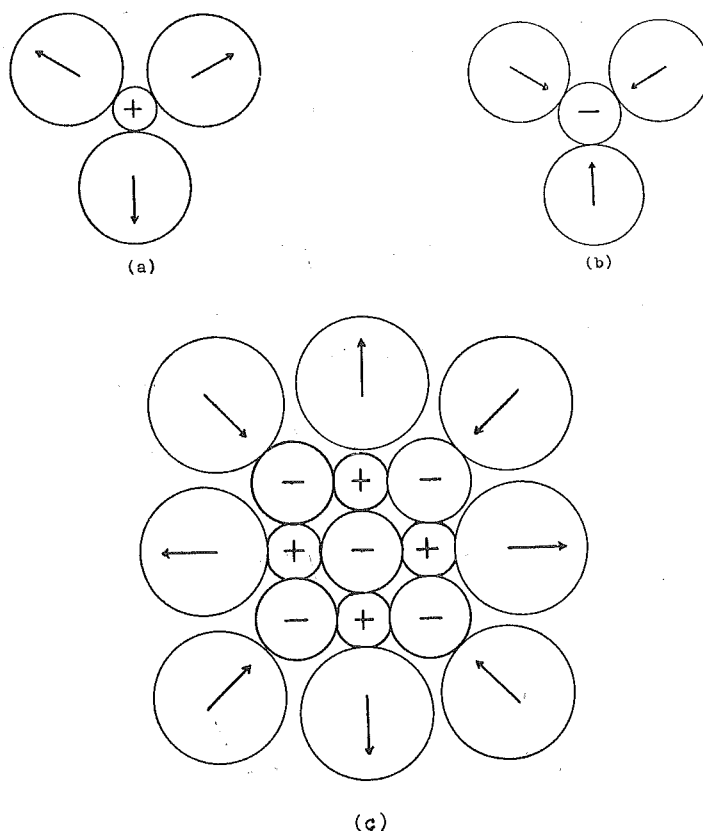


Fig. 4. Schema of the hydration of (a) the positive ion, (b) the negative ion and (c) the nuclear particle.

square of the distance between the ion and the water molecule, and it is obvious that the strength of the interaction will decrease suddenly with the increase of the distance. In this situation, evidently the binding of ions in an inner part of the crystal, perhaps even in the sixth or seventh atomic layer, is not appreciably affected by the adsorbed water. However, in the case of the embryo of any ionic crystal, which is thought to consist of very few ions, the solvation effect may be influential throughout the embryo.

The ability of orientation, to the point charge, of the water molecule in an aqueous solution can be estimated from the value of the dielectric constant of the solution. In other words, the dielectric constant of an aqueous solution gives a measure, of macro-scale, of the ability of orientation of the water molecules in the solution; a large dielectric constant of the solution means a large ability of orientation of the water molecules which compose the solution.

Undoubtedly the solubility of the ionic crystal is largely concerned with the dielectric constant of its mother solution. As it has been repeatedly stated, the bond energies of the surface ions are largely lost when the crystal is immersed in an aqueous solution of large dielectric constant. Then if it be supposed that the weakest bond energy on the immersed surface is  $U_0$ , the velocity of dissolution of the crystal,  $V_s$ , may be given approximately by the following equation:

$$V_s = a \cdot e^{-U_0/kT}$$

The velocity of growth of the crystal,  $V_c$ , on the other hand, may be proportional to the effective ion concentration of the solution:

$$V_c = b \cdot (\gamma \cdot S)^n$$

In these equations,  $a$  and  $b$  are constants,  $\gamma$  is the activity of the ion,  $S$  is the solubility of the crystal, and  $n$  may be  $> 1$ .

In the saturated solution, both velocities must be in equilibrium,  $V_s = V_c$ , thus the solubility of the crystal can be expressed by the following equation:

$$\ln S = C - U_0/nkT$$

In this equation, it is shown that  $\ln S$  is a linear function of  $U_0$ , since  $C$  is a constant. A rough estimation of the  $U_0$ -values has been done by GOTO

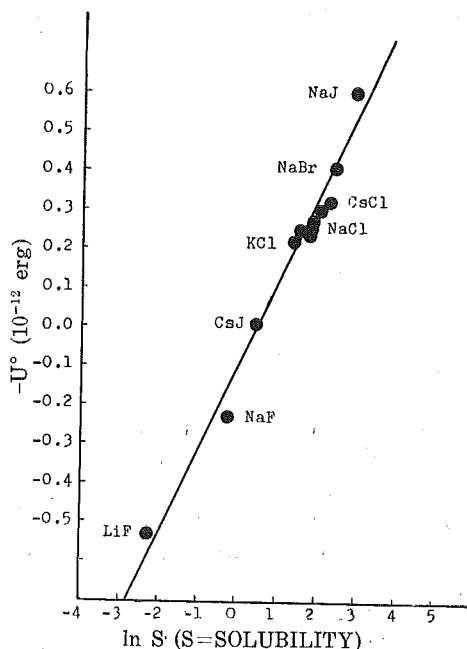


Fig. 5. Linear relation between  $\ln S$  and  $-U_0$ .

(1956) for alkali halide crystals in pure water of a enough quantity. Then, use being made of those values, the linear relation between  $\ln S$  and  $U_0$  can be shown as in Fig. 5.

In the above treatment, one can see the essential effect of the adsorption, or the solvation, of the water molecule. The solubility of the ionic crystal is mostly defined by the  $U_0$ -value, and the  $U_0$ -value depends much upon the ability of orientation of the water molecule. Thus it is evident that the nucleus, of any ionic crystal, which forms in the solutions of larger dielectric constant is more lossely bound than what forms in solutions of more small constant, since the  $U_0$ -value of the former is more diminished than that of the latter. It is also highly probable that the nucleus which forms in the solutions of very small dielectric constant must be contracted very tightly as supposed in the surface layer of the crystal which is free from any adsorption effect. As discussed in the preceding chapter, these structural compulsions operating on the nucleus may be apt to cause some change of modification of the nucleus.

An experimental confirmation of the solvation effect of water has been obtained by HARAD and GOTO (1957). This experiment is worth recapitulating, since it not only gives support to the above speculation, but also yields some important information about other effects such as those of the reaction velocity and of higher temperature.

#### *Method of Experiment*

Precipitates of  $\text{CaCO}_3$  were formed by the reaction:  $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{NaCl}$ , through the diffusion of the reactants in solutions of each different dielectric constants. The aqueous solutions of various concentrations of methyl alcohol, ethyl alcohol, ethylen glycol and glycerine were used for the purpose of obtaining these different dielectric constants.

TABLE 3. Properties of Each Precipitate.

Symbol	Name	Optics	Specific Gravity	Meigen's Reaction
dend.	dendritic aragonite	$\gamma=1.680$ $\alpha=1.530$ (—)	2.89~2.90	(+)
need.	needle-shaped " "	$\gamma=1.681\sim 3$ $\alpha=1.530$ (—)		(+)
rhom.	rhombohedral calcite	$\omega=1.655\sim 8$ $\varepsilon=1.485$ (—)		(—)
pyram.	pyramidal calcite	$\omega=1.658$ $\varepsilon=1.485$ (—)	2.70	(—)
s.rhom.	skeletal calcite	$\omega=1.660$ $\varepsilon=1.490$ (—)	2.72	(—)

Owing to the large viscosities of these solutions, the diffusions of reactants were very slow, so the reactions were kept up for five months.

Precipitates of various shapes, then, were grown to sizes which could be identified exactly by microscopic and physical methods such as the measurements of optics and specific gravity. The properties of each precipitates, which were examined by these methods, are shown in Table 3.

*Results of experiment*

It was shown in these measurements that all the precipitates consists of calcite and aragonite, whilst the most unstable modification  $\mu$ -CaCO<sub>3</sub>

TABLE 4.

No.	Composition of Solution (Alcohol wt %)		Calcite			Aragonite		
			Nc*	Form	Size ( $\mu$ )	N-ar.*	Form	Size ( $\mu$ )
1	Ethyl	11.3	95	rhom.	200~300	5	dend.	500~1000
2	Ethyl	20.4	100	rhom.	100	(+)**	dend.	1000
3	Ethyl	27.7	80	rhom.	100	20	dend.	400~500
4	Ethyl	33.8	80	rhom.	100~200	20	dend.	400~500
5	Ethyl	39.0	20	rhom.	100~200	80	dend. need.	200~300
6	Ethyl	43.3	10	rhom.	100~200	90	dend. need.	200~400
8	Methyl	8.2	100	rhom.	500	(+)	dend.	2000
9	Methyl	15.1	100	rhom.	200~500	(+)	dend.	1000
10	Methyl	21.1	90	rhom.	200~300	10	dend.	1000
11	Methyl	26.2	95	rhom.	100~300	5	dend.	600
12	Methyl	30.8	80	rhom.	300~400	20	dend.	400
13	Methyl	34.8	80	rhom.	300~500	20	dend.	500~ 600
14	Methyl	38.4	50	rhom.	300~500	50	dend.	800~1000
15	Glycol	14.7	100	rhom. pyram.	200~600	0		
16	Glycol	25.6	100	rhom. pyram.	200~300	0		
17	Glycol	34.1	100	pyram.	40~150	(+)	dend.	300~ 500
18	Glycol	40.8	100	pyram.	40~150	(+)	dend.	300~ 500
20	Glyce.	20.4	100	rhom. s.rhom.	200~400	(+)	dend.	50~ 100
21	Glyce.	33.8	100	s.rhom.	150~250	0		
22	Glyce.	43.4	100	?	v. fine	0		
23	Glyce.	50.5	100	?	v. fine	(+)	need.	300~ 500

\* Nc and N-ar. denote the relative number of particles of calcite and aragonite respectively.

\*\* (+) expresses a very small number of the particles.

was not present. All the results are arranged in Table 4.

#### *Considerations*

From the experiment of HARADA and GOTO, all the factors which have been considered to be responsible for the formation of aragonite have been carefully eliminated; Sr, Ba, Pb and Mg ions were absent in the solutions, the temperatures of the solutions were low, and the velocities of the reactions were very slow. Nevertheless, the predominant formation of aragonite can be seen in some examples of this experiment. In this respect the authors stated as follows:

(1) The presence of Sr, Ba, Pb, and Mg is not always necessary for the formation of aragonite.

(2) The results of the experiment prove the uncertainty of the effect of high reaction velocity, since the predominant formation of aragonite occurs rather in the examples of extremely slow reaction such as No.'s 5, 6 and 14.

(3) The most striking regularity can be found in the relationship between the N-ar. value of the product and the dielectric constant of the solution as shown in Table 5 and Fig. 6. It is obvious that aragonite forms more favorably in the solutions of comparatively smaller dielectric constants.

(4) As shown in Fig. 6, the predominant formation of aragonite occurs in the solutions which possess dielectric constants below 60. Then, it is very interesting to find that in ordinary inorganic aqueous solutions the predominant formation of aragonite is also possible when the dielectric constant of the solutions is lowered down to 60 by increasing temperature. This coincidence of the dielectric constant of 60 in both cases is very significant.

Evidently the experimental results of HARADA and GOTO are a positive proof of the solvation effect of water molecules. As seen in the results, the nucleus of open structure, of calcite, favorably forms under the prevalent effect of the solvation of water, while aragonite forms predominantly in the solutions in which the ability of orientation of the water molecule is much hindered.

#### *Temperature effect on aragonite formation*

Among the considerations of HARADA and GOTO, the suggestion on the temperature effect is especially interesting. This suggestion immediately leads one to notice the essential agent of the temperature effect on the aragonite formation, this is as follows:

*The ability of orientation of the water molecule may be variable effectively with the elevation of temperature. At high temperatures the thermal*

TABLE 5. Relation between N-ar. Values and Dielectric Constants of Solution.

No.	$\epsilon_0$	Nar.	No.	$\epsilon_0$	Nar.	No.	$\epsilon_0$	Nar.
1	73.8	5	9	73.3	0	16	72.9	0
2	68.5	0	10	70.5	10	17	70.3	0
3	64.0	20	11	67.9	5	18	68.0	0
4	60.3	20	12	65.2	20	20	74.5	0
5	57.0	85	13	63.5	20	21	70.6	0
6	54.2	59	14	62.0	50	22	67.6	0
8	76.7	0	15	76.1	0	23	65.5	5

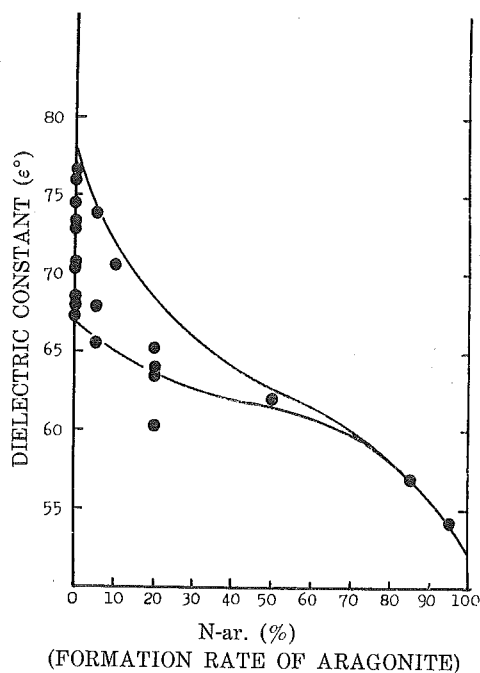


Fig. 6. Change of the formation rate of aragonite as a function of the dielectric constant of mother solution. (Harada &amp; Goto)

agitation of water molecules becomes violent, so that the ability of orientation of water molecule to the point charge is much hindered.

Of course aragonite is the modification of low temperature type, so one may expect that the increasing temperature would prevent the formation of aragonite. However, it should be noticed that raising the temperature up to only 80° probably does not affect the stability of aragonite

*nucleus in any appreciable amount, while the ability of orientation of the water molecule is certain to be very much decreased at this temperature. Evidently the negative effect, on the formation of aragonite, of the elevated temperature is overcome by the positive effect of the decreased action of water molecule within the temperature range from 60° to 100°.*

It has been known that many substances show a tendency to become less soluble with the elevation of temperature. As for calcite and aragonite, though they do not exhibit such a tendency, the difference in solubility between macro-calcite and macro-aragonite becomes diminished with the elevation of temperature as seen in Table 1; this fact shows that the stability difference between them also becomes less at high temperatures.

Then, in view of the special characters of the nuclear state particles as already discussed, it may be reasonably supposed that the stability relation between calcite and aragonite would be reversed in the nuclear state in the higher temperature range.

The decrease of the solvation effect of water with the elevation of temperature is thought to approach to a limit at the neighbourhood of the boiling point. It is certain, therefore, that the formation of calcite again becomes more active than that of aragonite above a temperature which may be not far above the boiling temperature.

According to FAIVRE (1946), the formation of aragonite reaches the maximum at 60°, then above this temperature it tends to diminish with the elevation of temperature as seen in Fig. 7. This seems to be a powerful support for the above speculation.

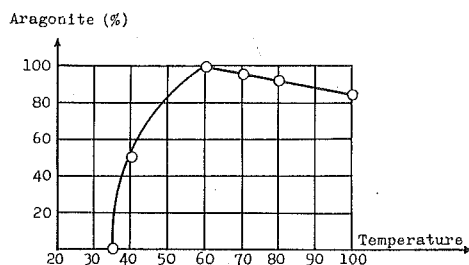


Fig. 7. Change of the formation rate of aragonite as a function of the temperature of mother solution. (Faivre)

## (6) Isomorphic Replacements in Calcite- and Aragonite-Group Minerals

The problem of isomorphic replacements in calcite- and aragonite-group minerals is in itself one of the most important problems in mineralo-



chemistry. Moreover, as shown in CHAPTER 4-III-c, this problem is connected intimately with the problem of the genesis of aragonite.

As is well known, the extent to which mixed crystal formation between two isomorphic crystals is possible is determined by the closeness of the correspondence of the atomic radii. GOLDSCHMIDT has shown that provided corresponding radii differ by not more than about 15 per cent of the smaller, a wide range of solid solution may be expected at room temperature.

The capability of mixed crystal formation of a crystal, however, is probably dependent on the thermodynamic nature of that crystal. For instance, as to calcite and aragonite, the high entropy structure of the former must have a larger capability of isomorphic replacement than the low entropy structure of the latter, and so the value of 15 per cent of GOLDSCHMIDT's prescription may be not applicable on the same footing to both structures. Possibly the chemical composition of calcite is more readily variable with the environment of its formation than that of aragonite, and if really so, it is certain to be a reliable proof of the as shown in CHAPTER 4-III-c.

#### I. Isomorphic Replacements in Calcite-Group Minerals

Mixed crystals of  $\text{CaCO}_3\text{-MnCO}_3$ ,  $\text{CaCO}_3\text{-CdCO}_3$  and  $\text{CdCO}_3\text{-MnCO}_3$  were synthesized in order to examine the above consideration. All the syntheses were made at room temperature and under room pressure; the

TABLE 6. Composition and Concentration of Reactants Used in Syntheses of  $\text{CaCO}_3\text{-MnCO}_3$  Mixed Crystals.

