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SOME FACTORS INFLUENCING CRYSTAL HABIT*

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Abstract

The influences of the following factors on crystal habit were investigated:

- 1. Temperature of pure aqueous solutions.
- 2. Presence of inorganic compounds in solution.
- 3. Presence of organic compounds in solution.
- 4. Presence of thickening substances.
- 5. Presence of suspensions.

Crystals were grown under temperature conditions varying from 5°C to 30° C. At a slow rate of crystal growth, the crystals of the salts investigated (barium nitrate, strontium nitrate, and lead nitrate) are of very simple habit when grown at low temperatures (5°C to 10° C), and become increasingly more complex with increase in temperature.

The presence of impurities in solutions was found to exert an influence on crystal habit. A number of anhydrous nitrates varying appreciably in solubility were employed to serve as inorganic impurities. An inorganic impurity of greater solubility than the salt crystallizing has the effect of producing crystals of simpler habit than those formed from a pure aqueous solution under similar temperature conditions and about the same rate of crystal growth. If, however, the salt present as an impurity is less soluble than the salt crystallizing from solution the crystals formed are more complex in habit.

The crystal habit was likewise influenced materially by the presence of organic substances added as impurities. The results in general suggest that the effect of some impurities, inorganic and organic, is due in part to the influence of the impurity upon the property of the water acting as the solvent. The influence of impurities on crystal habit is not always due to adsorption of the impurity by the crystal faces nor to the regular inclusion of the impurity by the crystal.

INTRODUCTION

HISTORICAL

One of the most interesting phenomena associated with the study of crystals is that of crystal habit. It is rather surprising to find that there has been very little intensive systematic study devoted to this fascinating subject. Investigators for some reason have not devoted much time and energy to solve the mysteries of

* From a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, June 4, 1926. crystal development. The subjects of definite polyhedral form, symmetry, and crystal structure have issued a stronger challenge.

It is a matter of general observation that there are a large number of minerals, each represented by several different crystal forms. Furthermore, these forms or combination of forms for any one mineral may vary considerably in relative size. These observations are most pronounced in the case of the more commonly occurring minerals. Calcite and pyrite, for example, are exceedingly common minerals represented by very pronounced difference in crystal forms and combination of forms. Good crystals illustrating this may be found in all museums exhibiting minerals, and full descriptions with drawings and photographs may be seen in any standard text on mineralogy.

Crystal habit in this paper is here considered to mean the crystal form, or any manner of combination of forms, by which a mineral, or any other crystalline substance, may be represented. Distortions, although often characteristic, as for example in the case of many quartz crystals, are not to be considered in this discussion under the term *habit*.

The terms dominant and predominant are used quite frequently in describing experimental results. The term dominant is applied to the form in combination which is relatively the larger or largest in size. The term predominant refers to the habit among a group of crystals that occurs more often than any other in that group.

To a crystallographer it is of extreme interest to know the factors that cause a substance, of definite chemical composition possessing in crystalline state well defined elements of symmetry and a definite crystal structure, to vary in crystal habit. It is the purpose of this paper to report some of the results obtained from a large number of experiments that have been conducted with the object of determining some of the factors that influence crystal habit.

In recent years, particularly, a number of investigators have been interested in the study of crystal habit. Apparently, the greatest amount of effort has been directed towards a study of the effect of foreign substances. Reports have been published quite widely dealing in some way with the effect of foreign substances on crystal habit.

Boydant¹ and several others have tried to determine why the presence of a foreign substance can produce an influence so as to

¹ Boydant: Report of Smithsonian Institution, 1908-09, p. 272.

modify crystal habit. However, their efforts to determine the exact nature of the influence have not been very successful. One reason quite generally advanced, credited to H. Marc,² is that the foreign substance is adsorbed by the crystal faces. Since the properties of the crystal faces of different forms vary, the amount of adsorption by these faces may likewise vary. This retards the development of certain forms producing crystals of different habit. Wherry³ suggests that in the case of crystals highly modified the effect is produced not only by one adsorbable impurity but by several.

P. Curie⁴ developed a very elaborate theory referred to sometimes as the "attractive theory." Curie sets forth with detailed mathematical calculations the idea that capillary action exists between the liquid and the crystal, and that this effect varies with the nature of the crystal face and the nature of the liquid. According to Curie the faces which develop require a minimum expenditure of capillary energy and that, therefore, the dominant forms are those whose constant capillarity is the least, and that since foreign substances influence the capillary constant, they, therefore, influence crystal habit.

