

ART. XXXVII.—*The Growth of Crystals Under External Pressure*; by STEPHEN TABER.

THE question whether it is possible for growing crystals to exert a linear pressure is of such great interest and importance to geologists that it is surprising the problem has received so little attention. Jean Lavalle, in 1853, appears to have been the first to assert that crystals do exert such a force.* He observed that crystals were pushed upward during their growth. This, however, was denied by Kopp, who, upon placing crystals of alum colored with a small amount of chrome alum in a solution of plain alum and allowing them to grow, noticed that no material was deposited on the under side of the colored crystals. He states that he was never able to observe anything tending to confirm the view that a crystal can raise itself in order to grow also on the side on which it rests.† Since that time several investigators have published their conclusions but they have reached no general agreement. It is not necessary to review here the literature bearing on the subject, a very complete bibliography of which has already been published by Dr. K. Andrée.‡

In 1905 Becker and Day published an account of their very interesting and suggestive experiments.§ Using alum, they found it possible "in a saturated solution of constant temperature to grow clear crystals a centimeter in diameter which would raise a weight of a kilogram through a distance of several tenths of a millimeter. The crystal was placed upon a piece of plate glass in a beaker containing saturated solution of the same material, and loaded as desired. Knowing the weight raised, it appeared an exceedingly simple matter to determine the force required, since it was only necessary to ascertain the actual area of contact between the weight and the crystal. Here, however, an unexpected difficulty was encountered."|| The under side of the crystal where it rests on the plate glass, instead of being plane consists of a terraced cavity so that the bearing surface is only a narrow rim around the outer edge of the crystal. The exact measurement of this area of contact is very difficult and uncertain, and, therefore, it is hard to estimate the force per unit area exerted by the crystal. However,

* Compt. Rend., vol. xxxvi, p. 493, 1853.

† Kopp, H., Über die Bildung von Krystallen mit Kernen, Ann. Chem. Pharm., vol. xciv, p. 124, 1855.

‡ Die geologische Bedeutung des Wachstumsdrucks kristallisierender Substanzen, Geologische Rundschau, vol. iii, pp. 7-15, 1912.

§ Becker, G. F., and Day, A. L., The Linear Force of Growing Crystals, Proc. Washington Academy of Sciences, vol. vii, pp. 283-288, 1905.

|| Ibid., pp. 285-286.

Becker and Day state that "It was at once evident that it amounted to many pounds per square inch, and as observations multiplied, it became reasonably certain that it is actually of the same order of magnitude as the ascertained resistance which the crystals offered to crushing stresses."*

Important as these conclusions are, the paper by Becker and Day did not attract the immediate and general attention that it deserved, possibly because it did not have as wide a distribution as it would have had if printed elsewhere than in the proceedings of a local society. And while it opened a wide field for further research no one seems to have taken advantage of it.

In 1913 two German investigators, Bruhns and Mecklenburg, published a paper† in which they claim to have repeated the experiments of Becker and Day with negative results, and they criticize the description of these experiments, stating that it is not so accurate and full as one might expect in the case of such a striking phenomenon.‡ Their own paper is certainly not open to this criticism, for they describe in the greatest detail the manner in which their experiments were conducted.

It is not necessary to repeat here all the details of their experiments, but one detail is important as it evidently explains why Bruhns and Mecklenburg obtained results differing from those described by the two American scientists. In a crystallizing dish containing a saturated solution of alum the German investigators placed *two crystals of alum* of approximately the same size and weight; *one of these was left uncovered, while the other was covered* with a glass plate on which was placed a weight of one kilogram.§ From time to time the crystals were removed from the solution and after being carefully dried, were measured and weighed. The experiments were repeated several times, the results obtained being tabulated. An inspection of the tables shows that the height of the unloaded crystals increased, while that of the loaded crystals remained practically the same. Both increased in weight, but the unloaded crystals gained nearly twice as much as the loaded ones.

Bruhns and Mecklenburg go further and state that the weight resting on the covered crystal plays, as such, no important rôle; the essential thing being the circumstance that the upper face of the crystal is protected from the addition of further substance.¶ In proof of this statement they describe another experiment in which four crystals of alum were placed

* Ibid., pp. 286-287.

† Bruhns, W. and Mecklenburg, Werner, Über die sogenannte "Kristallisationskraft," 6th Jahresbericht d. Niedersächsischen geologischen Vereins, pp. 92-115, 1913.

‡ Ibid., p. 96.

§ Ibid., p. 99.

¶ Ibid., p. 100.

in a saturated solution; two of the crystals being covered by light glass plates while the other two were left uncovered. The crystals were measured from time to time and the results tabulated as before. These results are in every way similar to those obtained in the previous experiments.

In the fall of 1914 the writer of the present paper began a series of experiments with the object of determining whether it is possible for growing crystals to exert a linear pressure, and if so, the conditions under which the pressure is developed; for, obviously it is not always in evidence, or such contradictory results as those cited above would never have been obtained by careful investigators. Some of the more important experiments conducted by the writer are described in the following pages, and the conclusions that may be drawn from them are also discussed. All of the questions growing out of this work have not been solved, but it was thought best to put on record such facts as have been established in order that others might aid in carrying on the investigation.

Before going into details it is advisable that the problem be clearly defined, for some observers have wrongly attributed to crystal growth certain phenomena that are without question due to other processes. Reference is here made to that class of phenomena which are due to chemical or physical changes taking place with increases of volume in a closed and insufficient space. The present investigation has been limited to those evidences of mechanical pressure accompanying crystallization that are not *obviously* to be explained in this way.

The writer began his investigations by growing crystals of alum in crystallizing dishes placed in desiccators containing sulphuric acid, care being taken to follow all of the precautions observed by Bruhns and Mecklenburg. The experiments were conducted in a room where the temperature fluctuations were not more than 5° C. Some of the crystallizing dishes contained both loaded and unloaded crystals, while other dishes contained only loaded crystals; otherwise the conditions were the same for all of the tests. At first the results were rather confusing, some crystals lifting their load several tenths of a millimeter, while others showed no increase in height. Later it was found that the loaded crystals were able to increase in height only when there were no unloaded crystals present in the same crystallizing dish. If unloaded crystals were placed in the crystallizing dish with a loaded crystal, or if volunteer crystals began to form soon after the experiment was started, then the loaded crystal did not show any increase in height, and in many cases there was an actual decrease in height.