No.	Mol Ratios Ca:Mn:CO <sub>3</sub> in Reactants	Reactant A (grms./100 cc soln.)			Reactant B (grms./100 cc soln.)
		CaCl <sub>2</sub> + 2H <sub>2</sub> O	MnCl <sub>2</sub> + 6H <sub>2</sub> O	NH <sub>4</sub> Cl	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O
1	0:100:150	0	3.958	3.5	5.0
2	10: 90:150	0.294	3.562	3.5	5.0
3	20: 80:150	0.588	3.167	3.5	5.0
4	30: 70:150	0.882	2.771	3.5	5.0
5	40: 60:150	1.176	2.375	3.5	5.0
6	50: 50:150	1.470	1.979	3.5	5.0
7	60: 40:150	1.764	1.583	3.5	5.0
8	70: 30:150	1.058	1.187	3.5	5.0
9	80: 20:150	1.352	0.792	3.5	5.0
10	90: 10:150	1.646	0.396	3.5	5.0
11	100: 0:150	1.940	0	3.5	5.0

TABLE 7. Composition and Concentration of Reactants Used in Syntheses of  $\text{CaCO}_3$ - $\text{CdCO}_3$  Mixed Crystals.

No.	Mol Ratios $\text{Ca}:\text{Cd}:\text{CO}_3$ in Reactants	Reactant A			Reactant B
		$\text{CaCl}_2 + 2\text{H}_2\text{O}$	$\text{CdCl}_2 + 2 \cdot 5\text{H}_2\text{O}$	$\text{NH}_4\text{Cl}$	$(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$
12	0:100:150	0	4.567	3.5	5.0
13	10: 90:150	0.249	4.110	3.5	5.0
14	20: 80:150	0.558	3.654	3.5	5.0
15	30: 70:150	0.882	3.197	3.5	5.0
16	40: 60:150	1.176	2.740	3.5	5.0
17	50: 50:150	1.470	2.284	3.5	5.0
18	60: 40:150	1.764	1.827	3.5	5.0
19	70: 30:150	2.058	1.370	3.5	5.0
20	80: 20:150	2.352	0.913	3.5	5.0
21	90: 10:150	2.646	0.457	3.5	5.0

TABLE 8. Composition and Concentration of Reactants Used in Syntheses of  $\text{CdCO}_3$ - $\text{MnCO}_3$  Mixed Crystals.

No.	$\text{Cd}:\text{Mn}:\text{CO}_3$ in Reactants	Reactant A			Reactant B
		$\text{CdCl}_2 + 2.5\text{H}_2\text{O}$	$\text{MnCl}_2 + 6\text{H}_2\text{O}$	$\text{NH}_4\text{Cl}$	$(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$
22	0:100:150	0	3.958	3.5	5.0
23	10: 90:150	0.457	3.562	3.5	5.0
24	20: 80:150	0.913	3.167	3.5	5.0
25	30: 70:150	1.370	2.771	3.5	5.0
26	40: 60:150	1.827	2.375	3.5	5.0
27	50: 50:150	2.284	1.979	3.5	5.0
28	60: 40:150	2.740	1.583	3.5	5.0
29	70: 30:150	3.197	1.187	3.5	5.0
30	80: 20:150	3.654	0.792	3.5	5.0
31	90: 10:150	4.110	0.396	3.5	5.0

compositions and the concentrations of the reactants used in these syntheses were as shown in Table 6, 7 and 8.

Reactions were performed in the apparatus shown in Fig. 8. In this apparatus, funnels A and B were filled each with 100 cc of the reactants A and B respectively, then the reactants were made to drop into the reaction vessel C through the capillary tubes. The frequency of dropping of the reactants can be controlled with the stopcocks S and S', and it was kept at

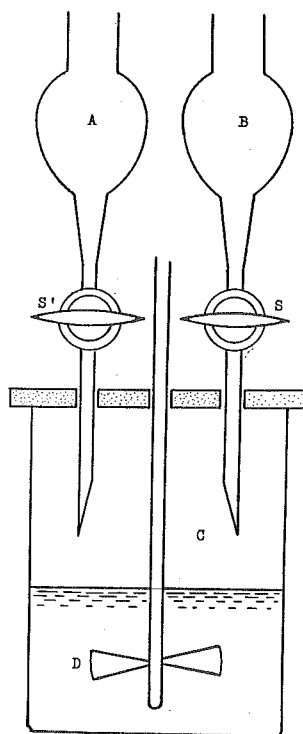


Fig. 8. Apparatus for the synthesis.

TABLE 9. X-ray Data of  $\text{CaCO}_3$ - $\text{MnCO}_3$  Mixed Crystals.

No. of Expt.	Ca/Mn Ratio in Solution	(10 $\bar{1}$ 2) d(Å)	(10 $\bar{1}$ 4) d(Å)	(11 $\bar{2}$ 0) d(Å)	(11 $\bar{2}$ 3) d(Å)	(20 $\bar{2}$ 2) d(Å)
1	0:100	3.669	2.8494	2.3953	2.1811	2.0081
2	10: 90	3.690	2.8660	2.4026	2.1869	2.0123
3	20: 80	3.699	2.8850	2.4088	2.1955	2.0204
4	30: 70	3.710	2.8949	2.4186	2.2035	2.0242
5	40: 60	3.724	2.9066	2.4251	2.2113	2.0352
6	50: 50	3.750	2.9340	2.4279	2.2263	2.0487
7	60: 40	3.767	2.9499	2.4490	2.2337	2.0504
8	70: 30	3.788	2.9760	2.4654	2.2514	0.0613
9	80: 20	3.819	2.9966	2.4721	2.2633	0.0733
10	90: 10	3.838	3.0169	2.4847	2.2754	0.0873
Iceland spar*		3.850	3.030	2.490	2.277	2.088

\* from Tunguska, SSSR.

(Nolenco., Cu-K $\alpha$ , 35 KV, 13 mA, 4-1-4,  $\frac{1}{2}^\circ$ /1 min., correction with Si)

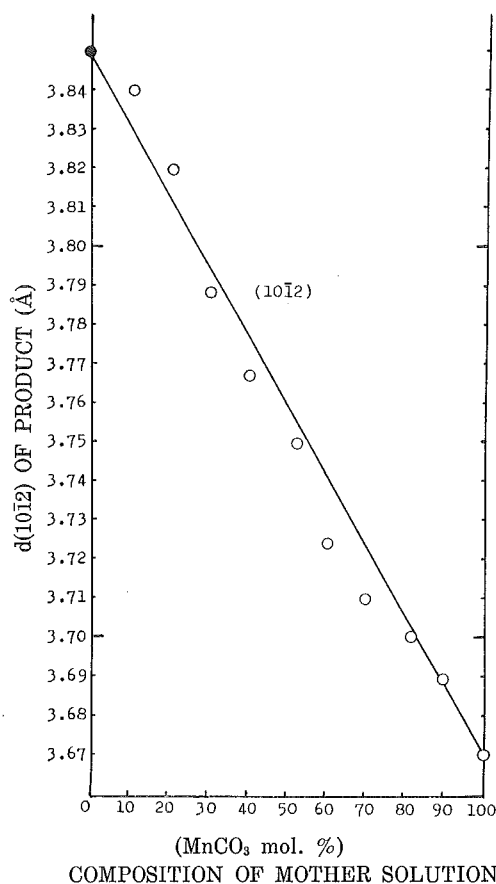


Fig. 9. Variation of  $d(10\bar{1}2)$  of artificial  $\text{MnCO}_3\text{-CaCO}_3$  mixed crystals. The blackened circle represents  $d(10\bar{1}2)$  of a natural iceland spar.

about 0.7 cc/min. for both the reactants. The reaction vessel was beforehand filled with 200 cc of 2.5%  $\text{NH}_4\text{Cl}$  solution; the reactions were carried out with vigorous stirring by the electric stirrer D.

The products thus obtained were left standing in the solutions for three days, and then were washed with water and dried in desiccator.

a)  $\text{CaCO}_3\text{-MnCO}_3$  Mixed Crystals

The products obtained by the above-described procedure were identified by X-ray analysis with the results shown in Table 9. In this table, gradual transitions of the lattice dimensions of the products in accordance with the compositions of their mother solutions are obviously seen.

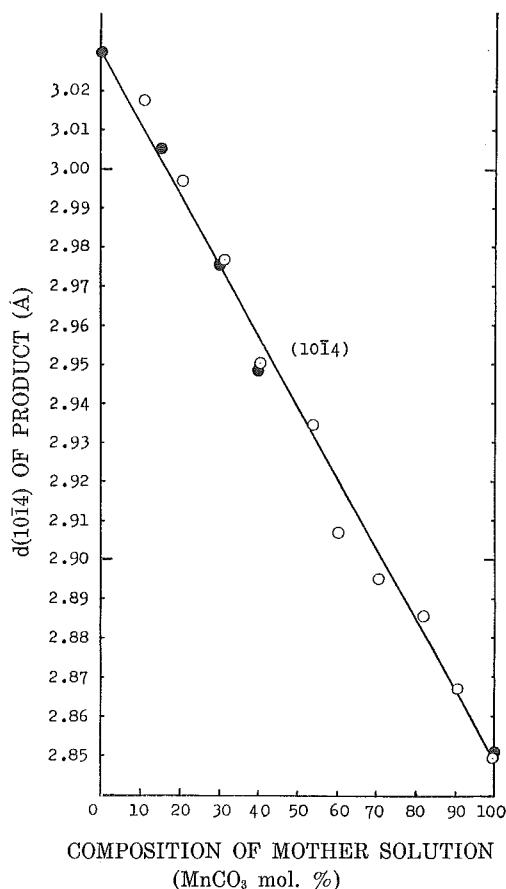


Fig. 10. Variation of  $d(10\bar{1}4)$  of artificial  $\text{MnCO}_3\text{-CaCO}_3$  mixed crystals. Blackened circles represent  $d(10\bar{1}4)$  of natural mixed crystals, the chemical composition of which is also shown on the same abscissa.

These transitions of the spacing  $d(10\bar{1}2)$ ,  $d(10\bar{1}4)$ ,  $d(11\bar{2}3)$ , and  $d(20\bar{2}2)$  are shown in Fig.'s 9, 10, 11 and 12. The smooth and nearly linear curves of those figures seem to be examples of the case in which VEGARD's law (VEGARD and DALE, 1928) is applicable; thus it may be reasonably supposed that the composition of each product has inherited the composition of the corresponding mother solution and so the products have the same Ca/Mn ratio as those of their mother solutions. This means nothing but the possibility of the perfect mixed crystal formation between  $\text{CaCO}_3$  and  $\text{MnCO}_3$ .

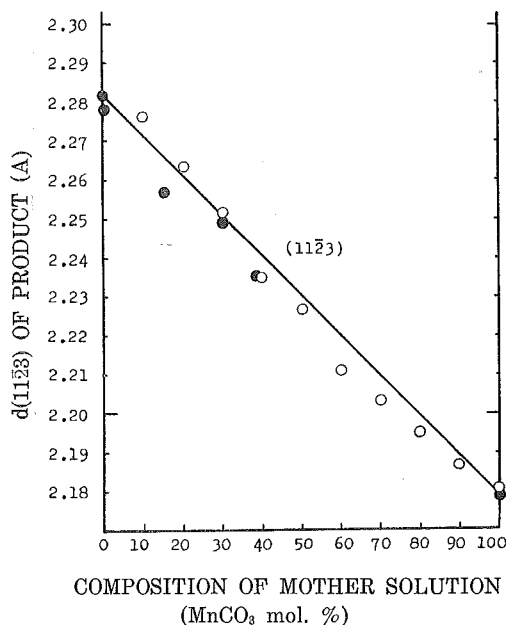


Fig. 11. Variation of  $d(11\bar{2}3)$  of artificial  $\text{MnCO}_3\text{-CaCO}_3$  mixed crystals. Blackened circles represent  $d(11\bar{2}3)$  of natural mixed crystals, the chemical composition of which is also shown on the same abscissa.

It is noteworthy that, considering the composition of each product to be the same as that of its mother solution, there can be seen also striking linear relation between these compositions of the products and their specific gravities calculated from lattice constants; this is in turn the best proof for the supposition that the respective compositions of the products are the same as those of the mother solutions. This relation between the compositions and the specific gravities is shown in Table 10 and Fig. 13.

The possibility of a perfect solid solution between calcite and rhodochrosite has been examined by many research-workers. VEGARD (1947) tried to synthesize the mixed crystals in this series in a similar way to that employed in the present work, and he found a wide discontinuous region from 85 to 25 mol.% of  $\text{CaCO}_3$ . GOLDSMITH and GRAF (1957) also have examined this problem experimentally, and have obtained the complete series of this mixture, but they considered it to be an unstable formation.

The high stability of these mixed crystals, however, may be proved by the fact that the mixed crystals covering the whole of the series are found to exist persistently in nature; KRIEGER (1930) first suggested the

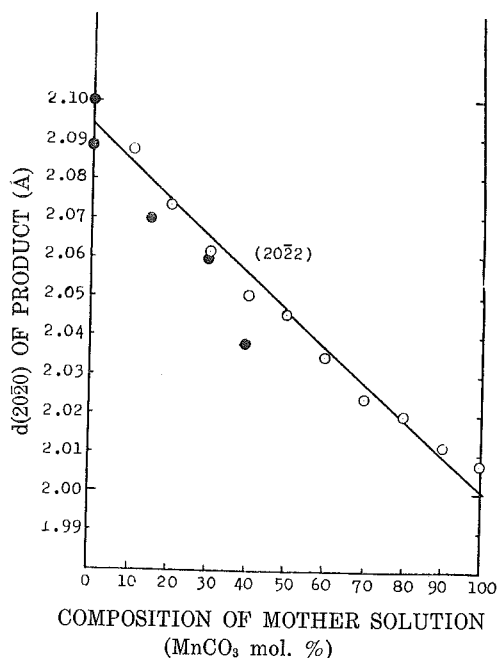


Fig. 12. Variation of  $d(2022)$  of artificial  $\text{MnCO}_3\text{-CaCO}_3$  mixed crystals. Blackened circles represent  $d(2022)$  of natural mixed crystals the, chemical composition of which is shown on the same abscissa.

TABLE 10. Lattice Constants of  $\text{CaCO}_3\text{-MnCO}_3$  Mixed Crystals.

No. of Expt.	a (Å)	c (Å)	c/a	$\alpha$ (Å)	$\alpha$ (deg).	Specific Gravity
1	4.798	15.650	3.262	5.908	47°55'	3.668
2	4.805	15.810	3.290	5.964	47°30'	3.570
3	4.822	15.949	3.308	6.003	47°23'	3.470
4	4.835	16.035	3.316	6.029	47°16'	3.393
5	4.853	16.095	3.317	6.054	47°16'	3.306
6	4.886	16.278	3.332	6.111	47°09'	3.184
7	4.891	16.470	3.367	6.170	46°40'	3.100
8	4.916	16.640	3.385	6.233	46°28'	2.988
9	4.949	16.766	3.388	6.281	46°26'	2.882
10	4.975	16.890	3.395	6.321	46°21'	2.794
*	4.983	17.04	3.418	6.368	46°06'	2.717

\* Iceland spar from Tunguska.

natural occurrence of a complete series of the mixture, and WAYLAND (1942), and HARADA and MATSUDA (1954) have confirmed it. The result of the present work described above is in agreement with their field evidences, and shows a large capability of mixed crystal formation of the

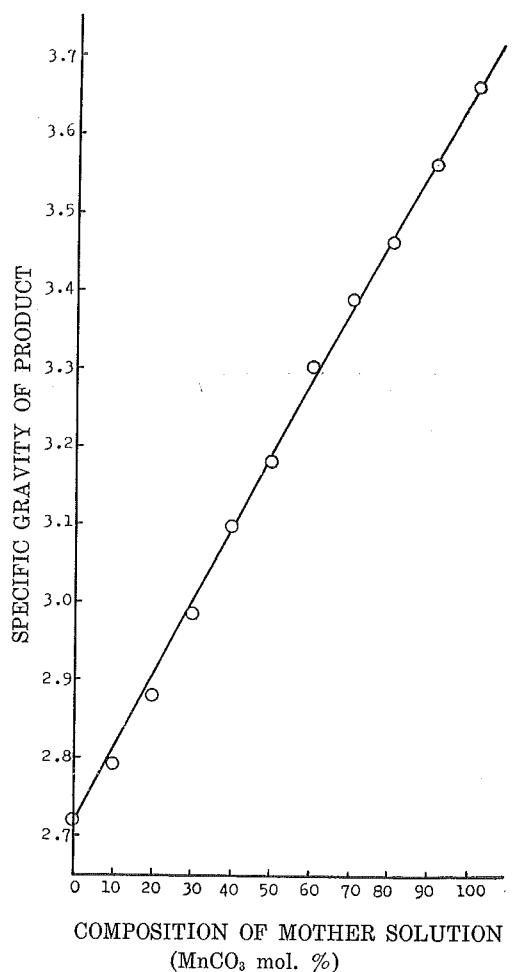


Fig. 13. Variation of the specific gravity of artificial (Mn, Ca) CO<sub>3</sub>.

calcite structure, since the ratio of atomic radii between Ca and Mn is somewhat exceeding the GOLDSCHMIDT law.

