ORIGIN OF AUTHIGENIC INCLUSIONS IN SYNTHETIC CRYSTALS

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ABSTRACT

Authigenic inclusions in natural crystals and crystals grown in the laboratory are described. Detailed description of the laboratory growth of ammonium dihydrogen phosphate is made to illustrate the development of inclusions during growth. It is suggested that these inclusions both in natural and synthetic crystals have their origin in some interruption of the growth process.

Visible inclusions are common optical defects of both natural and synthetic crystals. The term "inclusion" is given to any foreign body either solid, liquid or gas inclosed within the crystal.[1] One can recognize two classes of inclusions: primary—those inclusions associated with the growth of the crystal, and secondary—those inclusions which form after growth.[2]

Specific terms are used in the literature to describe the various forms of inclusions:[3]

- (*a*) Bubbles (Gordon, p. 284)—bubble shaped cavities of various sizes filled with vapor or solution.
- (*b*) Negative crystals (Ford, p. 201)—cavities having definite crystal shape.
- (*c*) Veils (Gordon)—thin sheets of small inclusions.
- (*d*) Phantoms or ghosts (Gordon, Johnston)—"oriented veils" (an envelope of planar veils each one of which is parallel to some possible crystal face usually, but not always, identical with the final crystal).
- (*e*) Clouds—aggregates of fine bubbles or cavities.
- (*f*) Solid crystals or mineral fragments—the included crystals may be:
  - (1) Foreign matter suspended in the mother liquor which is incorporated and overgrown, e.g., clay or chlorite in quartz (Johnston).
  - (2) Phases exsolved after growth is complete, e.g., bronzite (oriented ilmenite inclusions).
  - (3) From crystals that crystallize out of included mother liquor, e.g., NaCl in quartz vacuoles.

Although the inclusions sometimes occur in irregular arrangement (1, p. 202), more commonly they exhibit a definite orientation with respect to some common crystallographic direction. For example, the phan-

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[1] Ford, W. E., Dana's Textbook of Mineralogy, 4th Ed., p. 222, Wiley, N. Y., 1932.

[2] Laemmlein, G., *Zeit. Krist.*, **71,** 237–256 (1929) (41 references).

[3] Gordon, S. G., *Am. Mineral.*, **30** (5, 6), 284–285 (1945). Johnston, W. D., Jr., and Butler, K. D., *Bull. Geol. Soc. Am.*, **57,** 601–650 (1946).

toms in quartz where bubbles or mineral grains are arranged in a series of thin planes each one of which is parallel to some rhombohedral termination. Since the termination of such a crystal as quartz is related to the directions of most rapid growth, it is obvious that the phantom also reflects a stage in the growth process.

It must be recognized that some inclusions are probably post-growth (secondary) and are derived from local resolution, exsolution or chemical alteration. Examples of these are: nepheline (elaeolite) which has an oily or greasy luster probably due to oriented unmixed inclusion since pure nepheline is vitreous in luster,[4] and bronzite which owes its bronze sheen to exsolved thin plates of ilmenite.[4]

Phantoms or veils have been observed in the following crystals:

TABLE 1. ORIENTED AUTHIGENIC INCLUSIONS IN NATURAL CRYSTALS[2,3]

Mineral	System	Orientation
Quartz	Trig.	∥ to prism[5]
Beryl	Hex.	Hexagonal tubes ∥ to *c*[5] (negative crystals) also ∥ to prism
Diamond	Cubic	∥ to (111) (110)[6] Clouds ∥ to (110)
Barite	Ortho.	∥ to (110), (102), (210)[7]
Gypsum	Mono.	∥ to prism edge
Corundum	Hex.	1011 and 1120
Fluorite	Cubic	∥ to (111)
Calcite	Trig.	∥ to cleavage

Inclusions usually form during the growth when the rapidly growing crystal incloses mother liquor or other phases, either growing simultaneously, or introduced from outside the growth chamber. With slow growth the growing crystal usually rejects impurities ahead of the growing face resulting in a corresponding higher perfection. Interruption of growth may lead to inclusions as will be shown later. The self-purification during growth concentrates the impurities in the residual mother liquor until eventually they may precipitate, as illustrated in the pipe of a steel ingot or the center of an ice cube.

It will best serve our purpose to limit the discussion to authigenic inclusions of solution or vapor formed during the growth process since those are best illustrated by laboratory data.

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[4] Ramdohr, R., Klochmann's Lehrbuch der Mineralogie, 13th ed., Enke, Stuttgart, p. 221 (1948).