Another explanation quite generally met with, as one searches the literature bearing on crystal habit, is that the foreign substance is taken into the crystal from solution through simultaneous crystallization and is distributed in some orderly fashion. By virtue of this, the impurity modifies or influences the crystal habit. Paul Gaubert⁵ vigorously supports this idea and has reported somewhat at length on experiments using different dyes as foreign substances in solution to supply evidence in support of his view.

METHOD FOR GROWING CRYSTALS

For the purpose of growing crystals a combination of the following crystallizing dishes was used:

No. 1. 50 mm. diameter, 55 mm. deep. No. 2. 70 mm. diameter, 50 mm. deep. No. 3. 150 mm. diameter, 75 mm. deep.

² J. W. Mellor: A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 1, p. 630.

⁸ Edgar T. Wherry. At the Surface of a Crystal. Am. Mineral., 9, No. 3, p. 53.
⁴ Report of Smithsonian Institution, 1908–09, p. 272.

⁵ Paul Gaubert: Revue Scientifique, Paris, 41, No. 3, Jan. 15, 1910.

Each set up consisted of three dishes of No. 1 each containing the solution of the salt under consideration. These three dishes and one No. 2 dish containing concentrated sulphuric acid were covered by dish No. 3.

Solutions were made with distilled water and for most purposes 25 cc. of solution were placed in each dish. The majority of the experiments were carried on with three such sets of dishes for one experiment. It was highly desirable to make observations of crystals while they were growing in the mother liquor. In order to make observations for record on crystals grown from solutions which had not been disturbed, three sets of experiments, under the same conditions, were conducted simultaneously.

The dishes were placed on felt cloth which in turn was securely tacked to a wooden bench or wooden table top. The felt served as an insulation and also to reduce the effect of vibrations somewhat. The quantity of salt used in making up solutions was weighed carefully and the desired concentration was determined with the aid of solubility tables.

Temperature conditions in the room and in connection with any special experiments were determined by means of maximum and minimum thermometers. The experiments from which results were obtained for record were conducted under conditions where the temperature was controlled to within $\pm 2.5^{\circ}$ C.

Methods for growing crystals with the temperatures controlled by thermostats were considered for this work. While schemes such as described by Hostetter⁶ and others are most excellent for obtaining homogeneous crystals of fairly large size, they could not be used to advantage for the work undertaken.

Observations were made on crystals during the period of crystal growth, while the crystals were still in the mother liquor. Crystals were also carefully observed after being removed from the mother liquor. All observations were made with a 20 power Leitz binocular microscope. A special arrangement of lights was adapted so that crystals could be observed by reflected light or by transmitted light or by both simultaneously.

⁶ J. C. Hostetter: J. Wash. Acad. Science, 9, No. 4, pp. 85-94.

EXPERIMENTAL DATA

RATE OF CRYSTAL GROWTH

Since the rate of crystal growth will vary with the rate of evaporation, it follows that if the rate of evaporation is controlled so that it is fairly constant, the rate of crystal growth will also be fairly constant.

Four methods were used to vary the rate of evaporation:

A continuous partial vacuum was created by connecting a suction pump to a dessicator containing crystallizing dishes No. 1.
 Three crystallizing dishes, No. 1, containing the solutions, were placed under the large dish No. 3. Under this same dish was also placed dish No. 2 with some concentrated sulphuric acid. This arrangement allows a comparatively uniform rate of evaporation. (3) Dish No. 1 was covered first with filter paper, then with a glass plate placed immediately on top of the filter paper and finally a weight of at least 250 grams was placed on the glass plate. This arrangement was placed under dish No. 3. The filter paper absorbs some of the water vapor and consequently allows some evaporation to go on. However, the rate is much slower than in (2).
 A rubber stopper was tightly fitted to crystallizing dish No. 1. This prevented evaporation entirely.

The rate of crystal growth may also be influenced by rate of cooling. In general the solubility of a substance increases with the temperature of the solvent and this is true of all the salts used in these experiments.