Confirmatory experiments were made using other salts, such as copper sulphate and potassium sulphate, instead of alum.

In one of these experiments a crystal of potassium sulphate, 3.07 millimeters in thickness, was placed between two glass plates, held tightly together by rubber bands. The crystal and plates were then covered by a saturated solution of potassium sulphate and placed in a desiccator. Within a few days volunteer crystals began to form around the sides of the dish just above the surface of the solution, and a little later crystals appeared on the bottom of the dish. After several weeks the crystal pressed between the glass plates had gone completely into solution, while in the meantime the volunteer crystals had continuously grown in size.

From these experiments it would appear that when two crystals, similarly placed in a saturated solution, are subjected to unequal pressures the system is in unstable equilibrium. In other words a solution may become supersaturated with respect to a crystal placed under a relatively small pressure, while at the same time it tends to dissolve a crystal that is under a greater pressure. This probably explains why Bruhns and Mecklenburg failed to get the results that were obtained by Becker and Day.*

Experiments with results similar to those described above were performed by placing crystals in warm saturated solutions and allowing the solutions to cool down over night. In these tests supersaturation was induced by cooling, instead of by evaporation.

In another experiment a saturated solution of copper sulphate at room temperature (about 20° C.) was caused to flow slowly through a siphon to the bottom of a crystallizing dish, which was kept at a temperature of about 12° C. by surrounding it with running tap water. Another siphon with upturned ends kept the solution in the crystallizing dish at constant elevation. The arrangement of the apparatus is shown in fig. 1.

Before starting the flow of the solution through the apparatus, a crystal of copper sulphate, held tightly between glass plates surrounded by rubber bands, was placed in the crystallizing dish. The flow of solution was regulated by means of a pinch-cock so that about one liter passed through in twelve hours. At the end of twenty-four hours the growing crystal had pushed the plates apart, overcoming the resistance of the elastic bands, and had increased the distance between the plates from 1.21 to 2.63 millimeters. The experiment was discontinued

* On Dec. 29, 1915, several months after the completion of this work, the writer learned from Dr. J. C. Hostetter that, under the direction of Dr. A. L. Day, he had made experiments similar to those described above and reached the same conclusion. As the publication of Dr. Day's reply to Bruhns and Mecklenburg has been delayed, permission was courteously given to the writer to publish this paper without waiting for the appearance of that reply.

after a number of volunteer crystals had begun to develop in the crystallizing dish.

The foregoing experiments prove that under certain conditions the growth of crystals may be accompanied by the development of a linear force, and that the failure of some investigators to find evidence of this force is due to the conditions under which their experiments were conducted. The writer has formulated an hypothesis to explain the growth of crystals in directions in which mechanical hindrances oppose

FIG. 1.

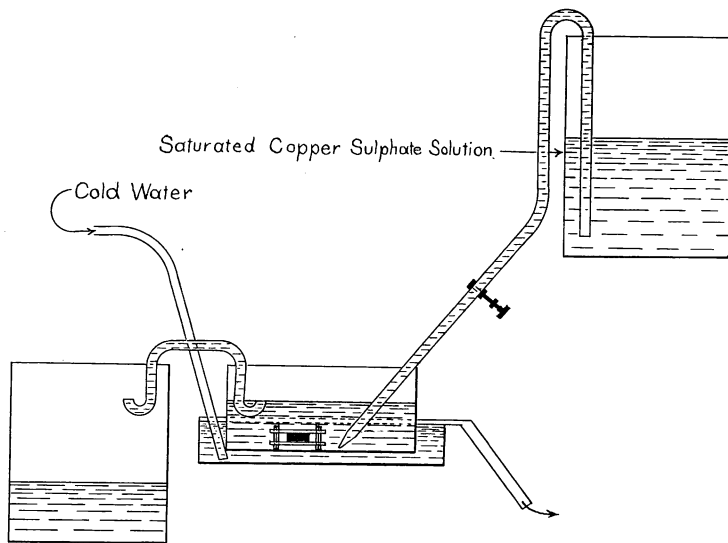


FIG. 1. Apparatus for growing crystals under pressure in a solution of approximately constant temperature.

growth, but since this problem is intimately related to the origin of the terraced cavities, it is necessary to consider both problems at the same time.

In all of the experiments described above, whenever a measurable lifting of a weight by a growing crystal took place, the crystal at the close of the experiment had a terraced cavity or hollow on its under side, and this was the case even when a crystal was used that had only plane faces in the beginning. In a very few instances indistinct shallow hollows seemed to be present also on the upper surface of covered crystals, but none had a depth of so much as 0.1 millimeter. Moreover, careful measurements show that the distances through which weights

are lifted by growing crystals are always the same as the amount by which their hollows are deepened. The results obtained in the experiment described below may be taken as typical.

A crystal of alum having a thickness of 2.18 millimeters was placed in a warm saturated solution and covered with a small glass plate. The solution was allowed to cool slowly in the crystallizing dish, which was left over night on a table in the laboratory. After about fifteen hours the crystal was taken from the solution, dried and remeasured. It was found to have increased 0.62 millimeter in total thickness, raising the glass plate through that distance, the cavity on the under side was deepened by 0.54 millimeter, and a shallow hollow, having a depth of 0.06 millimeter, was formed on the upper surface of the crystal. The increase in the depth of the cavities and the increase in the height of the crystal, therefore, differ by only 0.02 millimeter, which is well within the limits of error in making the measurements. All measurements were made with a screw micrometer graduated to 0.01 millimeter or with a spherometer similarly graduated, and the figures given above are the average of several independent determinations.

The hollows found on the under side of crystals are familiar to all who have grown them in glass vessels, for they are commonly formed on uncovered as well as covered and weighted crystals. Bruhns and Mecklenburg argue that the presence of these cavities does not indicate a lifting of the crystal by growth from below, and in support of this conclusion cite the experiment performed by Kopp in 1855, which they repeated with similar results.* They advanced the hypothesis that the formation of the narrow rim which surrounds the cavity and on which the crystal rests is due to adsorption, stating that the height of this rim does not increase with the growth of the crystal, and that it moves outward because of solution on the inner side, while it is continuously being built up anew on the outer edge. They further state that the height of the rim "about 0.12 millimeter" remains approximately constant during its outward growth, and that this is possibly connected with the thickness of the layer of solution between the crystal and its support.† It is clear that these statements do not agree with the results obtained in the experiments that the writer made with weighted crystals, but in order that there might be no uncertainty in this matter the following tests were conducted with crystals in free contact with the solution except, of course, on their under side, where they rested on the bottom of the crystallizing dish.