[5] Cameron, E. N., *et al.*, *Am. Mineral.*, **38,** 218–262 (1953).

[6] Gubelin, E., *Schweiz. Min. Petr. Mitt.*, **28** (1), 146–156 (1948).

[7] Whitlock, H. P., Report. Dir. N. Y. State Museum, p. 163 (1917).

No over-all generalization about the veiling tendency among various crystals can be made since it is definitely related to the habit of the crystal. Crystals show varying degrees of habit modification. For example, *ADP* ($NH_4H_2PO_4$) rarely shows more than two forms. More than fifty forms have been reported for quartz. During the growth of the crystal the solution composition (which dominates the habit) may change. Thus the phantom may not contain all of the forms shown by the final crystal. Independent of the degree of variation of habit the phantom or veil usually contains only the lower index forms and rarely shows the vicinal forms common to the final crystal.

TABLE 2. ORIENTED AUTHIGENIC INCLUSIONS IN SYNTHETIC CRYSTALS

Formula	System	Orientation
$LiSO_4 \cdot H_2O$	Mono.	‖ to (110)
NH_4Cl	Cubic	‖ to (100) (tubes)
$CuSO_4 \cdot 5H_2O$	Triclinic	
$NH_4H_2PO_4$(ADP)		
KH_2PO_4	Tetr.	‖ to (101)
KH_2AsO_4		
Rochelle Salt	Ortho.	
NaCl	Cubic	‖ to 100
$NaBrO_3$	Cubic	‖ to (−111)
$NaClO_3$	Cubic	‖ to (100)
$KClO_3$	Tetr.	‖ to (100)
CaF_2	Cubic	‖ to (111)
Alum	Cubic	‖ to (111)

There are several synthetic crystals which may occasionally grow without trace of a veil on the seed, e.g., HIO_3, quartz, and alum. In each case the solutions from which these crystals grow are of high concentration (high solubility) and show a high tendency to supersaturate. From a practical viewpoint the crystal grower can state that the "ease of growth" for these crystals is high.

The habit of a crystal is fixed to a high degree by the internal structure but can show some variation depending upon the environment during growth. One can modify the habit in some crystals within wide limits by changing the environment. For example, too rapid growth with poor agitation may yield dendrites or spherulites—incomplete crystals. The effect of pH is notable in the case of $NH_4H_2PO_4$ where growth is limited to the *c*-axis direction for low pH 4.0, but also takes place in the *a*-axis direction when the pH exceeds 6.0.

For each environment there appears to be maximum rate of growth which if exceeded results in poor crystals. As shown by numerous experiments this optimum rate is also a function of crystal size[8] both at the microscopic and macroscopic level.

An examination of the work of Groth[9] and Buckley[10] will show there are many instances demonstrating habit modification by change of solution composition. As yet no satisfactory correlation of these data is available.

If we examine the state of affairs during crystal growth we find we are dealing with a solid-liquid equilibrium. The solid is in some sort of equilibrium with the saturated solution—a liquid. However, the saturated solution may be regarded as an attenuated solid. There is some evidence that already in the supersaturated solution there is some preorganization of material directed toward the crystalline state, e.g., HIO_3 where dimers and trimers are found in the saturated solution.[11]

Speculating further, it is reasonable to assume that addition of some foreign ion would influence the solution and the preorganization for the following reasons: (*a*) The effect of addition is out of all proportion to the amount of the addition, 1% has a high effect. (*b*) The active habit-modifying impurities are preferentially absorbed. These impurities are also incorporated in the structure up to the saturation value (in $NaCl-PbCl_2$ system this is of the order of 5×10^{-4} mol % Pb^{++}).

As Wells[12] and others have pointed out, for each environment (solution) there is a characteristic set of endforms. If a crystal is shifted from one environment to another the new set of endforms is assumed. If we place two crystals with different endforms in the same environment (solution), nothing happens (the energy difference for macroscopic crystals of different face assemblage is too small) until growth is permitted whereupon both crystals assume the form characteristic of the solution.

If an anhedral fragment is allowed to grow, it will rapidly assume the equilibrium form but in so doing the interface between seed and new growth is usually cloudy or veiled. The relations between habit, seed, and veiling are well illustrated with the laboratory growth of ammonium dihydrogen phosphate.

The Laboratory Growth of Ammonium Dihydrogen Phosphate (ADP)

Ammonium dihydrogen phosphate (*ADP*) crystallizes in the tetragonal scalenohedral class of the tetragonal system. Its habit comprises

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[8] Egli, P. H., and Zerfoss, S., Discussions Farad. Soc., No. 5, 61–66 (1949).