SALTS USED IN THE EXPERIMENTS

The results reported in this paper were obtained largely from observations made upon the following three salts:

$$Pb(NO_3)_2$$

 $Ba(NO_3)_2$
 $Sr(NO_3)_2$

These three salts crystallize in the cubic system, in the tetrahedral pentagonal dodecahedral class of symmetry. Good crystals may be grown with very little difficulty, and for work dealing with crystal habit it is very important that the crystals obtained be sufficiently free from distortion to permit easy recognition and large enough so that the forms may be determined with the aid of a 20 power binocular microscope.

Other salts also were used in this study and crystals were grown of the following: NaCl, NaNO₃, NaBrO₃, NaClO₃, KI, KF, NaI, NaF, NaBr, and LiCl. The results were noted and were considered in connection with those of the three salts first mentioned, in arriving at interpretations.

Crystal growth was obtained by evaporation at fairly constant temperatures. The rate of evaporation was varied for different experiments. For most of the experiments two rates of evaporation were considered and for a few three rates. The rate of evaporation obtained by producing a partial vacuum with a suction pump will be referred to as "fast." The rate obtained under dish No. 3 in the presence of concentrated sulphuric acid will be referred to as "medium." The rate obtained under dish No. 3 by placing filter paper over the evaporating dish will be referred to as "slow." Experiments carried on with a rubber stopper tightly fitting the evaporating dish are regarded as "no evaporation."

The temperatures used were mainly the following:

5°C to 10°C 15°C to 20°C 20°C to 24°C 25°C to 30°C

The terms "medium" and "slow" refer to the method rather than to the actual rate of evaporation or of crystal growth. Experiments are reported, for instance, as evaporation "medium" with temperature conditions 15°C to 20°C. Experiments are also reported as evaporation "medium" with temperature conditions 20°C to 24°C. The scheme for allowing evaporation to take place is the same in each case. The actual rate must be somewhat different because there is a difference in temperature.

For highly quantitative work of a limited scope of this subject it would undoubtedly be important to define rate of crystal growth in terms of the actual increase in volume and the increase in the total surface area. This work, however, is in the nature of a preliminary report in this field and is approached from a fairly broad point of view. A quantitative consideration of rate of crystal growth, therefore, has for the present purpose of this work been omitted.

Experiments under the above conditions of evaporation and temperature were carried on (A) with pure aqueous solutions of the salts, and (B) with solutions containing impurities. The impurities considered were a set of inorganic salts, organic compounds, viscous liquids and suspensions.

A. CRYSTALS FROM PURE AQUEOUS SOLUTIONS

EVAPORATION "FAST"-TEMPERATURE 20°C-24°C

In each of three dishes was placed the following solution:

35 cc. H₂O 24 gm. Pb(NO₃)₂

At the time the experiment was started there were from 25 to 50 small crystals in the liquor in each dish. The three dishes were placed in a dessicator and the dessicator connected to a suction pump. The crystals in one dish were examined after 12 hours and in the remaining two after 36 hours.

All the crystals in the liquor were combinations of \pm tetrahedrons about equally developed. The crystals resembled slightly tabular octahadrons. All were milky and opaque. The above experiment was repeated with solutions of barium nitrate and strontium nitrate with the result that the crystals obtained in each case were all of the same habit as those obtained with lead nitrate. The crystals of barium nitrate were considerably smaller than those of lead nitrate or of strontium nitrate. The barium nitrate crystals were clear and transparent.

Evaporation "medium"—Temperature 5°C-10°C

In each of three dishes was placed the following solution:

25 cc. H₂O

2.2 gm. Ba(NO₃)₂

At the end of 12 hours of crystal growth the crystals of barium nitrate obtained were single tetrahedrons. The crystals were examined while in the liquor and a very interesting feature was noticed. The second tetrahedron could be seen to develop slowly while the crystals were being observed. The increase in temperature was not rapid enough to cause a solvent action to take place and produce a rounding of the edges and corners. The temperature in the room at the time of this experiment was but slightly higher than that of the interior of the box in which the experiments were set up. However, there was some heating effect from the light used for observation and the change in habit is explained as caused by this slight change in temperature. Crystal growth had not proceeded far enough to have reached a state of equilibrium. Because evaporation was taking place, the process of crystal growth continued even with a slight increase in temperature of the solution.