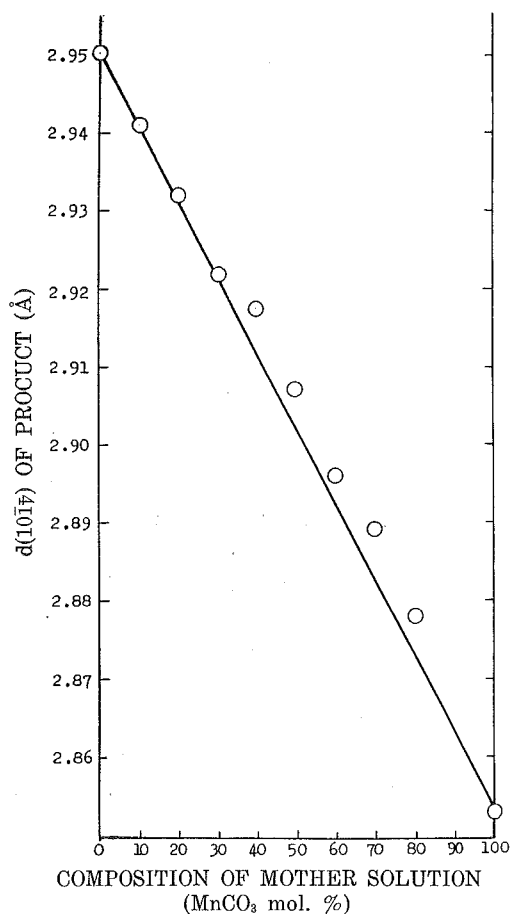
b) CdCO<sub>3</sub>-MnCO<sub>3</sub> Mixed Crystals

The results of X-ray analysis of the products are shown in Table 11, and the variation of  $d(10\bar{1}4)$  with composition is in Fig. 14. As seen in the figure, the curve of the variation is more linear than the case of the CaCO<sub>3</sub>-MnCO<sub>3</sub> mixed crystals, and thus it indicates the existence of the stable and complete series of mixture. In view of the experimental results, it is rather a wonder that no mixed crystal in this series has been found



TABLE 11. X-ray Analyses Data of  $\text{CdCO}_3$ - $\text{MnCO}_3$  Mixed Crystals.

No. of Expt.	Cd/Mn Ratio in Solution	(10 $\bar{1}$ 2) d(Å)	(10 $\bar{1}$ 4) d(Å)	(11 $\bar{2}$ 3) d(Å)	(20 $\bar{2}$ 2) d(Å)
22	0:100	3.688	2.854	2.182	2.010
23	10: 90	—	—	—	—
24	20: 80	3.705	2.878	2.197	2.022
25	30: 70	3.715	2.889	2.206	2.030
26	40: 60	3.720	2.896	2.210	2.033
27	50: 50	3.743	2.907	2.216	2.038
28	60: 40	3.751	2.918	2.222	2.045
29	70: 30	3.751	2.924	2.229	2.050
30	80: 20	3.767	2.932	2.236	2.056
31	90: 10	3.773	2.941	2.241	2.062
12	100: 0	3.789	2.950	2.246	2.066

(Nolecrco., Cu-K $\alpha$ , 35 KV, 13 mA, 4-1-4, 1°/1 min., corr. with Si)Fig. 14. Variation of  $d(10\bar{1}4)$  of artificial (Mn, Cd)  $\text{CO}_3$ .

in nature. This fact, probably, points out the importance of the geochemical differentiation of elements for the mixed crystal formation.

c)  $\text{CaCO}_3\text{-CdCO}_3$  Mixed Crystals

In view of much closeness in atomic radii of both cations  $\text{Ca}^{++}$  and  $\text{Cd}^{++}$ , a smooth and linear curve was expected for the transition of  $d(10\bar{1}4)$  like the transition curves in the foregoing two series. However, contrary to the expectation, the curve has larger curvature, which obviously shows that the compositions of the products do not coincide with those of their mother solutions.

Evidently the crystallization of a product the composition of which differs from that of the mother solution must cause the differentiation of the chemical composition of the mother solution with the progress of the crystallization; then it follows that the supplementary crystallization of one or more products of different composition takes place in conformity with the new chemical condition.

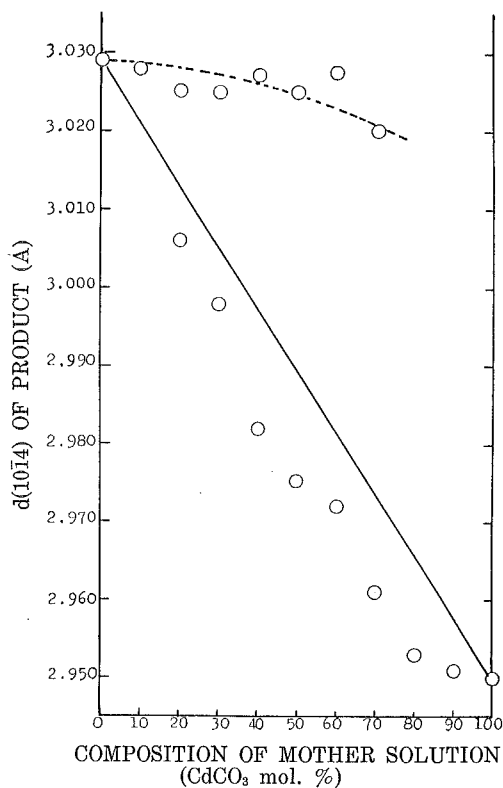
The existence of a supplementary product of such a kind is actually observable in this series as shown in Fig. 15 by dotted curve. In this figure it can be noticed that two chemically different products are appearing simultaneously in one solution. For instance, two mixed crystals which have the spacing  $d(10\bar{1}4)$  of 2.975 and 3.025 (Å) appear together in the solution of  $\text{Ca}_{50}\text{Cd}_{50}$ , as shown in Table 12 and Fig. 15.

The fact that the formation of the  $\text{CaCO}_3\text{-CdCO}_3$  mixed crystal is not in single series, but separates to two series in spite of great closeness of atomic radii, is very interesting. This fact would indicate the greater difficulty of the mixed crystal formation in  $\text{CaCO}_3\text{-CdCO}_3$  series than the

TABLE 12. Values of  $d(10\bar{1}4)$  of Products in  $\text{CaCO}_3\text{-CdCO}_3$  Series.

No. of Expt.	Ca/Cd Ratio in Solution	$(10\bar{1}4)_1$	I/I.	$(10\bar{1}4)_2$	I/I.
12	0:100	2.950	100	—	—
13	10: 90	2.951	100	—	—
14	20: 80	2.953	100	—	—
15	30: 70	2.961	80	3.020	20
16	40: 60	2.972	77	3.027	23
17	50: 50	2.975	75	3.025	25
18	60: 40	2.982	63	3.027	37
19	70: 30	2.998	55	3.025	45
20	80: 20	3.006	45	3.025	55
21	90: 10	—	—	3.028	100

(Nolerco., Cu-K $\alpha$ , 35 KV, 13 mA, Ni Fil., 4-1-4, 1/1, corr. with Si)

Fig. 15. Variation of  $d(1014)$  of artificial (Ca, Cd)  $\text{CO}_3$ .TABLE 13. Composition and Concentration of Reactants Used in Experiments in  $\text{CaCO}_3$ - $\text{SrCO}_3$  Series.

No.	Sr:Ca:CO <sub>3</sub> in Reactant	Reactant A (grms. in 100 cc Soln.)			Reactant B (grms. in 100 cc Soln.)
		SrCl <sub>2</sub> + 6H <sub>2</sub> O	CaCl <sub>2</sub> + 2H <sub>2</sub> O	NH <sub>4</sub> Cl	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O
33	10:90	0.533	2.646	3.5	5.0
34	20:80	1.067	2.352	3.5	5.0
35	30:70	1.600	2.058	3.5	5.0
36	40:60	2.133	1.764	3.5	5.0
37	50:50	2.666	1.470	3.5	5.0
38	60:40	3.200	1.176	3.5	5.0
39	70:30	3.733	0.882	3.5	5.0
40	80:20	4.266	0.588	3.5	5.0
41	90:10	4.800	0.294	3.5	5.0
42	100: 0	5.333	0	3.5	5.0

formations in the two series already mentioned. Probably this suggests the important contributions of factors other than atomic radii to the mixed crystal formation; the ionic potentials, the polarizing power and, perhaps, atomic weight of the corresponding atoms are among those factors.

## II. Isomorphic Replacements in Aragonite-Group Minerals

For the purpose of comparing the capabilities of mixed crystal formation of calcite and aragonite structure, attempts were made to synthesize the mixed crystals of the series  $\text{SrCO}_3\text{-CaCO}_3$ ,  $\text{BaCO}_3\text{-CaCO}_3$  and  $\text{BaCO}_3\text{-SrCO}_3$  under the same conditions as in the synthesis of calcite group. The compositions and the concentrations of the reactants used here are as shown in Tables 13, 14 and 15.

TABLE 14. Compositson and Concentration of Reactants Used in Experiments in  $\text{BaCO}_3\text{-CaCO}_3$  Series.

No.	Ba:Ca:CO <sub>3</sub> in Solution	Reactant A (grms. in 100 cc Soln.)			Reactant B (grms. in 100 cc Soln.)
		BaCl <sub>2</sub> + 2H <sub>2</sub> O	CaCl <sub>2</sub> + 2H <sub>2</sub> O	NH <sub>4</sub> Cl	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O
44	20:80	0.977	2.352	3.5	5.0
46	40:60	1.954	1.764	3.5	5.0
48	60:40	2.932	1.176	3.5	5.0
50	80:20	3.909	0.588	3.5	5.0

TABLE 15. Composition and Concentration of Reactants Used in Experiments in  $\text{BaCO}_3\text{-SrCO}_3$  Series.

No.	Ba:Sr:CO <sub>3</sub> in Solution	Reactant A (grms. in 100 cc Soln.)			Reactant B (grms. in 100 cc Soln.)
		BaCl <sub>2</sub> + 2H <sub>2</sub> O	SrCl <sub>2</sub> + 6H <sub>2</sub> O	NH <sub>4</sub> Cl	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> ·H <sub>2</sub> O
52	100: 0	4.886	0	3.5	5.0
54	90: 20	3.909	1.067	3.5	5.0
56	60: 40	2.932	2.133	3.5	5.0
58	40: 60	1.954	3.200	3.5	5.0
60	20: 80	0.977	4.266	3.5	5.0
42	0:100	0	5.333	3.5	5.0

### a) $\text{SrCO}_3\text{-CaCO}_3$ Series

Products were prepared in the appartus shown in Fig. 8, and by the same method as in the foregoing experiments. But this time each product

TABLE 16. X-ray Analysis Data of Products in  $\text{CaCO}_3\text{-SrCO}_3$  Synthesis (A)

C (hkil)	$\mu$ (hkil)	No. 33a d I	No. 34a d I	No. 35a d I	No. 36a d I	No. 38a d I	No. 40a d I	Na. 42a d I	S (hkil)
(10 $\bar{1}2$ )	(0002)	4.72	64.28	104.28	8	—	—	—	
		3.89	53.91	23.91	10	3.91	13	—	
	(10 $\bar{1}0$ )	3.59	313.60	393.60	28	—	—	—	
		—	—3.48	73.49	28	3.49	50	3.50 100	3.53 150
(10 $\bar{1}4$ )		—	—	—3.37	20	3.42	25	3.44 43	3.45 60
	(10 $\bar{1}1$ )	3.31	423.33	443.33	37	—	—	3.33 7	—
		3.056	453.066	303.076	44	3.079	67	—	—
		—	—	—2.957	5	2.974	8	2.994 15	3.013 20
(10 $\bar{1}2$ )		—	—	—2.794	11	2.794	11	2.815 15	2.839 20
	(10 $\bar{1}2$ )	2.738	402.751	502.758	37	—	—	—	—
		—	—	—	—	—	—	—	—
		—	—	—	—	2.720	2	2.728 5	—
(1 $\bar{2}10$ )		—	—	—	—	2.579	6	2.583 7 2.563 7	2.617 8 2.599 8
		—	—	—	—	—	—	2.527 10 2.509 11	2.545 14 2.533 15
		—	—	—	—	—	—	—	—
		—	—	—	—	—	—	—	—
(1 $\bar{2}10$ )		2.507	162.513	42.514	13	2.513	15	—	—
(11 $\bar{2}3$ )		—	—	—2.428	10	2.444 20 2.428 20	2.448 40	2.473 45 2.453 43	2.492 60 2.466 70
		2.296	82.296	62.308	6	2.298	8	—	—
		—	—	—	—	—	—	—	—
		—	—	—	—	2.149	5	2.166 8	2.175 12
(20 $\bar{2}2$ )		—	—	—	—	—	—	—	2.268 8
		2.125	52.130	72.137	7	—	—	—	—
		2.102	62.106	82.114	10	2.113	13	—	—
	(11 $\bar{2}0$ )	2.073	242.076	282.080	24	—	—	—	—
(10 $\bar{1}8$ )		—	—2.023	42.027	8	2.021	20	2.031 30	2.047 40
		—	—	—	—	—	—	—	—
		—	—	—	—	1.959 10 1.947 10	1.977 14	1.992 37	(041)
		1.926	151.936	61.941	12	1.943	20	—	—
(11 $\bar{2}6$ )		—	—	—	—	1.924	12	1.932 15	1.943 15
		—	—	—	—	1.906	13	—	—
		1.886	111.888	71.897	10	1.897	16	—	—
		—	—	—	—	1.880	13	1.883 20	1.900 27
(11 $\bar{2}6$ )		1.862	81.865	151.868	13	—	—	—	—
		1.829	201.833	251.833	17	—	—	—	—
		—	—	—	—	—	—	—	—
		—	—	—	—	1.790	12	1.802 25	1.819 30 1.812 25

C=calcite,  $\mu$ = $\mu$ -form, S=strontianite.(Cu-K $\alpha$ , 35 KV, 13 mA, Ni fil., 4-1-4, 1°/1 min.)

was made twice; one of the two products was left in contact with the mother solution for 30 days in order to see the persistency of product, while the other was left for 3 days as in the foregoing experiments.

Results of X-ray analyses of the products of 3 days standing are shown in Table 16, and those of 30 days standing are in Table 17. It is very interesting to see that the products consist of Sr-bearing calcite,  $\mu$ -CaCO<sub>3</sub> and Ca-bearing strontianite, while aragonite, pure and Sr-bearing, is not found in any of the examples.

*Sr-bearing calcite*

Sr-bearing calcite is found in products from the solutions which possess compositions of Sr/Ca ratios of less than about 50/50, in both the lots of 3 and 30 days standings. The interfacial spacings of these calcite crystals are appreciably larger than those of pure calcite, and the increase

TABLE 17. X-ray Analysis Data of Products in CaCO<sub>3</sub>-SrCO<sub>3</sub> Synthesis (B)

C (hkl)	No. 34 b d I		No. 36 b d I		No. 38 b d I		No. 40 b d I		S (hkl)
(10 $\bar{1}2$ )	3.89	24	3.88	10	—	—	—	—	
	3.49	40	3.49	135	3.49	160	3.52	180	(111)
	3.39	25	3.40	45	3.41	50	3.44	70	(021)
(10 $\bar{1}4$ )	3.056	140	3.056	63	—	—	—	—	
	2.974	6	2.976	10	2.980	18	3.005	20	(002)
	2.798	10	2.798	20	2.806	18	2.820	18	(012)
	2.560	10	2.562	13	2.569	8	2.577	13	(102)
	2.527	12	2.527	15	2.528	10	2.548	15	} (200)
	—	—	—	—	2.520	10	2.533	15	
(11 $\bar{2}0$ )	2.506	25	2.503	13	—	—	—	—	
	2.447	15	2.442	40	2.448	40	2.461	55	(112)
	2.419	14	2.416	30	2.428	35	2.447	50	(130)
(11 $\bar{2}3$ )	2.294	30	2.294	13	—	—	—	—	
	—	—	—	—	2.252	5	2.262	4	(211)
	2.161	7	2.161	10	2.161	10	2.173	10	(220)
(20 $\bar{2}2$ )	2.102	30	2.101	12	—	—	—	—	
	2.026	15	2.026	35	2.030	40	2.041	45	(221)
	—	—	1.947	15 }	1.956	16	1.973	15	(041)
	—	—	1.940	15 }					
(10 $\bar{1}8$ )	1.924	30	1.928	23	1.924	16	1.939	13	(202)
(11 $\bar{2}6$ )	1.883	30	1.879	28	1.878	24	1.894	28	(132)
	1.796	8	1.799	25	1.804	25	1.815	30	(023)

(Cu-K $\alpha$ , 35 KV, 13 mA, Ni Fil., 4-1-4, 1°/1 min.)

of these spacings with the increase of Sr/Ca ratio is obviously seen in the case of 3 days standing. Hence it is evident that the diadochic substitution of Ca by Sr takes place in them to some large extent. In view of the transition curve of  $d(10\bar{1}4)$  shown in Fig. 16, it is thought that the substitution in the products of 3 days standing may reach to about 30% for the maximum, while in the products of 30 days standing it is settled down to the neighbourhood of 10%.

$\mu$ - $\text{CaCO}_3$  (vaterite B)

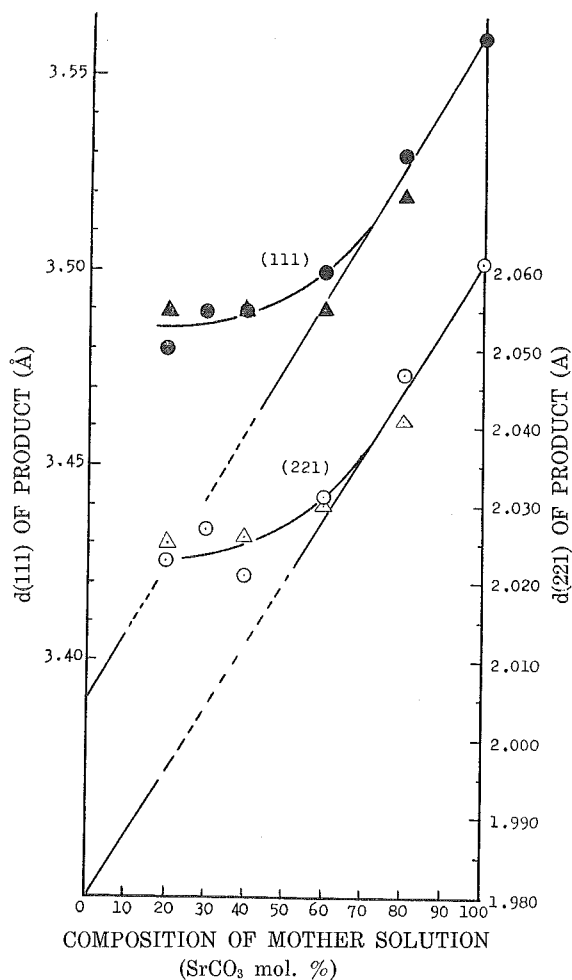


Fig. 16. Variation of  $d(111)$  and  $d(221)$  of artificial (Ca, Sr)  $\text{CO}_3$ . Circles represent products of 3 days standing, and triangles represent those of 30 days.