[9] Groth, P., Chemische Kristallographie, Leipzig, W. Engelmann (1908).

[10] Buckley, H. E., Crystal Growth, N. Y., Wiley (1951).

[11] Sidgwich, Chemical Elements and Their Compounds, Vol. 2, p. 1228, Oxford Press (1950).

Nayar, M. R., and Srivasta, L. N., *Phil. Mag.*, **39**, 800–805 (1948).

[12] Wells, A. F., *Phil. Mag.*, **37**, 184–199 (1946).

two forms, the second order prism (100) and the second order tetragonal bipyramid (101) (9, Vol. 2, p. 796). Groth does not report the basal pinacoid (001) as a form nor does it occur in the related potassium phosphates and arsenates. Growth from water solution is generally along the *c*-axis (pH = 4). However, thickening along the *a*-axis can be obtained by making the solution more basic (pH = 6).

Commercial production of *ADP* single crystals (2–3 pounds) takes place in two stages: (1) the production of a cap (equilibrium seed) from a seed plate, and (2) growth of the final crystal from the cap. Commercially both operations are done by a temperature-lowering operation rather than by the less easily controllable constant temperature evaporation method (Plate 1*A*).

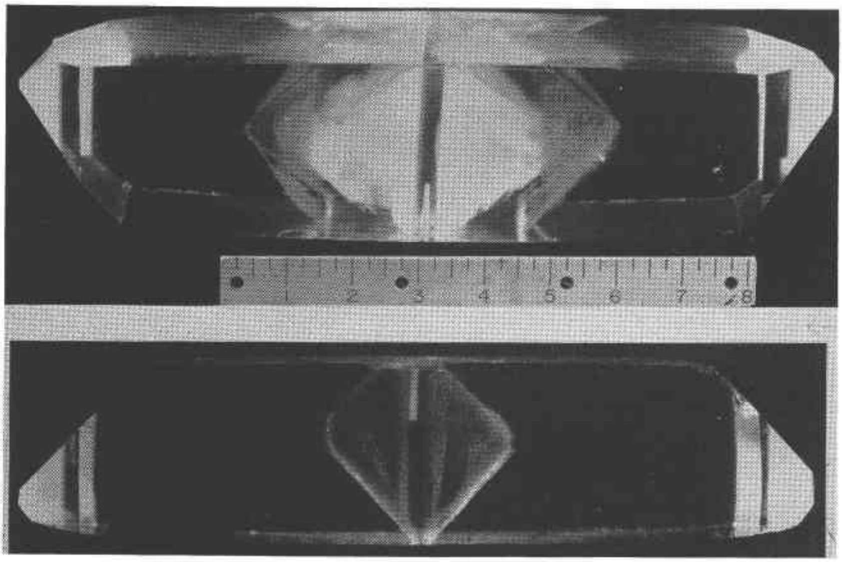

Plate 1. A. Ammonium dihydrogen phosphate (*ADP*) crystal grown from a cap by temperature lowering. The cap was grown from a seed plate cut parallel to 001. B. *ADP* grown from a "synthetic" cap. (Scale units in inches.)

In the first or capping operation a *Z*-cut plate (plate parallel to 001) is placed in a solution saturated at 50° C. and rapidly grown by temperature lowering into the doubly terminated (but cloudy) cap.

The various successive stages in the capping operation are shown in Fig. 1. Growth first takes place on the 8 corners of the two large faces of the seed plate (in the *Z*-direction) in the form of small pyramids. These pyramids gradually expand along the edges and in the *Z*-direction until they touch. If the capping operation is carried out sufficiently rapid,

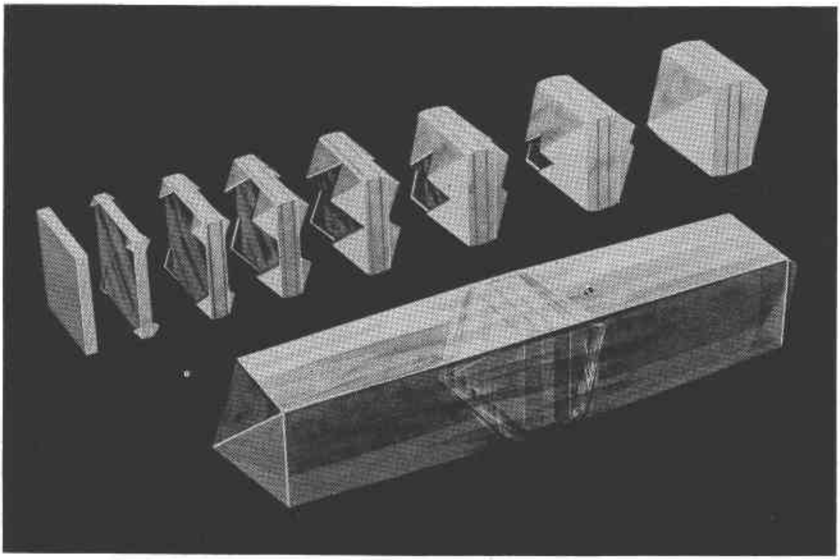

FIG. 1. Stages in the capping operation of a 001 seed plate of *ADP*.