After 36 hours the crystals in the two remaining dishes were single tetrahedrons and combinations of \pm tetrahedrons with a predominance of single tetrahedrons. Of the combinations one form was dominant. The maximum thermometer indicated that the temperature for a short period had been in the neighborhood of 10°C. During the first 12 hours it had not been above 7°C. The increase in temperature may account for the variation in habit.

EVAPORATION "MEDIUM"-TEMPERATURE 15°C-20°C

25 cc. H₂O

17 gm. Pb(NO₃)₂

Results after 12 hours of crystal growth showed a predominance of crystals with \pm tetrahedrons in combination of equal development. A minority of the crystals were combinations of \pm tetrahedrons with one form decidedly dominant. After 36 hours and 60 hours the predominance of \pm tetrahedrons of equal development had successively increased.

EVAPORATION "MEDIUM"-TEMPERATURE 12°C-20°C

25 cc. H₂O

 $2.2 \text{ gm}. \text{Ba}(\text{NO}_3)_2$

After 12 hours of crystal growth all the crystals of barium nitrate were combinations of \pm tetrahedrons with one form appreciably dominant. After 36 hours there were some crystals with combinations of \pm tetrahedrons equally developed. The crystals predominating were combinations of \pm tetrahedrons with one form dominant. After 60 hours all the crystals were combinations of \pm tetrahedrons with about 50% of the crystals having both forms equally developed while of the other 50% one form was dominant.

EVAPORATION "MEDIUM"—TEMPERATURE 20°C-24°C

Crystals were allowed to grow under the above conditions from solutions of lead nitrate, barium nitrate and strontium nitrate. Solutions were of the following concentrations:

25 cc. H ₂ O	20 cc. H ₂ O	25 cc. H ₂ O
17 gm. $Pb(NO_3)_2$	2.2 gm. Ba(NO ₃) ₂	18 gm. Sr(NO ₃) ₂

Observations on each set of solutions, after crystals first appeared, were made for record after 12 hours, 36 hours, and 60

hours of crystal growth, respectively. The following results were obtained:

After 12 hours the majority of the crystals were combinations of \pm tetrahedrons of equal development. An appreciable percent were \pm tetrahedrons in combinations with a cube with the \pm tetrahedrons equally developed and with the cube decidedly the subordinate form.

After successive intervals of 36 hours and 60 hours there was in each case an appreciable increase in the percent of crystals having \pm tetrahedrons in combination with a cube. The cube was relatively larger in the case of barium nitrate than in either of the other two salts. However, it was the subordinate form.

Qualitatively the results for each salt were the same.

EVAPORATION "MEDIUM"-TEMPERATURE 25°C-30°C

Crystals were obtained from solutions of lead nitrate, barium nitrate and strontium nitrate under conditions indicated above. The solutions were of the following concentrations:

25 cc. H_2O	25 cc. H ₂ O	25 cc. H ₂ O
18.5 gm. Pb(NO ₃) ₂	3 gm. Ba(NO ₃) ₂	22 gm. Sr(NO ₃) ₂

LEAD NITRATE. Crystals obtained from lead nitrate solutions were observed after 12 hours, 36 hours, and 60 hours of crystal growth. In each case, from 50 to 75 crystals were grown in each solution observed for record.

After 12 hours of crystal growth the majority of crystals were combinations of the cubes and + tetrahedrons with all three forms about equally developed. A smaller number were of the same combination, but the two tetrahedrons, equally developed, were the dominant forms. A few crystals, ten to fifteen, were of \pm tetrahedrons of equal development. After 36 hours the majority of the crystals were combinations of a cube and \pm tetrahedrons and a pyritohedron. The cube was the dominant form and the pyritohedron the subordinate form. The remaining crystals were combinations of a cube and \pm tetrahedrons with the cube the dominant form. After 60 hours the pyritohedron was present on a larger percent of crystals than previously, and had become relatively larger but was still the subordinate form.

The results obtained with barium nitrate and strontium nitrate are indicated in table No. 1.

EVAPORATION "SLOW"-TEMPERATURE 20°C-24°C

The solutions for this experiment were of the same concentration as for those under conditions of "medium" evaporation and temperature of $20^{\circ}C-24^{\circ}C$.