$\mu$ -CaCO<sub>3</sub>, the most unstable modification of hexagonal symmetry, is found in products from the solutions which possess Sr/Ca ratios of less than 40/60, only in the run of 3 days standing. The absence of this modification in the products of 30 days standing is probably in consequence of its unstable nature.

*Ca-bearing strontianite*

Strontianite is found in products from the solutions of Sr/Ca ratios of above 20/80. The appreciable decreases of  $d(111)$  of these strontianite crystals indicate the growth of the isomorphic replacement of Sr by Ca, which is estimated on the basis of VEGARD's law to be about 40% for the maximum, as shown in Fig. 16. It is noteworthy in connection with this fact that natural strontianite commonly contains Ca in some appreciable amount, and thus the lattice dimensions of such strontianites are smaller than those of pure artificial strontianite. The X-ray analysis data of natural strontianite, together with those of  $\mu$ -CaCO<sub>3</sub> which was synthesized by previous workers, are shown in Table 18.

b) BaCO<sub>3</sub>-CaCO<sub>3</sub> Series

Results of X-ray analysis of these products show that they consist of  $\mu$ -CaCO<sub>3</sub>, baryto-calcite and Ca-bearing witherite, and that no aragonite is found in this experiment similarly as in the case of the CaCO<sub>3</sub>-SrCO<sub>3</sub> series. The most significant features of the observation are the absence

TABLE 18. X-ray Analysis Data of  $\mu$ -CaCO<sub>3</sub> and Strontianite  
Given by Various Authors.

(hkil)	$\mu$ -CaCO <sub>3</sub>					
	d	(a) I/I <sub>0</sub>	d	(b) I	d	(c) I
(0002)	4.26	13	4.28	3	—	—
(1010)	3.58	63	3.575	6	3.59	s
(1011)	3.29	75	3.277	6	3.29	s
(1012)	2.73	100	2.715	8	2.719	s
	2.31	8	2.543	2	2.313	ff
(1120)	2.06	63	2.066	8	2.053	s
	1.87	15	—	—	1.85	f
(1014)	1.83	63	1.846	8	1.82	s
(2022)	1.65	31	1.645	6	1.64	m
			(The rest is omitted)		(The rest is omitted)	

(a) A. S. T. M. Card, 1-1033

(b) Olshausen: 1924,

(c) Gibson, Wyckoff & Merwin: 1925,



## Strontianite

(hkl)	(a)		(b)		(c)	
	d	I/I°	d	I	d	I
(110)	4.367	14	—	—	—	—
(020)	4.207	6	—	—	—	—
(111)	3.535	100	3.53	10	3.47	10
(021)	3.450	70	—	—	3.38	4
(002)	3.014	22	—	—	3.00	1
(121)	2.859	5	—	—	—	—
(012)	2.838	20	—	—	2.79	2
(102)	2.596	12	—	—	2.67	1
(200)	2.554	23	2.56	1	2.56	1
(112)	2.481	34	—	—	2.51	1
(130)	2.458	40	—	—	2.450	3
(022)	2.4511	33	2.45	4	2.416	5
(211)	2.2646	5	—	—	2.232	1
(220)	2.1831	16	2.18	1	2.149	2
(040)	2.1035	7	—	—	2.069	1
(221)	2.0526	50	2.05	4	2.022	7
(041)	1.9860	26	1.980	1	1.951	3
(202)	1.9489	21	—	—	1.921	3
(132)	1.9053	35	1.90	2	1.876	5
(113)	1.8253	31	—	—	—	—
(023)	1.8134	16	1.81	3	1.796	7

(a) A. S. T. M. Card, 5-0418

(b) Kitaigorodsky: 1952,

(c) Korzhinsky: 1956; this sample contains 10 % of  $\text{CaCO}_3$  mol.

of calcite and, instead of it, the persistent existence of  $\mu\text{-CaCO}_3$  even in the examples of 30 days standing. The results of analyses are shown in Table 19.

 *$\mu\text{-CaCO}_3$* 

This modification is found in the products formed from the solutions of low Ba concentration, of Ba (mol.%) up to 20. It is very interesting to see that in the products of 30 days standing this modification is found to be nearly the same in amount as in the corresponding products of 3 days.

*Baryto-calcite*

This monoclinic double salt of  $\text{Ca}\cdot\text{Ba}(\text{CO}_3)_2$  is found in nearly all the products in this run, especially dominantly in the products formed from the solutions of Ba/Ca from 20/80 to 60/40.

*Ca-bearing witherite*

TABLE 19. X-ray Analysis Data of Products in  $\text{CaCO}_3$ - $\text{BaCO}_3$  Syntheses.  
(A) Products of 3 Days Standing.

$\mu$ (hkil)	B.C	No. 44 a d I		No. 46 a d I		No. 48 a d I		No. 50 a d I		W (hkl)
(0002)	B. C	—	—	—	—	—	—	4.53	4	(110)
		4.24	4	—	—	—	—	—	—	
		3.97	27	3.97	25	4.00	15	4.04	3	
(1010)	B. C	—	—	—	—	3.70	35	3.70	70	(111)
		3.59	12	—	—	—	—	—	—	
		3.31	17	—	—	—	—	—	—	
(1011)	B. C	3.15	55	3.13	55	3.16	32	3.17	30	(002)
		2.739	18	—	—	—	—	—	—	
		2.553	16	2.547	16	2.586	16	2.600	37	(112); (130)
(1012)	B. C	2.149	15	2.148	13	2.154	—	—	—	(221)
		—	—	—	—	—	—	2.134	15	
		—	—	—	—	—	—	2.125	16	(041)?
(1120)	B. C	2.077	12	—	—	—	—	—	—	
		1.992	10	1.979	13	2.013	13	2.013	18	(132)
		1.946	10	1.932	12	1.951	10	—	—	
(1120)	B. C	—	—	—	—	1.941	8	—	—	
		—	—	—	—	—	—	1.926	18	(113)
		1.861	4	—	—	—	—	—	—	
$\mu$ (1014)		1.823	9	—	—	—	—	—	—	

B. C=baryto-calcite. W=withelite.

(B) Products of 30 Days Standing.

$\mu$ (hkl)	B. C	No. 44 b d I		No. 46 b d I		No. 48 b d I		No. 50 b d I		W (hkl)
(110)	B. C	—	—	—	—	—	—	4.49	3	(110)
		3.98	18	3.96	18	3.98	30	4.04	10	
(111)	B. C	—	—	—	—	—	—	3.67	30	(111)
		—	—	—	—	—	—	—	—	
(1010)	B. C	3.60	16	—	—	—	—	—	—	
(1010)		3.31	24	—	—	—	—	—	—	
(1012)	B. C	3.15	70	3.13	50	3.16	120	3.22	13	(002)
		2.749	24	—	—	—	—	—	—	
(1120)	B. C	2.554	10	2.552	10	2.563	20	2.596	17	(112)
		2.147	8	2.139	10	2.150	15	2.171	4	
(1120)	B. C	2.073	11	—	—	—	—	—	—	
		—	—	—	—	—	—	2.125	8	(221); (041)
(1120)	B. C	2.000	6	—	—	2.004	10	2.008	10	(132)
		—	—	1.981	12	1.992	8	—	—	
(1120)	B. C	—	—	1.971	8	1.951	11	—	—	
		—	—	1.916	12	1.924	5	1.926	5	(113)
$\mu$ (1014)		1.865	4	—	—	—	—	—	—	
		1.827	12	—	—	—	—	—	—	

(Cu-K $\alpha$ , 35 KV, 13 mA, Ni Fil., 4-1-4, 1/1)

TABLE 20. X-ray Analysis Data of Witherite, Baryto-calcite and Alstonite Given by Some Authors.

Witherite A. S. T. M., 5-0378 d I/I <sub>0</sub> (hkl)			Baryto-calcite A. S. T. M. d I/I <sub>0</sub>		Alstonite A. S. T. M. d I/I <sub>0</sub>	
4.56	9	(110)	3.96	50	4.51	7
4.45	4	(020)	3.16	100	3.93	25
3.72	100	(111)	2.54	40	3.68	100
3.68	53	(021)	2.14	30	3.12	62
3.215	15	(002)	2.00	30	2.60	31
3.025	4	(012)	1.94	25	2.54	10
2.749	3	(102)			2.27	4
2.656	11	(200)			2.13	37
2.628	24	(112)			2.00	17
2.590	23	(130)			1.92	31
2.281	6	(220)				
2.226	2	(040)				
2.150	28	(221)				
2.104	12	(041)				
2.048	10	(202)				
2.019	21	(132)				
1.940	15	(113)				

TABLE 21. X-ray Analysis Data of Products in BaCO<sub>3</sub>-SrCO<sub>3</sub> Series.  
(Products of 3 Days Standing)

(hkl)	No. 52 a d I		No. 54 a d I		No. 56 a d I		No. 58 a d I		No. 60 a d I		No. 42 a d I	
(110)	4.60	7	4.55	7	4.50	5	4.46	5	4.46	7	4.40	10
(111)	3.74	90	3.71	87	3.68	80	3.63	100	3.61	140	3.56	160
(021)	3.68	40	—	—	—	—	—	—	3.55	56	3.47	120
(002)	3.22	15	3.21	10	3.17	13	3.13	14	3.10	20	3.03	25
(012)	3.041	4	3.015	4	2.984	5	2.940	7	2.912	15	2.848	22
(102)	—	—	—	—	—	—	—	—	2.657	8	2.609	16
(200)	2.656	16	—	—	—	—	—	—	—	—	2.562	38
(112)	2.633	25	2.609	25	{ 2.583	30	2.554	33	2.528	46	{ 2.492	60
(130)	2.612	20	2.585	20								
(220)	2.291	5	2.268	5	2.241	5	2.225	8	2.212	10	2.19	200
(040)	2.236	3	—	—	—	—	—	—	2.149	6	—	—
(221)	2.154	22	2.135	22	2.120	19	2.097	23	2.081	38	2.061	75
(041)	2.109	10	2.090	8	2.076	8	2.045	10	2.021	15	1.992	37
(202)	2.053	10	—	—	2.013	9	1.992	12	1.988	15	1.954	30
(132)	2.021	20	2.009	18	1.988	15	1.967	18	1.940	26	1.912	50
(113)	1.945	17	1.928	14	1.906	15	1.878	18	1.859	30	1.832	43

(Cu-K $\alpha$ , 35 KV, 13 mA, Ni Fil., 4-1-4, 1°/1)

This is found in the products from the solutions of Ba/Ca above 60/40 in the run of 3 days standing, and from the solutions of above 20/80 in the 30 days'. The isomorphic replacement of Ba by Ca seems to reach some appreciable amounts in these products, but quantitative examination of this is impossible owing to the fact that most of the spacing of these witherite tend to coincide with spacings of baryto-calcite with the advance of the replacement.

The X-ray data of baryto-calcite, witherite, and alstonite given by some authors are shown in Table 20 for reference.

c)  $\text{BaCO}_3$ - $\text{SrCO}_3$  Series

Nearly complete mixed crystal formation is shown in this series as seen in Table 21 and Fig. 17. This condition is very natural in view of the closeness of atomic radii between Ba and Sr. Hence it is probable

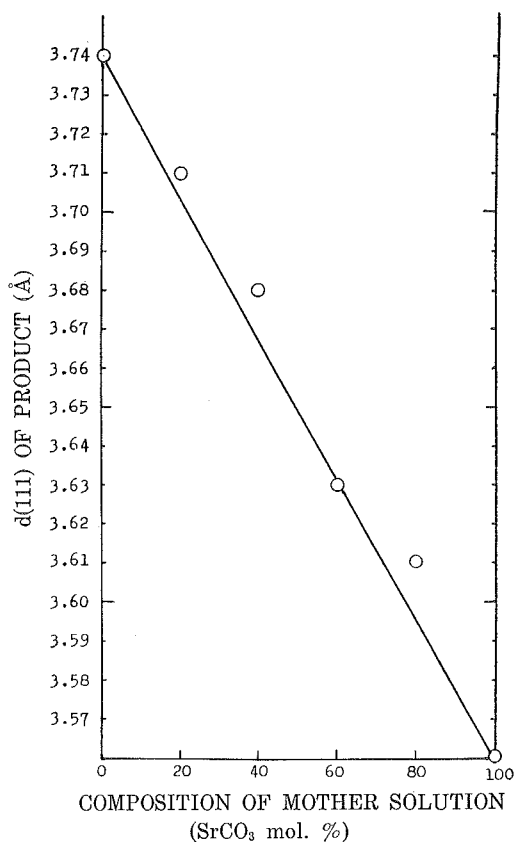


Fig. 17. Variation of  $d(111)$  of artificial (Sr, Ba)  $\text{CO}_3$ .

that less frequent occurrence of these mixed crystals in nature is due rather to geochemical factors than to crystallo-chemical.

### III. Considerations

In order to see the relative capability of mixed crystal formation of calcite- and aragonite-structure, attention must be paid, before everything, to the fact that in the case of  $\text{SrCO}_3\text{-CaCO}_3$  syntheses, aragonite is not found, while calcite which is present in place of aragonite is found to contain diadochically some appreciable amounts of Sr. This fact seems to show that Sr-bearing aragonite is more unstable than Sr-bearing calcite, or in other words, the stability of the nucleus of aragonite is much more affected by the replacement of Ca by Sr than that of the calcite nucleus, so that the aragonite nucleus is unable to exist and to grow in competition with the calcite nucleus.

This supposition may be confirmed by examination of the similar relation between calcite and  $\mu\text{-CaCO}_3$  in the  $\text{CaCO}_3\text{-BaCO}_3$  synthesis. In this series, the unstable  $\mu$ -form is able to remain without change for 30 days in the solutions in which calcite is unable to form. Probably in this case the stability of nucleus of calcite is spoiled by the absorption of large Ba ions, while the nucleus of  $\mu$ -form may be not so much affected by such absorption effect because of its very open and, perhaps, larger entropical structure; the specific gravity of  $\mu\text{-CaCO}_3$  is 2.54, this value is much smaller than 2.71 of calcite and 2.93 of aragonite.

The result of the present work shows the negative effects of Sr and Ba on aragonite formation; this is contrary to the opinion of most earlier researchers, who accepted the effect of Sr and Ba without question.

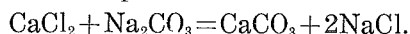
It should be noticed, however, that  $\mu\text{-CaCO}_3$  and Ca-bearing strontinite both have some properties on account of which they are apt to be mistaken for aragonite; the sensibility to chemical tests, such as Meigen's reaction, of both the species resemble that of aragonite, and they show somewhat similar patterns of X-ray diffraction to that of aragonite. Then it may be justly supposed that  $\mu\text{-CaCO}_3$  and Ca-bearing strontianite both may have sometimes been mistaken for aragonite in those earlier researches.

## (7) Effect of $\text{Mg}^{++}$ , $\text{Na}^+$ , $\text{K}^{++}$ and Other Ions on the Selective Formations of Calcium Carbonate

### I. Experiment

$\text{CaCO}_3$  was presipitated in reactions of  $\text{CaCl}_2$  with carbonates of Na, K and  $\text{NH}_4$  in the same apparatus and by the same method as the foregoing; the only exception was that this time the solutions which were filled in the

TABLE 22. Experiment-Data of Reactions;



(In each reaction, each 40 cc of 0.3 M  $\text{Na}_2\text{CO}_3$  and 0.25 M  $\text{CaCl}_2$  in which a give amount of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  was added were dropped into the reaction vessel containing 200 cc of an aqueous solution as specified in the table. All the reactions were performed at room temperature.)  $\text{Ca}:\text{CO}_3=25/30$

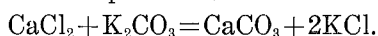
No. of expt.	Substance dissolved in reaction vessel (grams)	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ added in $\text{CaCl}_2$ (grams)	pH	Duration of reaction (minutes)	C/A/ $\mu$
70	non	non	5.5 ~9.5	45	140/0/0
71	NaCl 2.4	non	6.3 ~9.4	50	140/3/0
72	NaCl 7.0	non	6.4 ~9.7	60	140/4/14
73	NaCl 23.4	non	6.3 ~9.7	50	140/0/36
74	non	0.08	6.0 ~9.5	50	150/0/0
75	NaCl 2.4	0.08	6.8 ~9.85	55	140/0/18
76	NaCl 7.0	0.08	6.4 ~9.8	50	75/0/40
77	NaCl 23.4	0.08	6.4 ~9.65	50	15/0/55
78	non	0.4	5.5 ~9.3	45	140/0/0
79	NaCl 2.4	0.4	5.8 ~9.4	55	140/0/0
80	NaCl 7.0	0.4	6.0 ~9.3	50	150/0/0
81	NaCl 23.4	0.4	6.5 ~9.4	50	140/2/0
82	non	2.0	6.0 ~9.65	40	145/0/0
83	NaCl 2.4	2.0	6.0 ~9.65	50	145/2/0
84	NaCl 7.0	2.0	6.0 ~9.6	50	150/0/0
85	NaCl 23.4	2.0	5.95~9.65	40	150/2/0

reaction vessel were those of various concentrations of each NaCl, KCl,  $\text{KNO}_3$  and  $\text{NH}_4\text{Cl}$ , in place of  $\text{NH}_4\text{Cl}$  solution of a fixed concentration as in the foregoing experiments.  $\text{MgCl}_2$ , however, was not added in the solutions of the reaction vessel, but it was mixed with the reactant  $\text{CaCl}_2$ .