* Loc. cit., p. 101 and footnote 15, p. 113.

† Ibid., pp. 101-105.

Small crystals of alum colored with chrome alum (not more than 0.25 millimeter in diameter) were dropped into a warm saturated solution of plain alum, which was then allowed to cool down over night in the laboratory. Next morning, when the crystals were removed from the solution and measured they had an average diameter of 3 centimeters and height of 1.5 centimeters. The terraced hollows on the under side ranged from 2.38 to 3.21 millimeters in depth, and, at the top of each of these cavities, the small nucleal crystal, colored with chrome alum, could readily be distinguished; for it had not dissolved and no white alum had been deposited on its under surface. This means that these small nucleal crystals were elevated through a distance equal to about twelve times their original diameter.

In another test a small crystal of alum colored with chrome alum was placed in the solution of plain alum and allowed to grow until it had a diameter of 3 millimeters. It was then removed from the solution, dried, and the under surface given a thin coating of shellac. After the shellac had hardened, the crystal was replaced in a warm saturated solution, and allowed to grow over night as in the previous experiment. At the close of the test it was found that the impervious coating in no way had interfered with the deepening of the hollow, which was similar in every respect to the hollows formed in the crystals that had not been treated in this way.

Another crystal, with nucleus of chrome alum, was coated with shellac on all faces except the lower face, and then placed in a warm saturated solution as before. Deposition of new material took place first at the base and then gradually it covered all of the shellacked faces. The new faces were parallel to the old, but the new growth was easily broken from the original crystal along the shellacked surfaces, being firmly attached only at the base. The original crystal was elevated through a distance of 0.52 millimeter. A crystal, with all of its faces shellacked, did not grow in any direction when replaced in a saturated solution.

Most of the experiments outlined above were made with the alum crystals resting on an octahedral face, because flattened octahedrons are the commonest forms, and are also the easiest with which to work. When small (not more than 1 to 1.5 millimeters in height) these crystals frequently show only octahedral faces, but, as they grow more rapidly near the bottom than higher up, the larger crystals assume a terraced and roughly pyramidal form due to the alternation of octahedral faces and of octahedral and cube faces as shown in the cross-section, figure 2. In the several experiments made with crystals resting on cube faces, there seemed to be little if any

difference in their tendency to form cavities and raise the growing crystal.

One of the deepest hollows (2.93 millimeters) obtained by growing a crystal of alum in a solution that was allowed to cool down over night, was formed around an artificial plain surface which had been previously ground on the crystal in a direction not parallel to any of the natural faces. During the

FIG. 2.

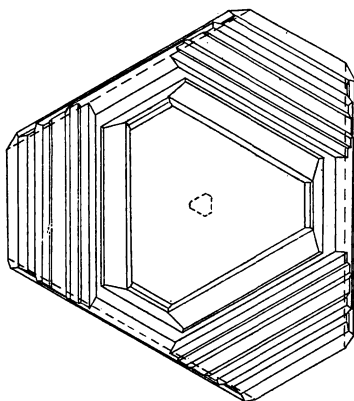
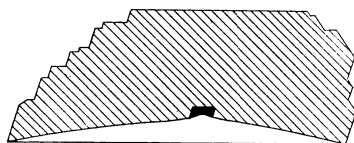


FIG. 2. Plan and cross-section of a large alum crystal with nucleal crystal colored with chrome alum. Crystal shows terraced pyramidal form and well-developed hollow on under surface.

growth of the crystal no appreciable change in the slope of the upper surface, which was a natural crystal face, could be observed.

When a crystal about 2 centimeters in diameter was placed upside down (i.e. with the hollow up) in a warm saturated solution, it grew a smooth surface on top similar in every way to the crystal that had not been reversed. Underneath the crystal a hollow, 0.6 millimeter in depth, was formed by the

downward extension of the new growth, the smooth flat face of the original crystal in the center of the hollow remaining unchanged. By coloring the original crystal with chrome alum the new growth could easily be distinguished from the old when the crystal was sectioned for examination.

The terraces on the under side of crystals are probably formed by the repetition of crystal faces, frequently they appear as minute striations parallel to the edges of the base, and sometimes they are unrecognizable, giving place to almost smooth sloping surfaces.

The experiments with weighted and unweighted crystals prove: (1) that a growing crystal resting on a smooth surface can raise itself and even a considerable additional load by building downward the advancing outward edge of the crystal; (2) that no material is deposited on the under side of the crystal except along the advancing outer edge; and (3) that the cavities are not formed by solution, but are due to the downward growth of the outer edge, while at the same time no material is being deposited on the under surface within this outer edge.

While it is true that there may be slow diffusion of molecules through solids and even through crystals, there is no ground for the belief that a crystal like an organism can grow from within. All of the experiments conducted by the writer support the theory that a crystal grows only through the addition of layers of material from without. If this is true, it follows that a crystal can grow only where it is in contact with a solution which furnishes it with the material necessary for growth. When crystals grow in contact with glass surfaces, as in the experiments described above, there is always a thin layer or film of solution between the crystal and the glass. The presence of this thin layer of solution is due to capillary attraction and adsorption. When the surrounding solution is more concentrated than the layer between the crystal and glass, diffusion is set up, tending to equalize the concentration, and, if the solution is supersaturated with respect to the base of the crystal, the crystal molecules present in excess of saturation are oriented and attached to the crystal as soon as they come within range of the molecular forces controlling crystal growth—a circumstance that must occur in such limited space not far from the outer edge of the crystal.

The area of contact between a crystal and the supporting surface is under greater pressure than the rest of the crystal, since it must bear the weight of the crystal as well as any added load. The solubility of most substances in aqueous solutions increases with the pressure, and therefore the supporting surface of a crystal of such a substance has a greater

solubility than the other parts of the crystal. Since a crystal is enlarged by deposition only at those points where it is in contact with a supersaturated solution, the degree of concentration necessary for crystal growth is greater at the base of the crystal than elsewhere. This means that a crystal is able to raise itself by downward growth, as in the experiments outlined above, only when its base is in contact with a solution supersaturated with respect to it, and that the degree of concentration necessary for growth increases with any increase in the weight supported per unit area of the supporting surface.