LEAD NITRATE. If lead nitrate crystals are produced under conditions of medium evaporation at temperatures of $20^{\circ}C-24^{\circ}C$ the first crystals formed are combinations of \pm tetrahedrons about equally developed. If such crystals are transferred from conditions of "medium" evaporation to conditions of "slow" evaporation, there is a marked influence on the crystal habit. In less than ten minutes, cube faces begin to form on some crystals in combination with the two tetrahedrons. The first appearance is as very narrow faces bevelling the edges of the crystals. After 12 hours the cube is the dominant form on the majority of the crystals. All crystals are combinations of a cube and \pm tetrahedrons. On some crystals the three forms are about equally developed, and on a small percent, the \pm tetrahedrons still dominate.

During the succeeding periods of 36 hours and 60 hours the percent of crystals on which the cube is the dominant form increases. However, no other forms occur in combinations.

BARIUM NITRATE. Barium nitrate crystals grown in an aqueous solution under conditions of "slow" evaporation and temperature $20^{\circ}C-24^{\circ}C$ after 12 hours of crystal growth are qualitatively the same in habit as lead nitrate crystals grown under the same conditions. The cube is relatively larger in size and also crystals on which the cube is the dominant form occur in larger percent. After 36 hours of crystal growth, the cube becomes more completely dominant. On some crystals there is only one tetrahedron in combination. After 60 hours some crystals are single cubes, some combinations of a cube and one tetrahedron and some a cube and \pm tetrahedrons with the cube decidedly dominant.

EVAPORATION "SLOW"-TEMPERATURE 25°C-30°C

Crystals from solutions of lead nitrate, barium nitrate, and strontium nitrate were allowed to grow under conditions of "slow" evaporation and temperatures of 25°C-30°C. The solutions were made of the same concentrations as for the experiments under conditions of "medium" evaporation and temperatures 25°C-30°C.

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It was found an advantage in all cases to allow crystals to develop first under conditions of "medium" evaporation with temperatures of 25° C- 30° C. The first crystals formed in all cases were combinations of \pm tetrahedrons. As soon as crystals have formed and the desired numbers are in the liquor the dishes may be transferred to conditions of "slow" evaporation. Observations for record were made after 12 hours, 36 hours and 60 hours of crystal growth.

LEAD NITRATE. Lead nitrate crystals developed under the above conditions after 12 hours of crystal growth are combinations of a cube, \pm tetrahedrons and a pyritohedron. This combination with the cube the dominant form occurs on the majority of crystals. Some crystals, however, are combinations of \pm tetrahedrons and a pyritohedron. Some crystals are combinations of a cube and a pyritohedron. The pyritohedron is present on all forms. After 36 hours of crystal growth the pyritohedron becomes more prominant; it constantly grows relatively larger.

After 60 hours the pyritohedron is relatively equal in size, on some crystals, to the other forms with which it is in combination. The development of the pyritohedron under temperatures around 30° C is very pronounced.

BARIUM NITRATE. Barium nitrate crystals placed under conditions of "slow" evaporation and temperatures of $25^{\circ}C-30^{\circ}C$ react very much the same as lead nitrate crystals during the first 12 hours of crystal growth. After 36 hours the pyritohedron is relatively equal in size to the \pm tetrahedrons. The cube is more generally in combination than on lead nitrate crystals and is relatively larger.

After 60 hours the crystals are all combinations of a cube, pyritohedron and \pm tetrahedrons. In some experiments conducted under these conditions a few crystals grew of the combination, cube, pyritohedron, \pm tetrahedrons and tetrahedral pentagonal dodecahedron. The crystals were practically perfect. The cube was the dominant form.

Table No. 1 represents in tabular form the results obtained from a set of experiments, a few of which have been described above, with crystals grown from pure aqueous solutions.