The pH of the solutions of reaction vessel was measured by a glass-electrode pH meter at the beginning and at the end of each reaction. The duration of reaction was kept to about one hour for the entire run, and the product was taken out from the solution as soon as possible when the reaction was finished, use being made of accelerated filtration with suction. The purpose of this instant filtration is to observe the nascent state of each product.

The observed data of the reactions are shown in Tables 22, 23, 24 and 25. The values of C/A/ $\mu$  in the last columns of these tables mean the ratio of the intensities of the most intensive diffractions of calcite, aragonite and  $\mu$ -form;  $d(10\bar{1}4)$  of calcite,  $d(111)$  of aragonite and  $d(10\bar{1}1)$  of

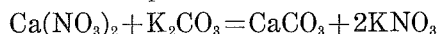
TABLE 23. Experiment-Data of Reactions;



(In each reaction, each 40 cc of 0.3 M  $\text{K}_2\text{CO}_3$  and 0.25 M  $\text{CaCl}_2$  in which a given amount of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  was added were dropped into the reaction vessel containing 200 cc of an aqueous solution as specified in the table. All the reactions were performed at room temperature.)  $\text{Ca}:\text{CO}_3=25/30$

No. of expt.	Substance dissolved in reaction vessel (grms.)	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ added in $\text{CaCl}_2$ (grms.)	pH	Duration of reaction (minutes)	C/A/ $\mu$
86	non	0	5.6 ~8.3	40	130/4/6
87	KCl 3.0	0	5.5 ~9.8	35	115/5/23
88	KCl 9.0	0	5.5 ~9.5	45	42/0/52
89	KCl 29.8	0	5.5 ~9.3	55	13/0/56
90	non	0.08	5.5 ~9.85	35	145/0/0
91	KCl 3.0	0.08	5.4 ~9.0	55	140/4/0
92	KCl 9.0	0.08	5.4 ~9.2	55	140/3/0
93	KCl 29.8	0.08	5.4 ~9.55	45	120/0/26
94	non	0.4	6.7 ~9.75	40	140/0/0
95	KCl 3.0	0.4	6.8 ~8.75	55	140/3/0
96	KCl 9.0	0.4	6.65~9.60	55	120/14/16
97	KCl 29.8	0.4	6.5 ~9.6	50	140/3/0
98	non	2.0	5.0 ~9.6	65	145/0/0
99	KCl 3.0	2.0	5.6 ~9.65	65	145/0/0
100	KCl 9.0	2.0	5.8 ~9.65	80	150/0/0
101	KCl 29.8	2.0	5.7 ~9.7	65	150/0/0

TABLE 24-1. Experiment-Data of Reactions;



(In each reaction, each 40 cc of 0.25 M  $\text{Ca}(\text{NO}_3)_2$ , in which a given amount of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  was added, and 0.3 M  $\text{K}_2\text{CO}_3$  were dropped into the reaction vessel containing an aqueous solution as specified in the table. All the reactions were performed at room temperature.)  $\text{Ca}:\text{CO}_3=25/30$

No. of expt.	Substance dissolved in reaction vessel (grms.)	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ added in $\text{Ca}(\text{NO}_3)_2$ (grms.)	pH	Duration of reaction (minutes)	C/A/ $\mu$
102	non	0	5.5~10.4	55	180/11/0
103	$\text{KNO}_3$ 4.0	0	5.4~ 9.75	60	140/0/17
104	$\text{KNO}_3$ 12.1	0	5.5~ 9.95	55	20/0/54
105	non	0.08	5.4~10.1	55	140/3/0
106	$\text{KNO}_3$ 4.0	0.08	5.6~ 9.95	55	160/0/0
107	$\text{KNO}_3$ 12.1	0.08	5.9~10.2	55	150/4/0
108	non	0.4	5.2~10.1	75	150/3/0
109	$\text{KNO}_3$ 4.0	0.4	6.7~10.2	60	150/3/0
110	$\text{KNO}_3$ 12.1	0.4	6.3~10.2	70	150/3/0

TABLE 24-2. Supplemental Experiments (1)

(In each reaction, each 40 cc of 0.25 M  $\text{Ca}(\text{NO}_3)_2$  and, this time, 0.20 M  $\text{K}_2\text{CO}_3$  were dropped. Hence Ca ion and  $\text{CO}_3$  ion are not equivalent in amount. Other factors are same as in the foregoing.)  $\text{Ca}:\text{CO}_3=25/20$

No. of expt.	Substance dissolved in reaction vessel (grms.)	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ added in $\text{Ca}(\text{NO}_3)_2$ (grms.)	pH	Duration of reaction (minutes)	$\text{C}/\text{A}/\mu$
102-x	non	0	$\sim 7.95$	60	100/0/45
103-x	$\text{KNO}_3$ 4.0	0	$\sim 8.65$	65	50/0/55
104-x	$\text{KNO}_3$ 12.1	0	$\sim 9.05$	65	40/0/52

TABLE 24-3. Supplemental Experiments (2)

(In each reaction each 40 cc of 0.25 M  $\text{Ca}(\text{NO}_3)_2$  and 0.4 M  $\text{K}_2\text{CO}_3$  were dropped into the reaction vessel.)  $\text{Ca}:\text{CO}_3=25/40$

No. of expt.	Substance dissolved in reaction vessel (grms.)	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ added in $\text{CaCl}_2$ (grms.)	pH	Duration of reaction (minutes)	$\text{C}/\text{A}/\mu$
102-z	non	0	$\sim 10.5$	65	32/0/60
103-z	$\text{KNO}_3$ 4.0	0	$\sim 10.5$	60	110/0/35
104-z	$\text{KNO}_3$ 12.1	0	$\sim 10.4$	70	45/0/57

TABLE 25. Experiment-Data of Reactions;  $\text{CaCl}_2 + (\text{NH}_4)_2\text{CO}_3$ 

(In each reaction, each 80 cc of 0.25 M  $\text{CaCl}_2$  and 0.4 M  $(\text{NH}_4)_2\text{CO}_3$  were dropped into the reaction vessel containing an aqueous solution as specified in the table.)  $\text{Ca}:\text{CO}_3=25/40$

No. of expt.	Substance dissolved in reaction vessel (grms.)	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ added in $\text{Ca}(\text{NO}_3)_2$ (grms.)	pH	Duration of reaction (minuter)	$\text{C}/\text{A}/\mu$
111	non	0	5.5~7.4	90	5/0/60
112	$\text{NH}_4\text{Cl}$ 2.1	0	5.9~7.4	90	140/0/7
113	$\text{NH}_4\text{Cl}$ 6.4	0	5.5~7.4	95	90/0/43
114	non	0.08	5.5~8.0	90	6/0/73
115	non	0.4	5.5~7.5	90	10/0/70
116	non	2.0	$\sim 7.65$	90	40/0/50

$\mu$ -form. These values may be available for finding the apparent ratio of the amounts of calcite, aragonite and  $\mu$ -form in a given product.

## II. Considerations

### a) Effect of $\text{Mg}^{++}$ on the Selective Formations of $\text{CaCO}_3$

It is seen in the tables that the addition of  $\text{Mg}^{++}$  effectively hinders the formation of  $\mu$ - $\text{CaCO}_3$ , and the formation of aragonite is not favoured



in the presence of  $Mg^{++}$ . This latter observation does not agree with that of most previous investigators, with exception of JOHNSTON et al., KOHLSCHÜTTER and EGG, ZELLER and WRAY, and others.

It is shown by X-ray analysis of the products that calcite which forms under the condition of the presence of  $Mg^{++}$  possesses smaller spacings than those of pure calcite. This indicates the growth of the isomorphic replacement of Ca by Mg, which may be more than 5 mol. %.

Since  $MgCO_3$  is isomorphous to calcite, evidently  $Mg^{++}$  is more fittable to the calcite structure than to the aragonite structure, and thus the absorption of  $Mg^{++}$  must result in larger lattice disorder for aragonite than for calcite. Therefore, the presence of  $Mg^{++}$  is unlikely to favour the formation of aragonite.

As for  $\mu$ - $CaCO_3$ , the small radius and the high ionic potential of  $Mg^{++}$  is unfit for the very open structure of  $\mu$ -form, then the absorption of  $Mg^{++}$  may cause some large distortion in  $\mu$ -form even if  $\mu$ -form has comparatively larger entropy. As seen already in the foregoing experiments, the structure of  $\mu$ -form is rather capable of absorbing the larger ions such as Ba and Sr, and/or the ions of lower ionic potential as Na, K and  $NH_4$ . The presence of  $Mg^{++}$ , therefore, must be an unfavourable factor for the formation of  $\mu$ -form.

b) Effects of Univalent Ions such as  $Na^+$ ,  $K^+$  and  $NH_4^+$  on the Selective Formations of  $CaCO_3$

It is clearly shown in the experiments that if  $Mg^{++}$  is not present the formation of  $\mu$ -form becomes more dominant in accordance with the concentrations of NaCl, KCl and  $KNO_3$ . It is also seen that among these three substances,  $KNO_3$  and KCl more effectively act on the  $\mu$ -form formation than does NaCl.

As seen in Table 26, calcite which forms in the solutions containing large amounts of NaCl, KCl or  $KNO_3$  shows some larger spacings than those of ordinary calcite, and hence the absorption of these univalent ions in calcite seems to be highly possible.

On the basis of these observations it can be reasonably concluded that the absorption, the admission according to GOLDSCHMIDT, of Na and K would grow more or less in every modification of  $CaCO_3$ , and that among these modifications  $\mu$ -form is the most insensible to this influence owing to its very open structure. Or it may be that "stuffing" of such ions would be necessary for the formation of the structure of unstable  $\mu$ -form as supposed in the case of low cristobalite, while the other two modifications may suffer much from loosening of structure caused by those univalent ions of low ionic potential.

The effect of  $\text{NH}_4\text{Cl}$  seems more complicated than that of  $\text{NaCl}$  and  $\text{KCl}$ . Although the formation of  $\mu$ -form is also dominant in the presence of this salt, there is some doubt whether it is due to the effect of the salt itself or due to the pH value of solution. Since the solution of  $\text{NH}_4\text{Cl}$  is a buffer solution, the pH value is kept lower through the reaction. Then it is likely that the concentrated  $\text{H}^+$  exerts some effect on the formation of  $\mu$ -form. More detailed discussion in this respect is as follows.

c) Effect of pH of Solution

The effect of pH on the selective formations in  $\text{CaCO}_3$  is not clearly seen. The following two facts only are observable.

(i) As mentioned briefly in the above paragraph, the formation of  $\mu$ -form is very active in the  $\text{NH}_4\text{Cl}$  solutions which possess relatively low pH value.

(ii) In the solutions which have final pH value of above 10, the formation of aragonite, if it is small in amount, is always seen.

In the latter case it is not clearly known whether the higher pH favours the formation of aragonite, or otherwise, the formation of aragonite cause the rise of the final pH in the solution. However, it seems more reasonable to suppose that under the violent attack of  $\text{H}^+$  the most open structure of  $\mu$ -form is more stable relative to the other denser structures of calcite and aragonite, especially of the latter.

d) Effect of Reaction Velocity.

All the reactions referred to in this chapter were carried out at the nearly same speed. It should be remembered that in the experiment of HARADA and GOTO described in CHAPTER (5) the speed of reaction was kept to one which is widely different from that of the present experiment; in the former the reactions were allowed to last for five months, while in the latter they were for only one hour. Then it is very interesting to see that no appreciable formation of aragonite is seen in the products of the present experiment.

It is, therefore, fully reasonable to think that the failure of the aragonite formation in the present experiment is attributable to some extent to the high velocity of the reaction, in addition to other factors such as mentioned above.

e) Effect of Unbalance in Quantities of  $\text{Ca}^{++}$  and  $\text{CO}_3^{=}$

It should be noticed that the diadochic absorption of foreign ions in a growing crystal may be promoted when the quantities of  $\text{Ca}^{++}$  and  $\text{CO}_3^{=}$  in solution are not balanced. Under the conditions which want, for instance, in  $\text{Ca}^{++}$  ions relative to  $\text{CO}_3^{=}$ , this deficiency of  $\text{Ca}^{++}$  would be complemented to some extent with obtainable cations other than  $\text{Ca}^{++}$  such

as  $\text{Mg}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Ba}^{++}$ , and even with  $\text{Na}^+$ ,  $\text{K}^+$  and others. Probably absorption of this kind may be promoted with the increasing velocity of reaction, and thus the effect of the higher reaction velocity on the selective formations in  $\text{CaCO}_3$  must be attributed, in part, to the diadochic absorption effect.

The result of the experiment on the effect of the unbalanced proportion of  $\text{Ca}^{++}$  for  $\text{CO}_3^{--}$  shows clearly that in the presence of a large amount of  $\text{KNO}_3$ , and  $\text{KCl}$ , the formation of  $\mu$ -form becomes increasingly dominant in the cases in which the amount of  $\text{Ca}^{++}$  is either lacking or excessive. This observation well agrees with the above suppositions.

Details of the result are shown in Table 24, Supplemental Experiments (1) and (2). Data of X-ray analyses of all the products are arranged in Table 26, with attached figures.

#### (8) Conclusions Regarding the Genesis of Aragonite

On the basis of the experiments and the considerations presented in the foregoing, the writer comes to the following conclusions as to the genesis of aragonite.

(i) The most important effect on the selective formation of aragonite, and of calcite, is the solvation of water molecules, which, acting upon the surface ions of nuclear particles, exerts a marked loosening effect upon the atomic bindings throughout the nucleus. The nucleus of the denser structure of aragonite is less stable than that of the open structure of calcite under the influence of the solvation effect, thus the formation of aragonite is expected to be favoured in the solutions in which the solvation effect of water is much diminished.

The solvation effect of water is effectively diminished by mixing the water with some polar liquids of low dielectric constant such as alcohols. It should be noticed that the secretion fluids of most organisms are supposed to be such polar liquids. The dominant formation of aragonite in the animal kingdom may be explained from this viewpoint.

The solvation of water is effectively hindered also by the thermal agitation of water molecules, and thus the formation of aragonite is more favoured at higher temperatures from  $60^\circ$  to the boiling point than at lower. To the writer's view, most of the aragonite formations in the mineral kingdom may be ascribed to the temperature effect.

(ii) In view of the low entropy structure of aragonite, it is very reasonable to suppose that the high velocity of reaction does not favour the formation of aragonite. Certainly, the slow reaction is one of the

primary requirement for the formation of aragonite. The slow reaction only, however, is by no means enough for the formation of aragonite, since slow reaction favours not only the formation of aragonite, but also the formation of high entropical structure of calcite to some larger extent. Namely, from the viewpoint of reaction velocity only, aragonite is always more difficult to form than calcite, and the difficulty of formation of aragonite increases with the increase of the reaction velocity.

(iii) A comparatively larger pH value of solution and the balanced proportion in quantities of  $\text{Ca}^{++}$  and  $\text{CO}_3^{=}$  may be favourable for the formation of aragonite. A high concentration of  $\text{H}^+$ , on the contrary, seems to favour the formation of the modifications of more open structure, calcite and  $\mu$ -form. Unbalance in quantities of  $\text{Ca}^{++}$  and  $\text{CO}_3^{=}$  may cause the absorption of foreign ions in the growing nuclei of each modification, and this in most cases is unfavourable to the formation of aragonite.

(vi) The presence of  $\text{Mg}^{++}$ ,  $\text{Sr}^{++}$ , and  $\text{Ba}^{++}$  does not favour aragonite formation; the presence of  $\text{Mg}^{++}$  is rather favourable for the formation of calcite, and the presence of  $\text{Ba}^{++}$  for the formation of  $\mu$ -form. It may be confidently said regarding these facts that the diadochic substitution of Ca by Mg makes calcite more stable relative to aragonite and  $\mu$ -form, and the substitution by Ba makes  $\mu$ -form more stable than the other two. It is a very interesting fact that, in the present experiments, no aragonite was found even in the presence of  $\text{Sr}^{++}$ , while calcite, in which an appreciable amount of Ca is replaced by Sr, could form under the same condition. These facts prove the chemically non-negotiable nature of aragonite, and this nature may be attributed to the low entropy structure of aragonite.

#### Acknowledgment

The writer wishes to express the sincerest thanks to Dr. Z. HARADA, Professor of Hokkaido University, under whose encouragement and guidance this work has been carried out.