When supersaturation is brought about either by evaporation or by cooling, the denser and therefore more concentrated portions of the solution tend to settle to the bottom, and in the latter case the bottom of the crystallizing dish is itself a cooling surface. It is possible that adsorption in some slight degree helps to increase the concentration of the layer of solution in contact with the bottom of the dish, but adsorption can not be the direct cause of the upward pressure developed by crystals in the foregoing experiments, for otherwise the presence of unweighted crystals in the same dish with weighted crystals would not prevent the upward growth of the latter. The weighted crystals fail to grow in height because the unweighted crystals, with their lesser solubility, prevent the necessary degree of supersaturation in the layer of solution resting on the bottom of the dish. Another reason for believing that adsorption is of no importance in the formation of cavities and upward growth of crystals is the absence of appreciable hollows on the upper surface of crystals grown under heavy weights or even under glass plates weighing only 0.17 gram. There are no grounds for assuming that adsorption is any more efficacious in producing hollows on the under than on the upper surface of a crystal when both surfaces are in contact with similar material. In the few cases where insignificant shallow hollows were observed on the upper surface of crystals they were probably due to the cover plate acting as a cooling surface.

The objections raised against the adsorption hypothesis apply with equal force to the theory that the pressure accompanying crystal growth, in the experiments described above, is in any considerable degree due to those forces which are peculiar to the growth of crystals and which determine the development of crystal faces. The thin layer of solution due to capillarity and adsorption is always found between the upper surface of a crystal and the cover glass, as well as between the lower surface and its support; and the concentration of the solution in contact with the upper surface can be increased by diffusion from a surrounding solution of higher concentration just as easily as the solution under the base of the crystal. The upper

and lower surfaces of the crystals used are crystallographically the same, and therefore the forces controlling the development of crystal faces must be the same at the top as at the bottom. The pressure on the upper surface of a crystal is always less than that applied to the base, for the latter must also support the weight of the crystal, and therefore, all other things being equal, a crystal should grow through additions at the top rather than at the bottom. That this did not take place in the foregoing experiments leads inevitably to the conclusion that the upward pressure developed by the growing crystal must be explained by the presence of a solution, in contact with the base, having a greater degree of concentration than the solution in contact with the other surfaces of the crystal.

It is a well-known fact that when solutions of a salt, such as alum, are subjected to concentration, the denser and therefore more concentrated portions of the solution tend to settle to the bottom of the container. The roughly pyramidal form of the larger alum crystals has already been commented on, and this shape is unquestionably due to the more rapid growth of the lower parts of the crystal where they are in contact with the more concentrated layers of the solution.

If a crystal of alum is suspended just below the surface of a saturated solution in a large beaker and another crystal is placed on the bottom of the beaker, the latter crystal will grow in size at the expense of the former, which will go slowly into solution.

A crystal of alum 3 milligrams in weight was placed on a small glass plate suspended 2 centimeters above the bottom of the crystallizing dish containing a warm concentrated solution, while a similar crystal was placed on the bottom of another dish containing a solution of the same concentration and temperature. Both were allowed to cool down over night under exactly the same conditions. When the crystals were examined the next morning it was found that the crystal resting on the suspended glass plate had been raised through a distance of only 1.1 millimeters, while the crystal that had grown at the bottom of the crystallizing dish had been raised 2.4 millimeters.

The experiment described below illustrates nicely the difference in the growth of a crystal on its upper and lower surfaces because of the greater concentration in the lower layers of the solution. A perforated metal screen covered with a piece of filter paper was supported on glass rods so that it rested 3 millimeters above the bottom of a crystallizing dish containing a warm concentrated solution of alum. A crystal of alum colored with chrome alum was placed on top of the filter paper and covered first with a small piece of filter

paper and then with a piece of the metal screen. The holes in the screen were 1.5 millimeters in diameter and were spaced 0.75 millimeter apart. The solution was allowed to cool down over night and the following morning the crystal was removed, sectioned vertically and carefully examined. It increased in height from 4.69 to 5.15 millimeters through the addition of material to the lower surface, and the hollow in the original crystal was almost entirely filled. Moreover, the crystal had grown downward in places through the pores of the filter paper, as there were several crystals, oriented parallel to the original crystal, attached to the under side of the lower metal screen. There was no deposition of new material on the upper face of the crystal and no growth through the paper such as was observed underneath, although the crystal grew outward until beyond the limits of the overlying filter paper and screen, and then upward and also inward until the new growth overlapped the screen on top. The pressure of the filter paper and screen, weighing less than 0.5 gram, was sufficient to prevent any growth on the upper surface of the crystal or in the pores of the filter paper. Growth continued downward through the pores of the lower filter paper because the concentration of the solution increased in that direction.

In another set of experiments, growing crystals of alum, copper sulphate and potassium sulphate were subjected to lateral pressure between pairs of vertical glass plates while in all other directions they were in free contact with supersaturated solutions. These crystals grew in every direction, except that in which the pressure was applied, forming flat tabular crystals. They could not overcome the external pressure resisting growth, because there was no provision for supersaturating the solution with respect to the faces that were under pressure and that were thereby rendered more soluble.

A consideration of the results obtained in the foregoing experiments leads to the following conclusions:

(1) A crystal will grow in a direction in which external forces oppose growth, if the surface on which the forces are acting is in contact with a solution that is supersaturated with respect to it; and, if the growing crystal is composed of a substance the solubility of which increases with pressure, then for any increase in the forces opposing growth a corresponding increase in the concentration of the solution is necessary.

(2) If a crystal of such a substance is subjected to a greater pressure in one direction than in others (as for example when a weight is placed on a crystal), the surfaces that are under the lesser pressure will tend to limit the concentration of the solution and prevent it from becoming supersaturated with

respect to the surfaces that are rendered more soluble because of greater pressure. In order that growth may also take place on the surfaces subjected to the greater pressure, some means must be provided for maintaining the supersaturation of the solution in contact with them.