			I ABLE I	
Salt	Rate of crystal growth	Hours of crystal growth	Temperature conditions	Results
Pb(NO ₃) ₂	"Fast"	12	20°C-24°C	All crystals \pm tetrahedrons in combination.
u	<i>66</i>	36	ű	a
u	"Medium"	12	5°C-10°C	All crystals combinations of \pm tetrahedrons; one form decidedly dominant.
u	u	36	u	ű
$Ba(NO_3)_2$	**	12	α	All crystals single tetra- hedrons.
ű	u	36	44	Predominance of single tetrahedrons; also \pm tetrahedrons in combination, one form dominant.
Sr(NO ₃) ₂	ĸ	12	"	All crystals combinations of \pm tetrahedrons; one form decidedly dominant.
u	ű	36	"	u u
Pb(NO ₃) ₂	u	12	15°C–20°C	Predominance of \pm tetra- hedrons equally developed; also \pm tetrahedrons, one form dominant.
u	(d.)	36	"	Increase in predominance of \pm tetrahedrons equally developed; \pm tetrahedrons, one form dominant.
u	u	60	**	"
Ba(NO ₃) ₂	ű	12	u	All crystals \pm tetrahedrons. one form dominant.
u	u	36	**	Predominance ± tetra- hedrons, one form dominant. Also ± tetrahedrons equally developed.

TABLE I

Salt	Rate of crystal growth	Hours of crystal growth	Temperature conditions	Results
Ba(NO ₃) ₂	"Medium"	60	15° C–20°C	$50\% \pm \text{tetrahedrons}$ equally developed. $50\% \pm \text{tetrahedrons}$, one form dominant.
Sr(NO ₈) ₂	"Medium"	12	15°C-20°C	Predominance of \pm tetra- hedrons equally developed; also \pm tetrahedrons, one form dominant.
"	a	36	ű	Greater predominance of tetrahedrons equally developed. \pm tetrahedrons, one form dominant.
4	#	60	4	"
Pb(NO ₃) ₂	R)	12	20°C-24°C	Predominance of \pm tetra- hedrons equally developed; also \pm tetrahedrons and cube, \pm tetrahedrons dom- inant.
a	u	36	ű	Predominance of \pm tetra- hedrons equally developed. Increase \pm tetrahedrons and cube.
"		60	4	a
Ba(NO ₃) ₂		12	ш	Predominance of \pm tetra- hedrons equally developed; also \pm tetrahedrons and cube, tetrahedrons dominant
ü	#	36	"	Same as for Pb(NO ₃) ₂ ; cube relatively larger.
u	a	60	12	"
Sr(NO ₃) ₂	a	12	.6	Same as for $Pb(NO_3)_2$.
<i>u</i>	() 4 4	36	ű	"
и	a	60	u	u

Salt	Rate of crystal growth	Hours of crystal growth	Temperature conditions	Results
Pb(NO ₃) ₂	"Medium"	12	25°C–30°C	Predominance of \pm tetra- hedrons and cube; also \pm tetrahedrons and cube, \pm tetrahedrons dominant; also \pm tetrahedrons.
42	,44	36	46	Predominance of cube, \pm tetrahedrons, pyritohedron, cube dominant; also cube, \pm tetrahedrons, cube domi- nant.
	ш	60	"	Increase in percent of pyrito- hedrons.
Ba(NO3)2	4	12	<i>₩</i>	Predominance of cube, \pm tetrahedrons. Also cube, \pm tetrahedrons, pyritohedrons.
a	- -	- 36	4	Increase in percent of pyrito- hedrons.
μ.	"	60	#	u .
$Sr(NO_3)_2$	"	12		Predominance of cube, \pm tetrahedrons. Also cube, \pm tetrahedrons, pyritohedrons.
4	ű.	36	"	Increase in percent of pyrito- hedrons.
u	æ	60	4	"
Pb(NO ₃) ₂	"Slow"	12	20°C-24°C	Predominance of cube, \pm tetrahedrons, cube dominant. Cube, \pm tetrahedrons, all equally developed. \pm tetra- hedrons and cube, tetra- hedrons dominant.
, ^u		36	u	Increase of cube dominance.
u	ű	60	4	42