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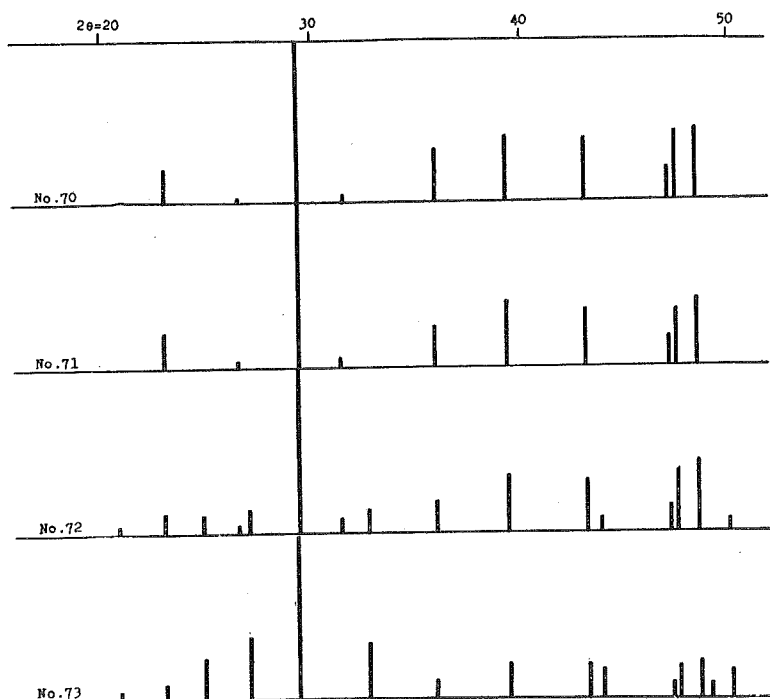
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TABLE 26. X-ray Analysis Data of Precipitates Shown in TABLE 22-25  
(with attached figures)(Cu-K $\alpha$ , 35 KV, 13mA, Ni Fil., 4-1-4, 1°/1 min.)

TABLE 26-1

C (hkil)	A (hkl)	$\mu$ (hkil)	No. 70		No. 71		No. 72		No. 73	
			d	I	d	I	d	I	d	I
(10 $\bar{1}$ 2)	(111)	(0002)	—	—	—	—	4.28	3	4.28	4
			3.88	20	3.88	20	3.88	14	3.88	8
		(10 $\bar{1}$ 0)	—	—	—	—	3.59	8	3.59	22
(10 $\bar{1}$ 4)	(111)		—	—	3.38	3	3.39	4	—	—
		(10 $\bar{1}$ 1)	—	—	—	—	3.30	14	3.30	36
			3.046	140	3.050	140	3.052	140	3.054	110
(0006)			2.855	4	2.855	4	2.855	7	—	—
		(10 $\bar{1}$ 2)	—	—	—	—	2.736	12	2.741	31
(11 $\bar{2}$ 0)			2.506	32	2.503	24	2.506	18	2.503	9
(11 $\bar{2}$ 3)			2.285	40	2.294	38	2.291	34	2.293	20
(20 $\bar{2}$ 2)			2.102	38	2.102	34	2.102	28	2.102	19
		(11 $\bar{2}$ 0)	—	—	—	—	2.071	8	2.067	15
(02 $\bar{2}$ 4)			1.932	20	—	—	1.932	15	1.926	10
(1018)			1.913	42	1.915	34	1.914	40	1.916	19
(11 $\bar{2}$ 6)			1.879	44	1.881	39	1.876	45	1.879	22
		$\mu$	—	—	—	—	—	—	1.857	8
		(10 $\bar{1}$ 4)?	—	—	—	—	1.827	6	1.826	15

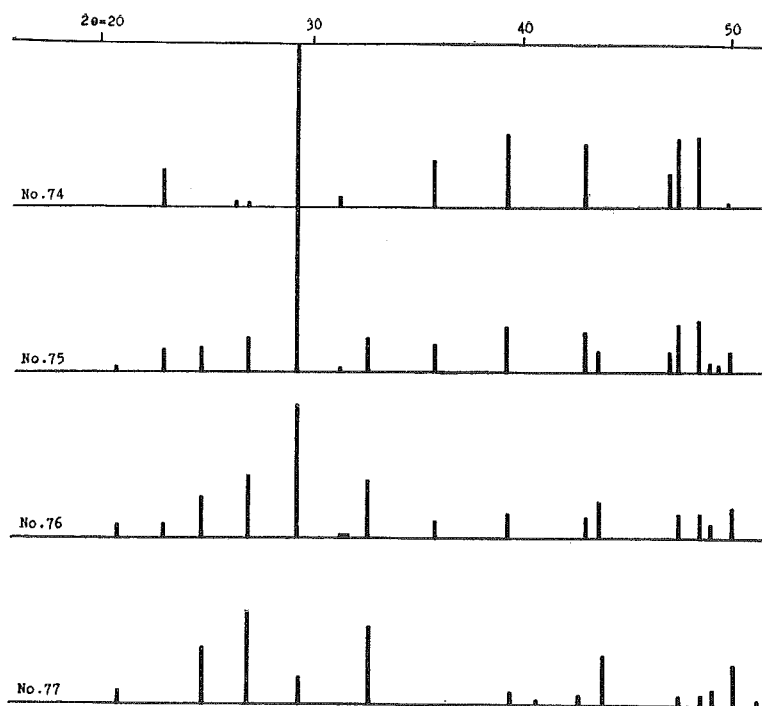


Attached Fig. 26-1.



TABLE 26-2

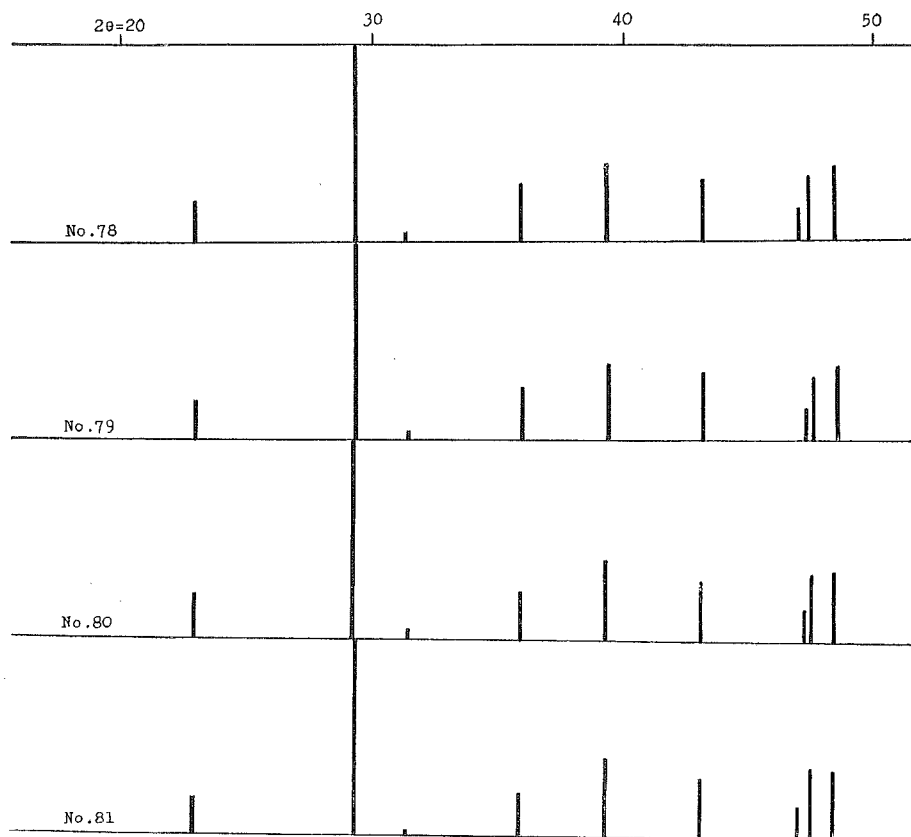
C (hkl)	A (hkl)	$\mu$ (hkil)	No. 74		No. 75		No. 76		No. 77	
			d	I	d	I	d	I	d	I
(10 $\bar{1}2$ )		(0002)	—	—	—	—	4.27	7	4.25	7
			3.89	20	3.88	10	3.87	7	—	—
		(10 $\bar{1}0$ )	—	—	3.60	12	3.59	24	3.59	34
(10 $\bar{1}4$ )		(10 $\bar{1}1$ )	—	—	3.81	18	3.80	40	3.80	55
			3.046	150	3.050	140	3.047	75	3.037	15
(0006)			2.846	5	—	—	—	—	—	—
		(10 $\bar{1}2$ )	—	—	2.744	10	2.739	32	2.733	46
(11 $\bar{2}0$ )			2.503	27	2.506	16	2.501	10	—	—
(11 $\bar{2}3$ )			2.283	45	2.291	26	2.289	15	2.285	5
(20 $\bar{2}2$ )			2.102	37	2.102	24	2.098	12	2.102	5
		(11 $\bar{2}0$ )	—	—	2.074	12	2.071	22	2.065	28
(02 $\bar{2}4$ )			1.932	17	1.932	12	—	—	—	—
(10 $\bar{1}8$ )			1.916	40	1.916	27	1.913	15	1.913	5
(11 $\bar{2}6$ )			1.879	42	1.879	30	1.875	15	—	—
		$\mu$	—	—	—	—	1.858	8	1.857	9
		(10 $\bar{1}4$ )	—	—	1.823	18	1.823	18	1.823	22



Attached Fig. 26-2.

TABLE 26-3

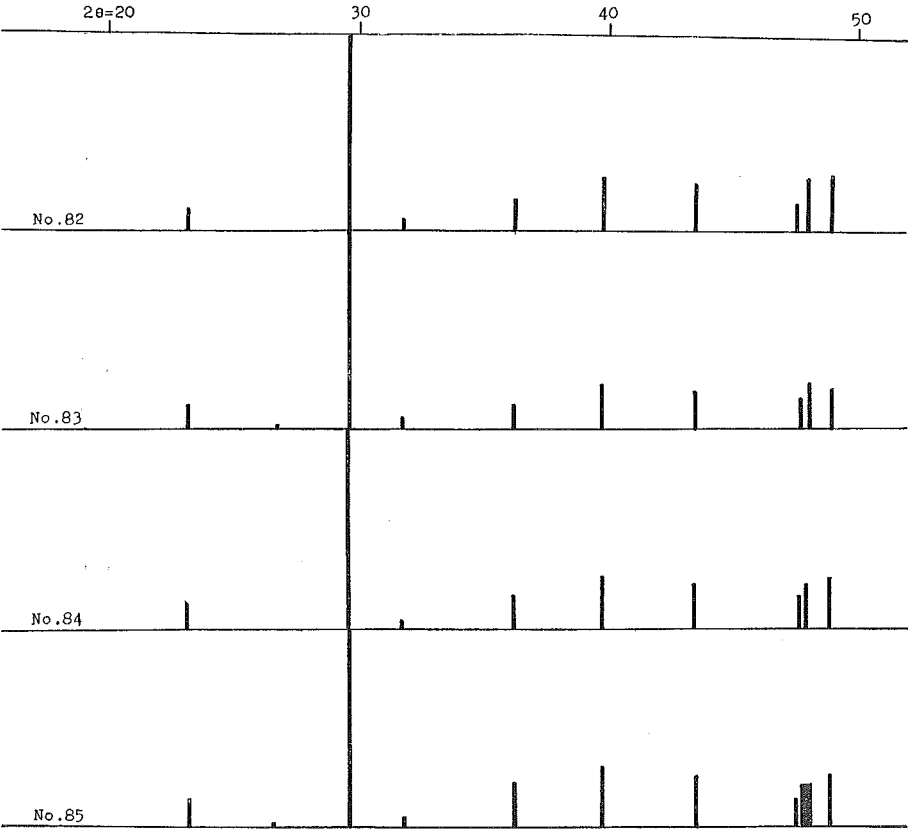
C (hkl)	A (hkl)	$\mu$ (hkl)	No. 78		No. 79		No. 80		No. 81	
			d	I	d	I	d	I	d	I
(10 $\bar{1}$ 2)	(111)		3.86	19	3.86	20	3.86	22	3.86	19
			—	—	—	—	—	—	3.36	2
(10 $\bar{1}$ 4)			3.041	140	3.039	140	3.046	150	3.035	140
(0006)			2.855	4	2.838	4	2.841	5	2.841	3
(11 $\bar{2}$ 0)			2.497	28	2.494	26	2.497	23	2.497	23
(11 $\bar{2}$ 3)			2.285	40	2.285	38	2.285	40	2.285	40
(20 $\bar{2}$ 2)			2.096	30	2.097	34	2.097	30	2.097	30
(02 $\bar{2}$ 4)			1.928	16	1.923	15	—	—	1.928	15
(10 $\bar{1}$ 8)			1.913	33	1.911	32	1.911	35	1.911	36
(11 $\bar{2}$ 6)			1.875	35	1.875	37	1.875	36	1.875	35



Attached Fig. 26-3.

TABLE 26-4

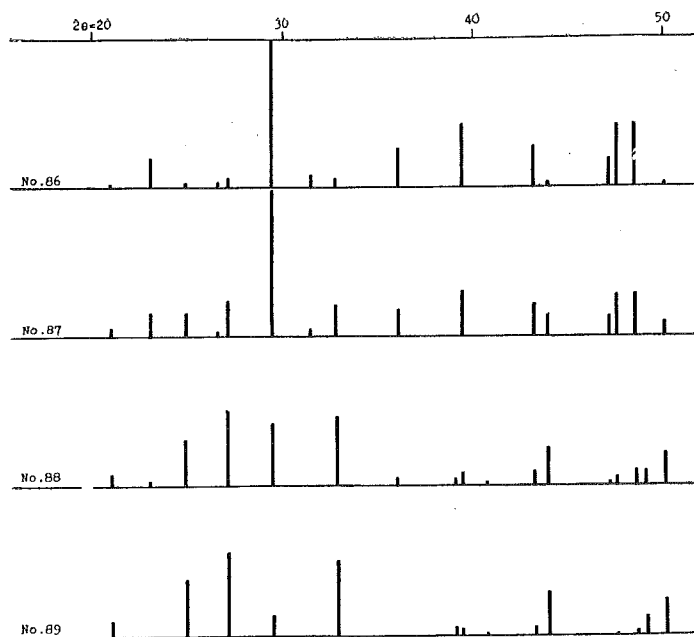
C (hkl)	A (hkl)	$\mu$ (hkl)	No. 82		No. 83		No. 84		No. 85	
			d	I	d	I	d	I	d	I
(10 $\bar{1}$ 2)	(111)		3.85	11	3.84	12	3.86	14	3.86	14
			—	—	3.34	2	—	—	3.37	2
(10 $\bar{1}$ 4)			3.005	145	3.015	145	3.025	150	3.017	150
(0006)			2.820	5	2.829	5	2.833	4	2.829	5
(11 $\bar{2}$ 0)			2.486	16	2.481	12	2.493	16	2.493	22
(11 $\bar{2}$ 3)			2.268	27	2.271	22	2.277	26	2.279	30
(20 $\bar{2}$ 2)			2.085	24	2.086	19	2.089	22	2.088	30
(02 $\bar{2}$ 4)			1.913	13	1.905	14	1.913	16	1.914	15
(10 $\bar{1}$ 8)			1.897	25	1.896	23	1.903	23	1.905	20
(11 $\bar{2}$ 6)			1.865	28	1.865	20	1.868	25	1.868	25



Attached Fig. 26-4.

TABLE 26-5

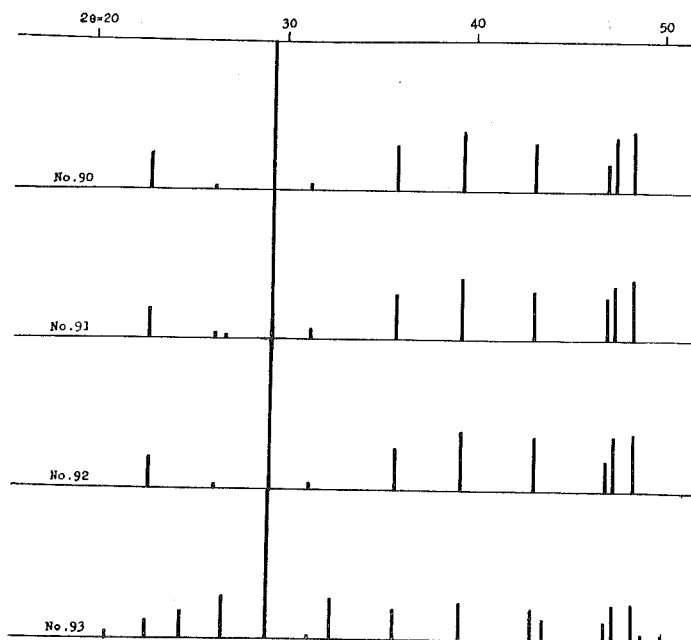
C (hkil)	A (hkl)	$\mu$ (hkil)	No. 86		No. 87		No. 88		No. 89	
			d	I	d	I	d	I	d	I
(10 $\bar{1}2$ )	(111)	(0002)	—	—	4.27	6	4.26	7	4.27	10
			3.86	20	3.88	16	3.88	4	—	—
		(10 $\bar{1}0$ )	3.59	3	3.59	17	3.59	32	3.59	38
			3.39	4	3.36	5	—	—	—	—
(10 $\bar{1}1$ )		3.30	6	3.30	23	3.30	52	3.30	56	
(10 $\bar{1}4$ )		3.046	130	3.048	115	3.046	42	3.050	13	
(0006)		2.855	7	2.855	5	—	—	—	—	
(10 $\bar{1}2$ )		2.744	5	2.736	21	2.738	46	2.736	50	
(11 $\bar{2}0$ )		2.499	26	2.505	18	2.503	6	2.506	3	
(11 $\bar{2}3$ )		$\mu$	—	—	2.325	4	2.319	5	2.319	5
			2.288	42	2.291	29	2.291	9	—	—
		$\mu?$	—	—	—	—	2.220	3	—	—
(20 $\bar{2}2$ )	$\mu?$	—	—	—	—	2.120	5	2.125	6	
		2.102	28	2.101	22	2.099	9	2.102	6	
	(11 $\bar{2}0$ )	—	—	2.067	13	2.067	26	2.067	28	
(02 $\bar{2}4$ )		1.932	18	1.932	13	1.932	4	—	—	
(10 $\bar{1}8$ )		1.913	42	1.913	27	1.913	6	1.916	5	
(11 $\bar{2}6$ )		1.879	42	1.878	29	1.879	10	1.875	7	
	$\mu$	—	—	1.857	6	1.857	10	1.857	15	
	(10 $\bar{1}4$ )	—	—	1.826	10	1.823	22	1.826	25	



Attached Fig. 26-5.