In their conclusions concerning the area of contact between a growing crystal and the supporting surface, Becker and Day state that "there is reason to believe that this area changes constantly as the crystals grow, and is less for a smaller load than for a larger one."* When a supersaturated solution is diffusing under the edge of a growing crystal, growth is most rapid on the outermost edge, and the concentration of the solution decreases rapidly with the distance that it has to diffuse under the crystal. As growth takes place and the crystal is raised this tends to keep the outer edge, supporting the weight of the crystal, as narrow as possible, but the area of the edge must always be large enough to keep the pressure per unit area less than the crushing strength. Moreover since the solubility increases with the pressure the area of the supporting surface must always be sufficient to maintain the relative supersaturation of the solution with respect to it and prevent re-solution. This argument leads to the conclusion that the area of support may also be dependent on the relative concentration of the solution with which it is in contact. It is difficult to obtain the quantitative data that would confirm this conclusion, but observation seems to support the view that the area is smaller when in contact with a highly supersaturated solution than when the solution is almost at the saturation point.

The molecular forces enabling crystals to grow in directions in which they must overcome external pressure, furnish the most plausible explanation of certain geologic phenomena; but hollow faces such as those obtained in the foregoing experiments are not common in minerals, and their absence has been used as an argument against this hypothesis. In nature, however, crystal growth usually takes place at a much slower rate than is feasible in laboratory experiments, and the rock masses in contact with a growing crystal are more or less permeable to solutions. That solutions are active agents even in relatively impervious rocks, like granite, is indicated by the reactions that take place not only in fractures but also along the contact between different minerals and even along the cleavage planes of the minerals themselves.

In attempting to reproduce under laboratory control the needle-like ice columns that are commonly found on bare clayey soils after a cool night, the writer observed that water

* Loc. cit., p. 287.

in fine capillary tubes remained in a liquid state at very low temperatures.* This suggested the following experiment: A half-inch glass tube and a fine capillary tube were filled with a concentrated solution of copper sulphate and sealed. The

FIG. 3.

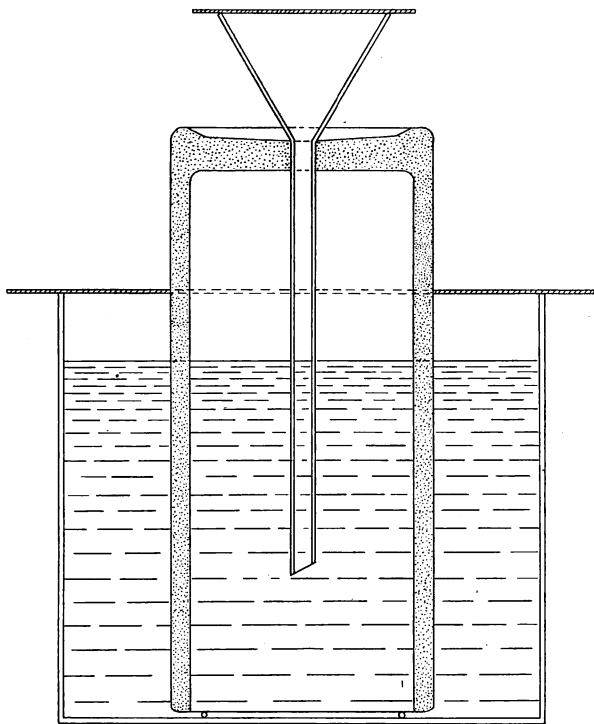


FIG. 3. Porous battery cell in a saturated solution of copper sulphate. The solution is drawn up through the capillary pores and on evaporating from the upper surfaces deposits crystals which rupture the cell and gradually form veinlets.

temperature was then lowered until crystals began to separate out in the large tube, but crystallization did not take place in the capillary tube even when it was kept at a much lower temperature for several days. The discovery of this fact led to a series of experiments with porous materials, two of which are described below.

*This fact seems first to have been observed and recorded by Sorby, *Phil. Mag.* (4), vol. xviii, p. 105, 1859.

A porous battery cell was placed bottom up in a glass jar, about three-fourths full of a saturated solution of copper sulphate, and a piece of paraffine-coated cardboard was cut to fit snugly around the cell and rest on top of the jar, as shown in figure 3. The purpose of the cardboard was merely to prevent evaporation from the surface of the solution in the jar. The battery cell was 18 centimeters high and 8 centimeters in diameter while its walls averaged 6 millimeters in thickness. The stem of a glass funnel was inserted through a small hole drilled in the bottom of the cell so that the solution could be replenished and kept at the same elevation. The solution was slowly drawn up through the capillary pores of the cell allowing evaporation to take place from the exposed surface. After a couple of days a coating of copper sulphate began to form here and there in irregular spots. These spots gradually increased in size and thickness to form thin crusts, and, later, groups of short needle-like columns of copper sulphate normal to the surface of the cell, could be observed gradually pushing the crusts outward. The columnar crystals also appeared in large and small groups elsewhere on the surface of the cell, and on the outer ends of some of these, small fragments of the cell could be distinguished. After about ten days narrow cracks were seen forming in the walls of the cell. At first they seemed, for the most part at least, to be open fissures, but the openings were gradually filled with copper sulphate so as to form veinlets, and, as the veinlets became larger, it could be seen that the copper sulphate crystals were in the form of needle-like columns or fibers with their axes normal to the walls of the fracture. The veins were usually enlarged by growth from both sides, as was shown by the presence of an irregular parting near the center marked by a line of small cell fragments. Occasionally where one side was cut off from additional supplies of solution the crystals would grow without break across the entire vein. In structure and appearance these veins closely resemble the asbestos veins in serpentine, and this suggests that the latter have possibly grown out from the walls in a somewhat similar manner. In places the veins give way to a brecciated zone in which the individual fragments are separated from one another and held in place by the copper sulphate. When the experiment was discontinued some of the veins had a width of over 3 millimeters, and the columnar crystals growing normal to the surface of the cell had a length of about 1 centimeter.

After several attempts to break glass receptacles with growing crystals a method was devised that proved successful. In this experiment crystals of copper sulphate were grown in a bulb-shaped chamber 4.5 centimeters in diameter, blown in a

glass tube having an interior diameter of 7 millimeters. The walls of the chamber were about 0.3 millimeter thick. The apparatus was set up as shown in figure 4. A saturated solution of copper sulphate at room temperature (about 20° C.)

FIG. 4.