Salt	Rate of crystal growth	Hours of crystal growth	Temperature conditions	Results
Ba(NO ₃) ₂	u	12	ŭ	Predominance of cube, \pm tetrahedrons. Also cube, \pm tetrahedrons, equally de- veloped. Small percent \pm tetrahedrons, cube.
u	#	36	<i>a</i>	Predominance of cube, \pm tetrahedrons. Cube, single tetrahedron.
u	546 () 	60		Predominance cube, \pm tetra- hedrons. Cube, single tetra- hedron. Cube.
Sr(NO ₃) ₂	μ.	12	. "	Cube, \pm tetrahedrons, cube dominant.
u	u	36	u	Cube becomes more domi- nant.
u	u	60	4	"
Pb(NO ₃) ₂	"Slow"	12	25°C-30°C	Predominance of cube, ± tetrahedrons, pytitohedron. ± tetrahedrons, pyrito- hedron. Cube, pyritohedron.
u	u.	36	#	Pyritohedron relatively larger.
u	u	60	"	
Ba(NO ₃) ₂	u	12		Predominance of cube, ± tetrahedrons, pyritohedron. ± tetrahedrons, pyrito- hedron. Cube, pyritohedron.
u	"	36	"	Cube, \pm tetrahedrons, pyritohedron.
a	u	60	ű	Predominance of cube, pyri- tohedron, ± tetrahedrons. Cube, pyritohedron, ± tetrahedrons, tetrahedral pentagonal dodecahedron.

Salt	Rate of crystal growth	Hours of crystal growth	Temperature condensities	Results
Sr(NO ₃) ₂	"Slow"	12	25C°-30C°	Predominance of cube, \pm tetrahedrons, pyritohedron. Cube, \pm tetrahedrons.
	u	36	u	Cube, \pm tetrahedrons, pyritohedron.
4	u	60	4	Predominance of cube, \pm tetrahedrons, pyritohedron. Cube, pyritohedron, \pm tetrahedrons.

SUMMARY AND CONCLUSIONS OF CRYSTALLIZATION FROM PURE AQUEOUS SOLUTIONS

The results obtained from the experiments reported above point very strongly to the conclusion that the crystal habit of crystals from pure aqueous solutions may be influenced in a marked manner by:

- 1. The rate of crystal growth;
- 2. The temperature of crystal growth,

Crystals growing at a rapid rate have a tendency to develop as simple forms, even at high temperatures. Crystals formed at any temperature below the boiling point of the aqueous solutions of the salts used, under ordinary pressure conditions, if grown rapidly, are developed as simple forms. In the case of the salts lead nitrate, barium nitrate and strontium nitrate, the crystals formed rapidly at high temperatures are combinations of \pm tetrahedrons equally developed so that the crystals resemble small octahedrons.

If the rate of crystal growth is slow the temperature at which crystals develop seems to be a very strong factor in determining crystal habit. This is very evident from all the results obtained and especially so in the case of barium nitrate. Single tetrahedrons were developed at temperatures of $5^{\circ}C-10^{\circ}C$ and at temperatures between $25^{\circ}C$ and $30^{\circ}C$ complex crystals of a cube, pyritohedron, \pm tetrahedrons and a tetrahedral pentagonal dodecahedron were obtained.

Observations of the influence of temperature on crystal habit have been recorded in scientific literature; however, reports of systematic work on this subject have not been found. Levy and Lacroix⁷ in describing Boricky's method of procedure in micro-chemical analysis report that the temperature at which crystallization is allowed to proceed has a perceptible influence on the crystal form of the hydrofluosilicate obtained. George Kalb⁸ states that among ice crystals formed near 0°C the tabular habit prevails, while lower temperatures favor the production of the prismatic habit.

If crystals of a complex habit formed at a temperature near 30° C and slow rate of crystal growth are suddenly changed to conditions of rapid crystal growth, while still in the mother liquor, either by suddenly lowering the temperature or by means of rapid evaporation, they are rapidly changed to crystals of simple habit. The complex forms may often be seen enclosed in the nature of a phantom crystal in the simple crystals of \pm tetrahedrons.

It has been suggested that the change in viscosity of an aqueous solution due to a change in temperature is a factor that should be considered as influencing crystal habit. This is undoubtedly a very valuable suggestion. Since the interpretations offered do not, at present, seem to fit the results obtained, and as a careful consideration of this factor is a problem in itself it has been left open for future consideration.

A very interesting observation has been reported by Hostetter,⁹ that if the solvent action on octahedrons of alum crystals caused a rounding of edges, the rhombic dodecahedron was formed in combination with the octahedron when crystal growth was resumed. The action of solution of a similar nature has been observed in this work. The form which resulted, however, after crystal growth was resumed was determined by the temperature of the solution.

Tutton's idea of "over crystallization"¹⁰ seems to be well substantiated in practically all of the results obtained from conditions of "medium" rate of crystal growth. In fact results obtained from all other conditions of evaporation, "medium" or "slow" and at temperatures between 20° to 30°C may be considered to substantiate it.