TABLE 26-6

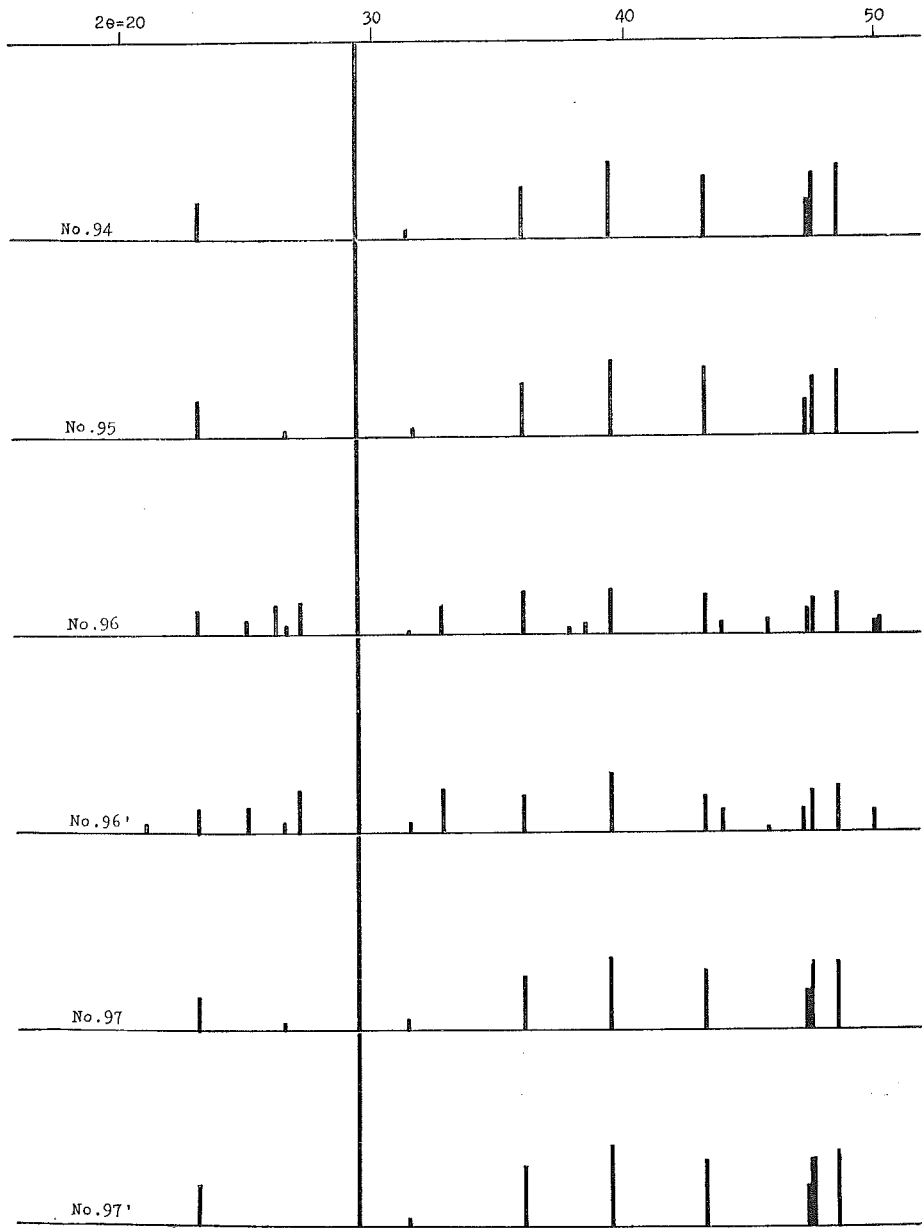
C (hkl)	A (hkl)	$\mu$ (hkil)	No. 90		No. 91		No. 92		No. 93	
			d	I	d	I	d	I	d	I
(10 $\bar{1}$ 2)	(111)	(0002)	—	—	—	—	—	—	4.27	4
			3.86	23	3.86	18	3.86	20	3.88	10
		(10 $\bar{1}$ 0)	—	—	—	—	—	—	3.59	16
			—	—	3.39	4	3.39	3	—	—
(10 $\bar{1}$ 4)		(10 $\bar{1}$ 1)	—	—	—	—	—	—	3.312	26
			3.041	145	3.041	140	3.044	140	3.046	120
(0006)			2.854	5	2.846	8	2.855	5	2.855	3
		(10 $\bar{1}$ 2)	—	—	—	—	—	—	2.736	28
(11 $\bar{2}$ 0)			2.499	30	2.499	25	2.498	27	2.499	15
(11 $\bar{2}$ 3)			2.285	40	2.287	40	2.291	37	2.291	22
(20 $\bar{2}$ 2)			2.100	33	2.100	30	2.101	35	2.100	19
		(11 $\bar{2}$ 0)	—	—	—	—	—	—	2.070	14
			—	—	—	—	—	—	2.065	14
(02 $\bar{2}$ 4)			1.932	18	1.931	18	1.932	20	—	—
(10 $\bar{1}$ 8)			1.913	35	1.913	35	1.916	35	1.913	20
(11 $\bar{2}$ 6)			1.875	40	1.878	40	1.875	40	1.879	20
		(10 $\bar{1}$ 4)	—	—	—	—	—	—	1.823	12



Attached Fig. 26-6

TABLE 26-7

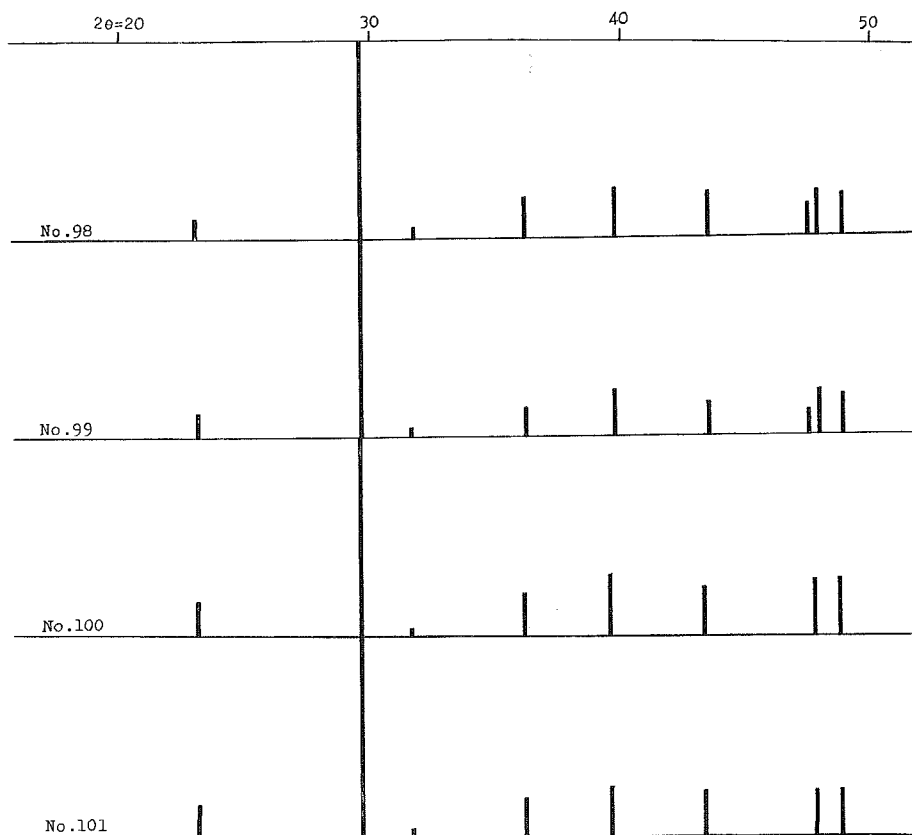
C (hkil)	A (hkl)	$\mu$ (hkil)	No. 94		No. 95		No. 96		No. 97	
			d	I	d	I	d	I	d	I
(10 $\bar{1}$ 2)			3.86	17	3.86	18	3.87	12	3.87	17
		(10 $\bar{1}$ 0)	—	—	—	—	3.60	5	—	—
		(10 $\bar{1}$ 0)	—	—	—	—	3.57	6	—	—
	(111)		—	—	3.36	3	3.41	14	3.38	3
		(10 $\bar{1}$ 1)	—	—	—	—	3.295	16	—	—
(10 $\bar{1}$ 4)			3.041	140	3.035	140	3.035	120	3.046	140
(0006)			2.837	5	2.832	4	—	—	2.855	5
		(10 $\bar{1}$ 2)	—	—	—	—	2.736	14	—	—
(11 $\bar{2}$ 0)			2.497	25	2.493	27	2.499	20	2.496	25
	(031)		—	—	—	—	2.415	3	—	—
	(112)		—	—	—	—	2.382	5	—	—
	(130)		—	—	—	—	2.343	5	—	—
(11 $\bar{2}$ 3)			2.282	38	2.279	35	2.283	21	2.282	34
(20 $\bar{2}$ 2)			2.102	28	2.095	32	2.097	19	2.097	31
		(11 $\bar{2}$ 0)	—	—	—	—	2.065	6	—	—
	(212)		—	—	—	—	1.983	8	—	—
(02 $\bar{2}$ 4)			—	—	1.927	16	—	—	—	—
(10 $\bar{1}$ 8)			1.913	30	1.910	28	1.913	18	1.913	33
(11 $\bar{2}$ 6)			1.875	34	1.872	31	1.877	20	1.875	33
	(230)		—	—	—	—	1.819	5	—	—



Attached Fig. 26-7.

TABLE 26-8

C (hkl)	A (hkl)	$\mu$ (hkl)	No. 98		No. 99		No. 100		No. 101	
			d	I	d	I	d	I	d	I
(10 $\bar{1}$ 2)			3.85	10	3.85	13	3.86	16	3.86	15
(10 $\bar{1}$ 4)			3.019	145	3.021	145	3.025	150	3.029	150
(0006)			2.825	5	2.838	5	2.838	5	2.829	5
(11 $\bar{2}$ 0)			2.485	15	2.486	13	2.493	20	2.493	18
(11 $\bar{2}$ 3)			2.271	24	2.274	23	2.279	30	2.279	25
(20 $\bar{2}$ 2)			2.080	21	2.088	16	2.092	23	2.092	23
			—	—	2.083	16	—	—	—	—
(10 $\bar{1}$ 8)			1.901	23	1.901	20	1.909	27	1.904	21
(11 $\bar{2}$ 6)			1.865	20	1.868	19	1.872	27	1.872	23

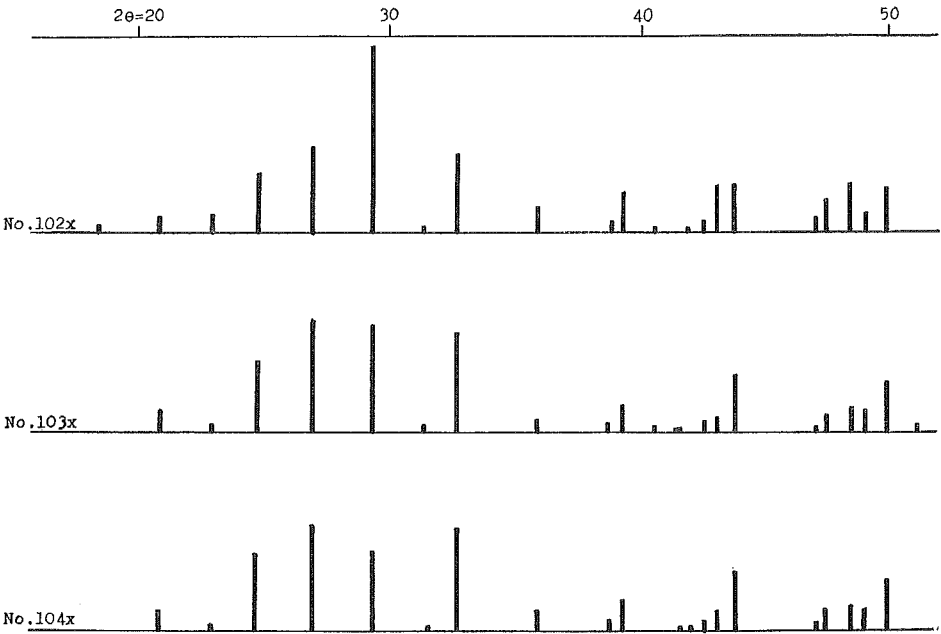


Attached Fig. 26-8.



TABLE 26-9a

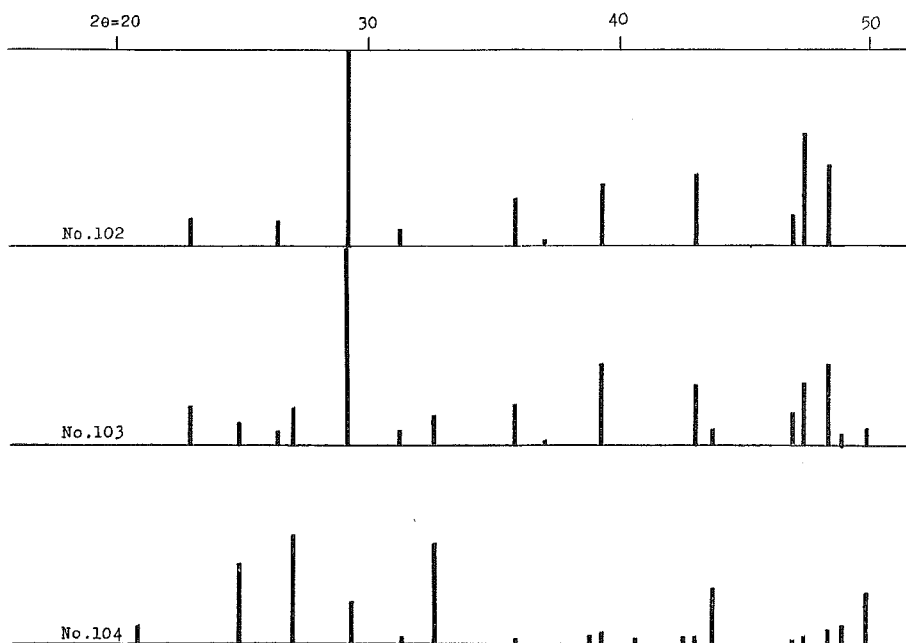
C (nkil)	A (hkl)	$\mu$ (hkil)	No. 102-x d I		No. 102 d I		No. 102-z d I			
(10 $\bar{1}$ 2)	(111)	(0002)	4.27	8	—	—	4.27	10		
			3.87	8	3.86	12	—	—		
		(10 $\bar{1}$ 0)	3.59	28	—	—	3.59	35		
(10 $\bar{1}$ 4)		(10 $\bar{1}$ 1)	3.31	45	3.37	11	—	—		
			3.046	100	3.037	180	3.31	60		
			2.857	3	2.852	8	3.050	32		
(11 $\bar{2}$ 0)	(10 $\bar{1}$ 2)	2.736	40	—	—	2.738	53			
		2.501	10	2.495	23	2.503	3			
	(11 $\bar{2}$ 3)		—	—	2.421	4	—	—		
(031)			2.293	20	2.287	30	2.296	8		
			2.124	5	—	—	2.123	5		
		(20 $\bar{2}$ 2)		2.101	23	2.100	35	2.102	8	
			(11 $\bar{2}$ 0)		2.065	23	—	—	2.067	30
					1.932	7	1.932	15	—	—
	(02 $\bar{2}$ 4)			1.916	16	1.914	58	1.917	5	
(10 $\bar{1}$ 8)		1.881	24	1.876	40	1.878	9			
(11 $\bar{2}$ 6)		1.861	10	—	—	1.857	12			
	$\mu?$		1.828	20	—	—	1.825	25		
	(10 $\bar{1}$ 4)									



Attached Fig. 26-9a.