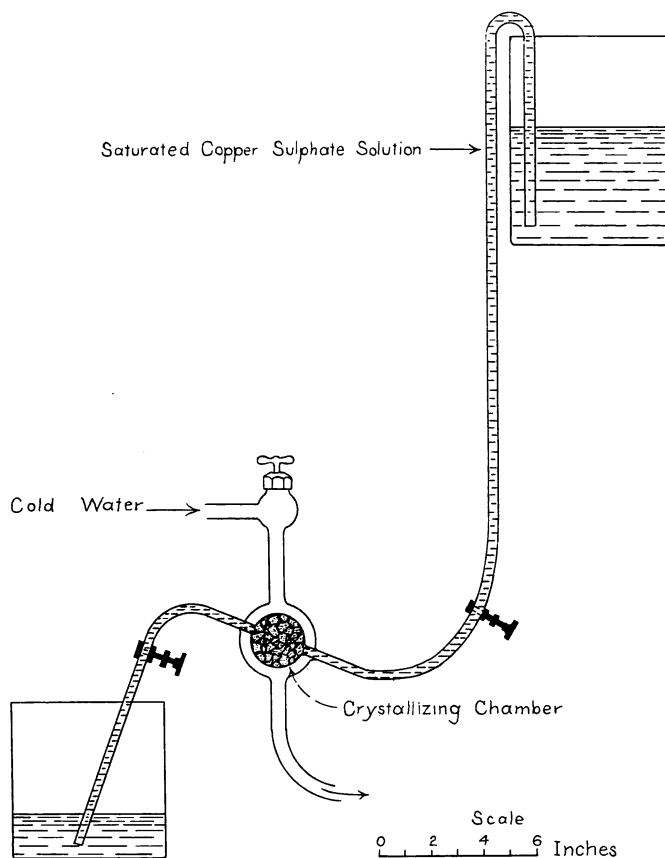


FIG. 4. Apparatus for growing crystals under pressure, with glass crystallizing chamber ready to be ruptured by growing crystals.

was drawn from a large reservoir by means of a glass siphon and passed through the crystallizing chamber, the rate of flow being controlled by a pinchcock placed near the end of the outflow tube. The surface of the solution in the reservoir stood at an average elevation of about 50 centimeters above the crystallizing chamber. The latter was kept at a

lower temperature than the reservoir by surrounding it with running tap water having an average temperature of about 12° C. The chamber was first filled with fragments of a broken battery cell together with a few small crystals of copper sulphate to induce crystallization, and then the interstices were filled up with clean, fine quartz sand. Upon admitting the solution, care was taken to remove, as far as possible, all air bubbles from the apparatus. In the beginning the flow of the solution was regulated so that about two liters passed through in twenty-four hours, but toward the close of the experiment, as the passageways became choked with crystals, the flow became slower and slower. After starting the experiment, it was kept in continuous operation until the chamber was ruptured, which occurred at the end of 9 days in one test and 7 days in another.

After one of these tests, the mass filling the ruptured chamber was immediately broken to pieces and carefully examined. The outer portion of the mass was thoroughly cemented together so that the surface in contact with the glass was almost smooth, but near the center some of the spaces were only partly filled by deposition. The crystals of copper sulphate had sharp boundaries along their contact with the quartz grains and cell fragments. No fibrous or columnar crystals could be found, and, when freshly broken pieces were examined under a bifocal microscope, magnifying to 78 diameters, no copper sulphate crystals were observed in the pores of the cell fragments except occasionally where there were unusually large openings.

After completing the other test, the ruptured glass chamber, with its contents, was set aside and allowed to stand undisturbed for several weeks. The solution remaining in the chamber at the close of the experiment gradually reached the surface by capillary attraction, and evaporated where exposed to the air along the fractures in the glass. The evaporating solutions built up crystals in the fractures, and the glass fragments were pushed farther apart, but none of these crystals showed a columnar or fibrous structure.

During these investigations another observation was made that throws some additional light on the manner of crystal growth under varying conditions. After a test in which the flow of solution through the glass crystallizing chamber had been nearly stopped by crystal growth, the apparatus was disconnected without rupture having occurred, and, with the tubing still full of solution, was placed in a beaker, as shown in fig. 5, where it was allowed to stand undisturbed for three months during the summer. The pressure of the solution standing in the longer tube caused the solution to flow very

slowly from the open end of the shorter tube, where it evaporated. At first the solution ran down between the tube and the beaker for a distance of 8 centimeters, forming on evaporation a crust that in places attached the tube to the beaker. Later, the flow became adjusted to the evaporation in such a

FIG. 5.

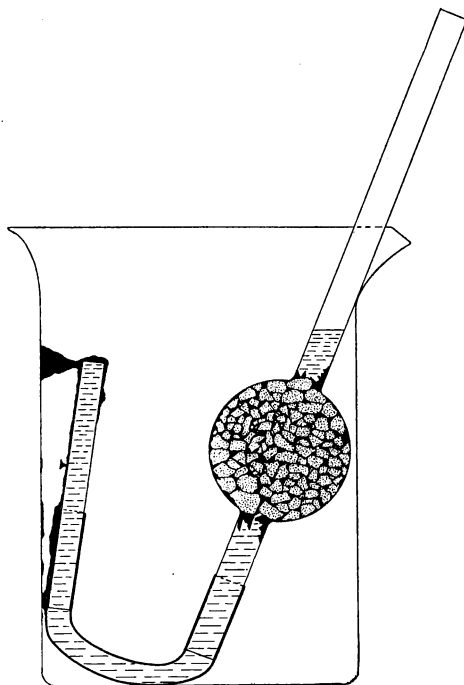


FIG. 5. Diagram showing glass tube gradually being pushed back from the side of the beaker by a growing mass of copper sulphate crystals.

way that crystal growth continued only where the crust of copper sulphate was in contact with the beaker near the top of the tube. Gradually a hollow growth, shaped somewhat like a stalactite, was formed between the end of the tube and the beaker. As it increased in size the tube was pushed back 1.3 centimeters against the elastic resistance of the rubber tube connecting the two glass tubes, and the mass that had formed lower down between the tube and beaker was pulled apart, leaving fragments adhering to both. Additions of material seemed to take place only where the formation was in contact

with the side of the beaker, and the rate of growth was probably not uniform, as rings of growth varying in thickness and also in fineness of crystallization could be distinguished. The successive rings gradually increased in diameter so that the formation was largest at the end in contact with the beaker. The rings are probably due to variations in the rate of growth resulting from changes in temperature and humidity. In this case the material for growth diffused under the growing mass from within instead of from without.