⁷ Levy and Lacroiz: Les Mineraux des Roches, p. 125.

⁸ Centr. Min. Geol., 1921, pp. 129-34.

9 J. C. Hostetter: Jour. Wash. Acad. of Science, Vol. 9, Nov. 4, pp. 93.

¹⁰ A. E. H. Tutton: Crystallography and Practical Crystal Measurement, Vol. 1, pp. 16-17. In all cases the crystals at first are of a simpler habit than after a period of 36 hours and 60 hours of crystal growth. According to Tutton, when crystals are first formed the process of crystallization proceeds so rapidly that it continues until the concentration of the solution has become lower than the theoretical state of equilibrium. Since crystallization in these experiments resulted because of evaporation the state of equilibrium was undoubtedly restored before solvent action took place sufficiently to cause a rounding of the edges as Tutton observes.

Tutton's idea explains very nicely why the crystal habit should become more complex after the first few hours of crystal growth, provided the temperature is above the point where simple crystals form. If the state of concentration has been reduced below the theoretical state of equilibrium, it seems quite likely that as the solution approaches a state of supersaturation, brought on by evaporation, the presence of a number of crystals of appreciable size will make it quite impossible for the solution to again reach a very high state of supersaturation. The process of crystallization will continue the moment the state of saturation exceeds the theoretical state of equilibrium. Under conditions of "medium" or "slow" evaporation the rate of crystal growth will, therefore, undoubtedly progress much more slowly after the first few hours of crystal growth or after the state of "over crystallization" has been obtained, than before that time. If the temperature, then, is high enough the crystals will, because of a slower rate of crystal growth, be more complex in habit.

The word "complex" is used quite frequently in this paper and in conformity with general usage is employed to distinguish simple crystals of one form from crystals of two or more forms. A crystal of the \pm tetrahedrons in combination with a cube, for instance, is referred to as being more complex than a crystal of just \pm tetrahedrons. However, a crystal of a more complex paramentral ratio is regarded as more complex than a crystal expressed by a simple paramentral ratio. The pyritohedron (hko) is regarded as more complex, therefore, than either the tetrahedron (111) or the cube (100). Likewise, a combination of a cube and a pyritohedron would be regarded as a more complex crystal than a cube in combination with either one or two tetrahedrons.

The results obtained in these experiments indicate that the pyritohedron is formed to advantage at a higher temperature

than the cube or the tetrahedrons. The cube, likewise, forms at a slightly higher temperature than the \pm tetrahedrons, and the combination of the \pm tetrahedrons forms at a higher temperature than the single tetrahedron. The rate of evaporation for each case is considered "slow."

A combination of crystal forms, in the light of the above experiments, may for some crystals be considered to be the result of a successive change of conditions. If conditions favorable to any one crystal form exist for a sufficiently long period of time that form will be the dominant form or it may even grow as a single form to the exclusion of all other forms. This result has been obtained in the case of the cube. The most favorable temperature for the cube of barium nitrate seems to be about 23°C. If this temperature can be successfully maintained for a period of three days, the majority of the barium nitrate crystals in the mother liquor will be cubes. Such results have been obtained repeatedly.

(To be continued)

EUHEDRAL OLIGOCLASE OF PERICLINE HABIT FROM MEDICINE BOW MOUNTAINS, WYOMING

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INTRODUCTION

The purpose of this article is to place on record an American occurrence of oligoclase crystals of pericline¹ habit, an unusually rare form of a common mineral. They occur at Gold Hill, Wyoming, on the west flank of Medicine Bow Mountains or Snowy Range, about three miles due west of Medicine Peak. Specimens were collected by the writer in July, 1925, while acting as field assistant to Professor Eliot Blackwelder. These were studied in the mineralogical laboratory at Stanford University and this article prepared under the direction of Professor Austin F. Rogers, whose stimulating criticism is gratefully acknowledged.

OCCURRENCE

The oligoclase lines the walls of an irregular vein in an altered pre-Cambrian dike, a dark-colored, mediosilicic rock, typical of many similar dikes which here traverse the ancient sediments.

¹ Pericline is a variety of albite in which the crystals are elongated parallel to the b-axis. The variety of albite with this habit should not be confused with the twinning-law bearing the same name. No necessary connection exists.