TABLE 26-9b

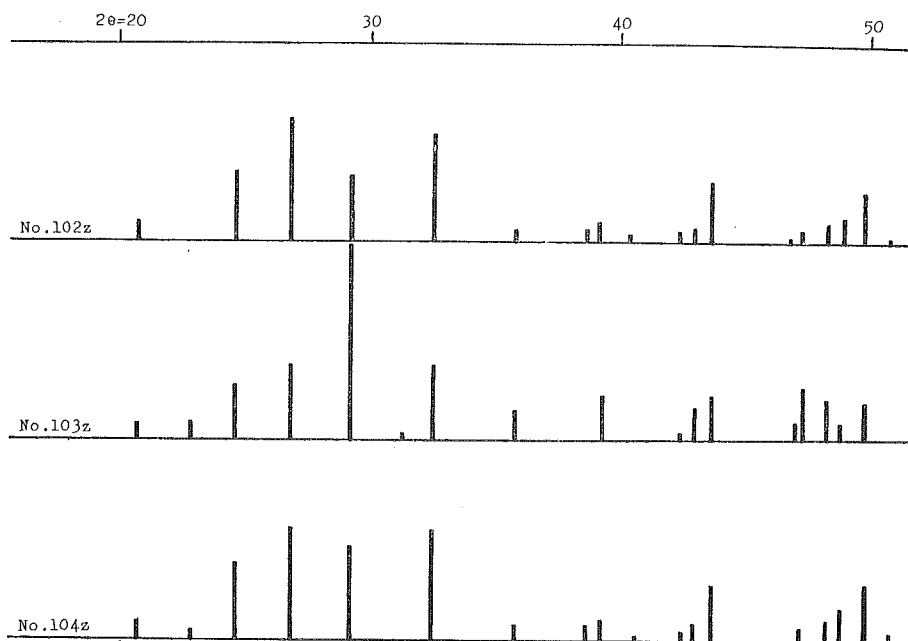
C (hkl)	A (hkl)	$\mu$ (hkl)	No. 103-x d I		No. 103 d I		No. 103-z d I	
(10 $\bar{1}$ 2)		(0002)	4.26	10	—	—	4.27	6
			3.88	3	3.88	18	3.89	7
		(10 $\bar{1}$ 0)	3.59	35	3.60	10	3.59	26
(10 $\bar{1}$ 4)		(10 $\bar{1}$ 1)	3.31	55	3.31	17	3.31	35
			3.046	50	3.046	140	3.050	110
			2.855	3	2.853	6	2.855	3
(11 $\bar{2}$ 0)		(10 $\bar{1}$ 2)	2.738	45	2.740	14	2.738	35
			2.505	5	2.506	19	2.506	15
			2.293	13	2.291	40	2.293	23
(11 $\bar{2}$ 3)			2.225	3	—	—	—	—
		$\mu?$	2.124	5	—	—	2.125	3
			2.102	7	2.102	30	2.102	15
(20 $\bar{2}$ 2)		(11 $\bar{2}$ 0)	2.070	28	2.066	7	2.070	22
(10 $\bar{1}$ 8)			1.916	8	1.913	33	1.916	25
(11 $\bar{2}$ 6)			1.879	13	1.879	40	1.879	20
		$\mu?$	—	—	1.863	5	1.865	8
			1.857	11	—	—	1.857	8
		(10 $\bar{1}$ 4)	1.329	25	1.824	8	1.826	18
			1.789	3	—	—	—	—



Attached Fig. 26-9b.

TABLE 26-9c

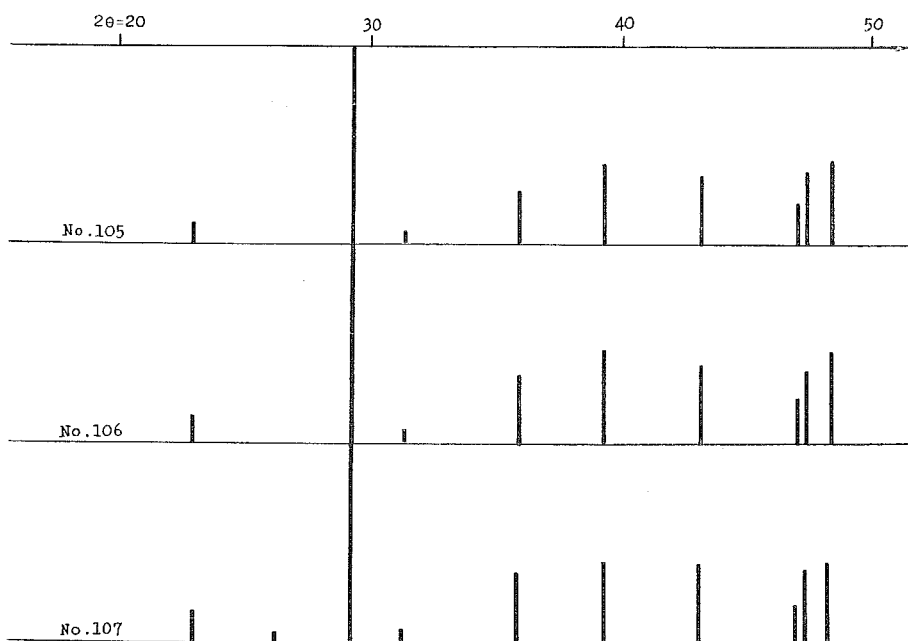
C (hkl)	A (hkl)	$\mu$ (hkl)	No. 104-x		No. 104		No. 104-z	
			d	I	d	I	d	I
(10 $\bar{1}2$ )		(0002)	4.27	10	4.27	8	4.27	10
			3.88	3	—	—	3.89	4
		(10 $\bar{1}0$ )	3.59	38	3.59	39	3.59	38
(10 $\bar{1}4$ )		(10 $\bar{1}1$ )	3.809	52	3.302	54	3.302	57
			3.052	40	3.044	20	3.050	45
		(10 $\bar{1}2$ )	3.736	50	2.738	50	2.738	54
(11 $\bar{2}0$ )			2.503	10	2.501	1	2.506	7
(11 $\bar{2}3$ )		$\mu$	—	—	2.322	3	2.325	8
			2.293	15	2.292	5	2.292	10
		$\mu?$	2.125	5	2.125	4	2.125	4
(20 $\bar{2}2$ )			2.101	10	2.102	4	2.102	8
		(11 $\bar{2}0$ )	2.067	30	2.068	27	2.068	28
			—	—	1.932	3	—	—
(02 $\bar{2}4$ )			1.918	10	1.915	4	1.920	6
(10 $\bar{1}8$ )			1.879	13	1.878	6	1.880	10
(11 $\bar{2}6$ )		$\mu$	—	—	1.867	10	—	—
		$\mu$	1.857	10	1.857	10	1.860	15
			—	—	1.847	8	—	—
			1.828	25	1.825	26	1.826	28
		(10 $\bar{1}4$ )	—	—	—	—	1.792	3



Attached Fig. 26-9c.

TABLE 26-10

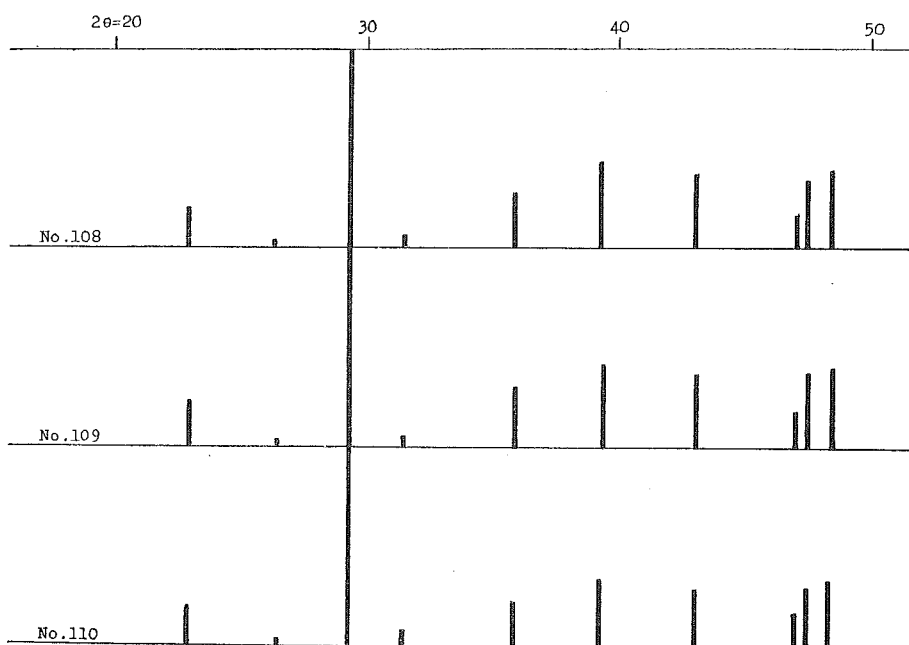
C (hkil)	A (hkl)	$\mu$ (hkil)	No. 105 d I		No. 106 d I		No. 107 d I	
(10 $\bar{1}$ 2)	(111)		3.86	19	3.88	23	3.88	25
			3.38	3	—	—	3.39	4
(10 $\bar{1}$ 4)			3.039	140	3.046	160	3.046	150
(0006)			2.845	5	2.858	6	2.855	7
(11 $\bar{2}$ 0)			2.493	27	2.506	32	2.503	34
(11 $\bar{2}$ 3)			2.287	40	2.291	45	2.293	40
(20 $\bar{2}$ 2)			2.097	33	2.102	37	2.100	38
(02 $\bar{2}$ 4)			1.924	20	1.932	18	1.932	18
(10 $\bar{1}$ 8)			1.913	35	1.917	34	1.917	37
(11 $\bar{2}$ 6)			1.875	40	1.880	45	1.877	40



Attached Fig. 26-10.

TABLE 26-11

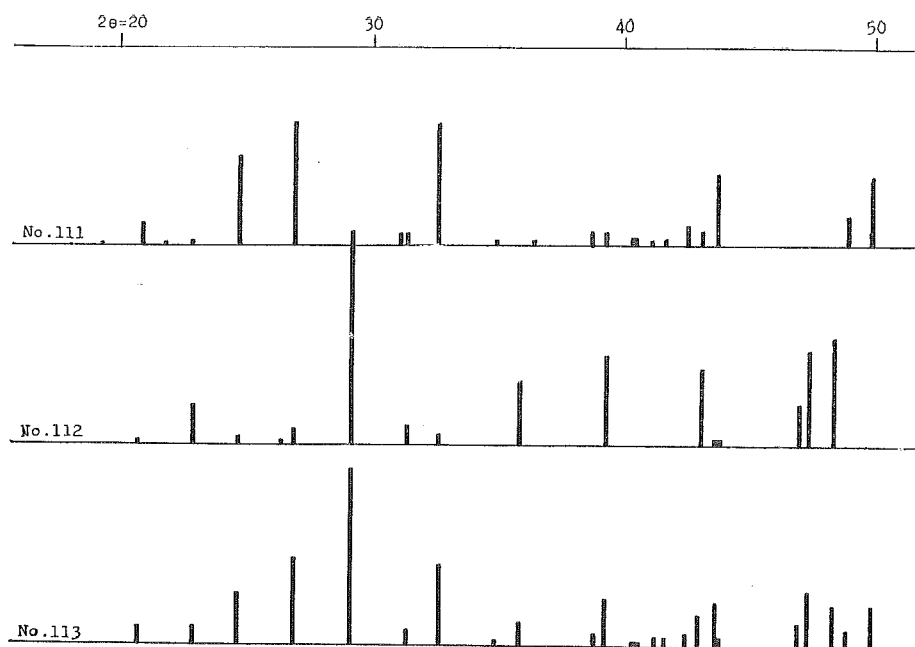
C (hkil)	A (hkl)	$\mu$ (hkil)	No. 108		No. 109		No. 110	
			d	I	d	I	d	I
(10 $\bar{1}$ 2)	(111)		3.88	20	3.86	24	3.86	20
			3.39	3	3.37	3	3.36	3
(10 $\bar{1}$ 4)			3.042	150	3.041	150	3.040	150
(0006)			2.845	7	2.852	5	2.838	8
(11 $\bar{2}$ 0)			2.503	27	2.499	30	2.493	23
(11 $\bar{2}$ 3)			2.291	40	2.288	40	2.291	33
(20 $\bar{2}$ 2)			2.099	35	2.097	35	2.094	30
(02 $\bar{2}$ 4)			1.928	16	1.928	17	1.926	17
(10 $\bar{1}$ 8)			1.913	33	1.913	36	1.909	30
(11 $\bar{2}$ 6)			1.875	38	1.875	40	1.875	32



Attached Fig. 26-11.

TABLE 26-12

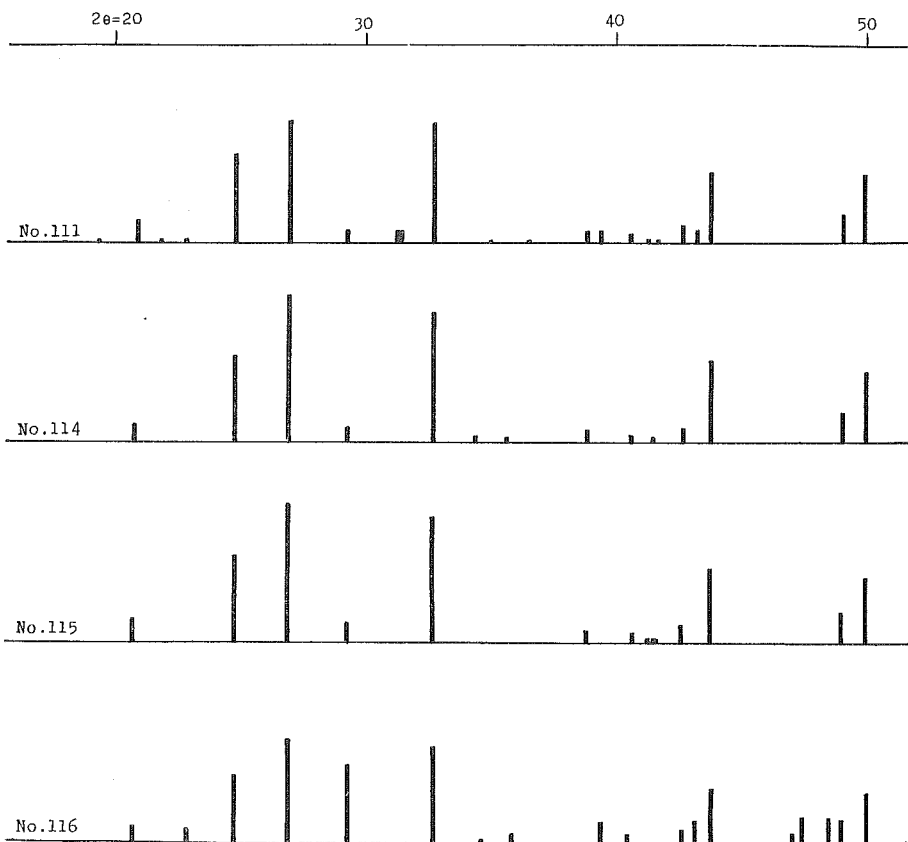
C (hkl)	A (hkl)	$\mu$ (hkl)	No. 111		No. 112		No. 113	
			d	I	d	I	d	I
(10 $\bar{1}2$ )		(0002)	4.25	10	—	—	4.27	8
		(10 $\bar{1}0$ )	—	—	3.86	20	3.88	10
		(10 $\bar{1}1$ )	3.59	45	3.60	5	3.59	27
(10 $\bar{1}4$ )			3.31	60	3.31	7	3.30	43
(0006)			3.052	5	3.048	140	3.050	90
(11 $\bar{2}0$ )			2.846	2	2.855	8	2.855	7
		(10 $\bar{1}2$ )	2.743	57	2.744	5	2.744	40
(11 $\bar{2}3$ )	$\mu$		—	—	2.499	30	2.503	12
			2.325	5	—	—	2.319	5
			2.296	6	2.289	45	2.294	24
(20 $\bar{2}2$ )			2.120	8	—	—	2.120	7
			2.102	7	2.098	38	2.102	15
		(11 $\bar{2}0$ )	2.069	35	—	—	2.071	20
(02 $\bar{2}4$ )			—	—	1.932	20	1.932	12
(10 $\bar{1}8$ )			—	—	1.913	47	1.916	28
(11 $\bar{2}6$ )			—	—	1.876	54	1.879	20
	$\mu$		1.857	14	—	—	1.861	8
		(10 $\bar{1}4$ )	1.827	33	1.823	2	1.826	20



Attached Fig. 26-12.

TABLE 26-13

C (hkil)	A (hkl)	$\mu$ (hkil)	No. 111		No. 114		No. 115		No. 116	
			d	I	d	I	d	I	d	I
(10 $\bar{1}2$ )		(0002)	4.25	10	4.27	10	4.26	10	4.27	10
			—	—	—	—	—	—	3.87	5
		(10 $\bar{1}0$ )	3.59	45	3.59	43	3.59	42	3.59	33
(10 $\bar{1}4$ )		(10 $\bar{1}2$ )	2.31	60	3.30	73	3.31	70	3.30	50
			3.052	5	3.053	6	3.052	10	3.044	40
		(0006)	2.846	2	—	—	—	—	—	—
(11 $\bar{2}3$ )		(10 $\bar{1}2$ )	2.743	57	2.736	65	2.738	65	2.736	50
			2.325	6	2.325	5	2.321	6	—	—
			2.296	6	—	—	—	—	2.288	10
(20 $\bar{2}2$ )			2.120	8	2.122	6	2.125	8	2.118	6
			2.102	7	—	—	—	—	2.099	10
		(11 $\bar{2}0$ )	2.069	35	2.067	40	2.070	36	2.065	28
(02 $\bar{2}4$ )			—	—	—	—	—	—	1.932	5
(10 $\bar{1}8$ )			—	—	—	—	—	—	1.914	12
(11 $\bar{2}6$ )			—	—	—	—	—	—	1.875	12
		$\mu$	1.857	14	1.857	15	1.861	15	1.857	12
		(10 $\bar{1}4$ )	1.827	33	1.823	35	1.824	33	1.823	25



Attached Fig. 26-13.