The shape of a crystal is the resultant of several different factors, and under varying conditions these factors vary greatly in their relative importance. In the ideal case of a growing crystal, everywhere in contact with a solution of uniform saturation, it is probable, as suggested by Lehmann, that the form assumed is the resultant of the forces of surface tension and molecular orientation.* The tendency is always to build that form for which the total surface energy is a minimum, and in crystals the surface tension is not the same in different directions. Otherwise the stable form would be a sphere.

In nature this ideal condition can seldom be attained, and in most cases the form of a growing crystal is determined by the external forces resisting growth and the accessibility of the material from which the crystal is built rather than the tendency to form crystal faces. The tendency to form crystal faces is much stronger in some substances than in others, but it is never so strong as to cause growth on a face which is not in contact with a supersaturated solution, and, even if a growing surface is in contact with a supersaturated solution, the relative rate of growth is chiefly controlled by the rapidity with which the material for growth is made available.

If a solution remains in contact with two substances, A and B, it will in time become saturated with respect to both, and should the conditions change so that the solution is supersaturated with respect to A, then the crystals of A will begin to grow. With increase in size a crystal of A will finally approach so close to a crystal of B that the latter will offer resistance to further growth in that direction. If, under existing conditions, A has a relatively weak tendency to form crystal faces and a relatively rapid rate of growth, the crystal of A will grow around the crystal of B, which will then become an inclusion; but on the other hand, if A has a relatively strong tendency to form crystal faces and a relatively slow rate of growth, so that there will be sufficient time for diffusion to supply new material to the surface of A along its contact with the crystal of B, then B must make room for the crystal of A.

* Quoted in J. V. Elsdon's "Principles of Chemical Geology," p. 60. London, 1910.

It may do this in two ways: if the pressure exerted by the crystal of A on B renders the latter more soluble, and sufficient time is allowed, B will go into solution where the pressure is greatest, and crystallize out again where the pressure is least; but should conditions be otherwise, B must be pushed out of the way by the growing crystal of A.

Water is universally present in rocks, though often in very small quantities, and the recrystallization of minerals is largely brought about through the agency of aqueous solutions. The growth of garnet crystals in certain quartz-mica schists studied by the writer furnishes a good illustration of the processes described above. The garnets referred to are of later origin than the schistosity of the rock, which, under the microscope, is seen to consist essentially of elongated quartz grains and small flakes of mica, the two minerals being interleaved to form thin layers or imperfect alternating bands. The garnets in their growth have pushed aside the relatively insoluble plates of mica so that opposite the garnets the mica layers run closer together, while the more soluble quartz has been removed from these points of greatest pressure, and redeposited between the folia, where the supporting effect of the garnets resulted in a reduction of pressure. The recrystallized quartz grains are roughly elongated and oriented, so that their longer dimensional axes radiate outward from the garnets.*

So far in this discussion only the growth of individual crystals has been considered. In the growth of crystalline aggregates the molecular forces controlling the formation of crystal faces can have little to do with the shaping of the mass as a whole, which is, therefore, determined by the external forces resisting growth and the accessibility of the material from which the growing mass is composed. During the growth of such a mass, the tendency is to produce that form which requires the least expenditure of energy, and if the resistance to growth were equal in all directions, the growing body would tend to become spherical; but usually the accessibility of material is an influential, if not the controlling, factor. The shape of calcareous concretions formed in shales furnishes an illustration of the growth of crystalline masses where growth is opposed by the resistance of external forces.

The hollow faces and also the needle-like columnar crystals, obtained in the experiments described in this paper, are to be attributed to the limited accessibility of the materials necessary for growth. The formation of the hollow faces, as already explained, is due to the rapid growth of the outer edge of a crystal face in contact with a smooth supporting surface, and

* Taber, S., *Geology of the Gold Belt in the James River Basin, Virginia*, Va. Geol. Surv., Bull. No. VII, pp. 29-30 and 228-229, 1913.

the consequent reduction in the concentration of the solution tending to diffuse in under the crystal. A concave surface is less soluble than a plane surface, and, therefore, hollow faces are soon filled up except in those cases where crystal growth is so rapid as to reduce the concentration of the solution faster than diffusion can supply material to the less exposed surfaces.

The form of the needle-like columnar crystals of copper sulphate obtained by the writer is determined by the fact that each crystal is in contact with the solution furnishing the material for its growth only at its base. The material for growth is supplied through capillary openings so small that their surface tension is sufficient to prevent the solution from creeping up the crystals. The enlargement of these columnar crystals takes place only in the direction of greatest pressure, but this phenomenon is due merely to the circumstance that in other directions the crystals are not in contact with the solution. The long slender columnar form is never found in crystals of copper sulphate that have grown normally with the solution in contact with several surfaces, because this form is not the most stable. The total surface energy of one of the columnar crystals is great as compared with the mass, and, therefore, they are dissolved by solutions that are supersaturated with respect to more stable crystal forms. If the columnar crystals are placed in saturated solutions with normal crystal forms, the latter tend to grow at the expense of the former in the same way that large crystals replace smaller ones.

The same argument applies to the formation of ice columns. The ice columns are usually capped by sand grains, small pebbles, etc., which, as pointed out by Prof. Abbe,* have probably acted as refrigerating surfaces and served as nuclei for the crystallization of the ice. These nuclei are not essential, however, and are sometimes absent even in nature. Numerous experiments carried on by the writer with different kinds of material, varying quantities of water, and different methods of insulation and refrigeration all lead to the same conclusion: The essential condition for the formation of ice columns is that the water for the growth of the ice column must be delivered through a small capillary opening to the base of the growing crystal which must not elsewhere come in contact with water.

There are of course other ways in which elongated, columnar and even fibrous crystals may be formed. In some crystals, such as rutile needles, the form is probably due solely to the molecular forces controlling the formation of crystal faces; while in other cases external forces have been the controlling

* Abbe, Cleveland, Ice Columns in Gravelly Soil, *Monthly Weather Review*, vol. xxxiii, pp. 157-158, 1905.

factor. Where the elongated form develops chiefly as a result of external pressure, the longer dimensional axes are normal to the direction of greatest pressure and parallel to the least pressure. Van Hise and others have explained the development of elongated crystals during the recrystallization of rocks on the theory that solution takes place along the line of greatest strain and deposition along the line of least resistance and normal to the maximum stress. This theory is confirmed by the experiments of F. E. Wright in the formation of crystals of wollastonite, diopside and anorthite under vertical pressure.* If the normal habit of a mineral is columnar, then those crystals that are oriented with their longer axes parallel to the least pressure will tend to grow at the expense of those that are not so favorably oriented. When columnar crystals develop parallel to the direction of the greatest pressure, as in the experiments with copper sulphate and ice described in this paper, the orientation is in spite of the pressure and not because of it.

Attention has been called to the fact that crystallization does not take place so readily in very small capillary spaces. It is possible that the high surface tension and extremely small volume of the solution may tend to prevent the development of centers of crystallization.

The solution, furnishing the material necessary for growth to a crystal surface that is under pressure, may consist of a layer so thin that the space occupied must be classed as subcapillary rather than capillary in size. A subcapillary opening, as defined by Van Hise, is one in which the attraction of the solid molecules extends from wall to wall.† The flow of solutions through such extremely minute openings must be exceedingly slow, and therefore it is probable that the material for growth reaches the growing surface largely as a result of diffusion even in the case of natural crystals which have grown gradually through a long period of time. It would be very difficult, if not impossible, to expel solutions from subcapillary openings solely through the application of pressure, and therefore, under favorable conditions, the material for growth may be able to reach a crystal that is under very great pressure—a pressure that is perhaps several times the crushing strength of the crystal.

The pressure that may sometimes be observed during the growth of a crystal is probably due to the molecular forces associated with the separation of solids from solution and the

* Wright, F. E., *Schistosity by Crystallization, A Quantitative Proof*: this Journal, vol. xxii, pp. 224-230, 1906.

† Van Hise, C. R., *Treatise on Metamorphism*, U. S. Geol. Surv., Monograph 47, p. 135, 1904.

attraction and orientation of the physical molecules as they are brought into position on the surface of a growing crystal, but the exact mechanical process (or processes) is uncertain. It seems probable that several closely related processes are involved. While the forces that control the development of crystal faces may enable a growing crystal to exert a linear force that is greater in some directions than in others, "this crystallizing force" is probably small. This force was not quantitatively determined in the experiment by Becker and Day, and it is doubtful if it can be directly determined.

A crystal surface will not grow under pressure and therefore will not do work in overcoming external forces resisting growth unless the surface is in contact with a supersaturated solution. From this it follows that any factor affecting the solubility of the surface will correspondingly affect the amount of work which may be done by a growing crystal in contact with a definite quantity of supersaturated solution. If a growing crystal is everywhere in contact with a solution of uniform concentration, then the pressure that may be developed in any given direction will depend upon the solubility of the crystal in that direction and the way in which the solubility varies under pressure. In crystals, the solubility is equal along all parallel directions, and, with certain exceptions, it is unequal along directions which are not parallel. The solubility of most substances increases with the pressure, and in crystals the rate of increase is probably the same only in parallel directions. A convex surface has a greater solubility and a concave surface a less solubility than a plane surface, and, therefore under uniform conditions, the tendency is always to form plane surfaces. The crystal faces that most commonly develop are normal to the directions of greatest solubility under the existing conditions, while the crystal edges and crystal angles develop in the directions of least solubility. The writer suggests that the intensity of the "crystallizing force" for a crystal of any substance under given conditions might be estimated after experimentally determining the relative solubilities under varying pressures in different directions.

It is possible that the pressure effects studied in this paper are not limited to crystals, for it is readily conceivable that the same forces of molecular cohesion, which enable any solid to resist external forces tending to cause rupture, could exert, during the enlargement of the mass, a pressure that would be of the same order of magnitude as the forces necessary to produce rupture. Moreover there is another factor involved that may be of prime importance. Most substances, so far as we know, dissolve in water with a net decrease in the volume of the system. In some cases the volume of the solution is even

less than the volume of the water alone.* All the salts used in the experiments described in this paper go into solution with contraction in volume. The writer has tried to obtain some evidence of pressure during the crystallization of ammonium chloride, one of the few salts that dissolve in water with an expansion in the volume of the solution, but so far has obtained only negative results. This question, however, is not regarded as settled, and the experiments are being continued.

Pressure tends to increase the solubility of a salt that goes into solution with a contraction in the total volume. The separation of such a salt from solution must be accompanied by a corresponding increase in volume, and if the separation takes place in a closed and limited space, the pressure developed may be enormous, probably many times the crushing strength of the substance.

If a crystal or crystalline mass should be so enclosed by other matter that the material for growth reached it only by diffusion through subcapillary openings, then the pressure developed during crystallization might be very largely due to the accompanying increase in volume. If this hypothesis proves to be true it may help to explain the variation in the character of the concretions found in rocks that differ in texture. Those concretions, that largely exclude the material composing the rock in which they grow and in so doing push apart the planes of lamination, seem to be limited chiefly, if not entirely, to the fine-grained rocks, such as shales and slates, in which the openings are for the most part subcapillary in size. On the other hand there are many concretions that are relatively impure, because they include much of the surrounding material, and these do not show any evidence of having exerted pressure on the inclosing rock, since the bedding planes of the latter may often be traced through the concretions without break in their continuity.

This class of concretions seems to be limited largely if not entirely to sandstones and other coarser-textured rocks in which the openings are for the most part capillary and supercapillary in size. In extreme cases the concentrated matter merely fills the interstices and cements loose-textured material together to form indistinct nodular masses.

Highly pure siliceous concretions and pyrite crystals may develop in limestones and similar calcareous rocks without distorting the enclosing material, for such rocks are relatively

*Thomsen, *Therm. Untersuch.*, I, 45, 1882. MacGregor, *Trans. Roy. Soc. Can.* 1890, 19; 1891, 15. *Trans. Nova Scotia Inst. Sci.*, vii, 368, 1890. Traube, *Zs. anorg. Chem.*, iii, 1, 1892. These references cited in G. P. Baxter's "Changes in volume upon solution in water of the salts of the alkalis," *Jour. Am. Chem. Soc.*, vol. xxxiii, p. 922, 1911.

soluble, and go easily into solution where subjected to pressure by a growing body.

The writer believes that the forces developed during crystal growth have played an exceedingly important part in the formation of many veins. In an earlier publication some of these veins were described in detail and many of the facts supporting this hypothesis were given,* but additional evidence is now available. A paper is at present under preparation in which the experimental data so far established, together with such observational data as have been collected, will be used in attempting to explain various geologic phenomena, especially the formation of veins.