the pyramids eventually coalesce into a doubly terminated crystal. If the capping operation is too slow the pyramids end up as parallel growth forms.*

Growth on the central portion of the original seed surfaces is incomplete as far as filling out the volume. The cap is usually hollow on both sides of the seed plate and contains solution in the cavity. Poor diffusion *within* the central portion of the seed surfaces during the rapid capping accounts for the failure to complete the crystal interior.

The specification for the initial seed plates requires only that the edges (where growth takes place) be as perfect and unstrained as possible. The condition of the portion of the surface of the seed within the edge is unimportant; in fact the seed can be a "square-toroid."

The growth of the final crystal then proceeds from the cap in a second operation. The cap is planted in a solution saturated at 50° C. With appropriate agitation the solution and cap are allowed to cool to room temperature in a sealed container at a rate of 0.5°/day.

The interface between the cap and new growth also shows a cloudiness or veil that has the shape of the cap. Occasionally during the growth of the main crystal or bar stock thin planar veils perfectly parallel to each

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* If the capping is done on crystals mounted on a seed tree which is rotated in the solution with the *c*-axis on the direction of rotation, the front face may cap over nicely while the trailing face may show parallel growth for low speeds of rotation. If the rate of rotation is increased or the direction is reversed at intervals this defect is corrected.

of the four terminal faces (101) may appear. One such crystal is shown in Plate 2. Complete phantoms occur in *ADP* only when growth along the *a*-axis is permitted.

These veils appear as planes of bubbles parallel to a pyramid face. The veil may be a single plane or a series of parallel planes separated by clear material. The veil may be a complete "phantom" of four planes arranged pyramidally or only a faint incomplete plane. The veil consists of round or elongated bubbles or tubes with their long axis parallel to a line made by the prism-pyramid intersection. The contents of these bubbles have not been determined.

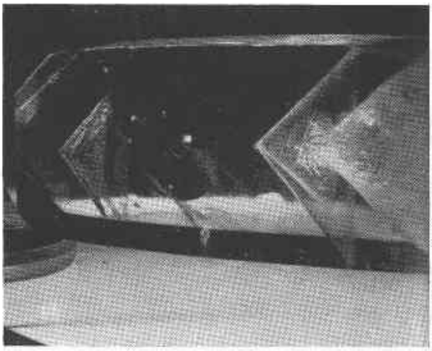

PLATE 2. Repeated veils in *ADP*.

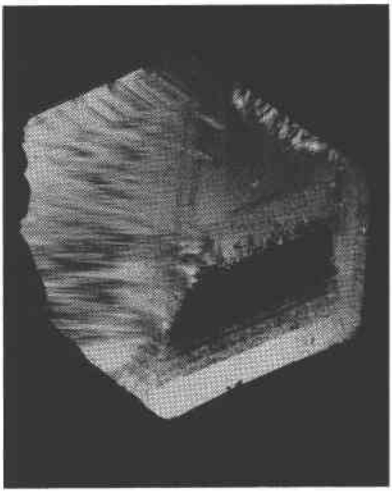

PLATE 3. Basal section of quartz between crossed polaroids showing two growth stages separated by a veil.

Two types of veils or inclusions are recognized—those formed during capping and those formed during growth of the main crystal. Both types of veils have a common origin as will be shown.

The transition from seed to cap is illustrated in Fig. 1. This is in reality the transition from a non-equilibrium endform to the endform in equilibrium with this particular environment (solution). Since *ADP* does not exhibit the base 001 as a part of the endform, the use of the basal cut as seed is responsible for the intensive veiling and inclusion during the capping operation.

One step, in line with the theory of endform equilibrium, can be taken to reduce the initial veiling and increase the yield of useful material. This step involves planting a "synthetic" cap—one ground out of clear oriented material to simulate the one obtained by the capping of a seed plate.* The initial success of this refinement is shown in Plate 1*B*. It will be noted that the veiling is reduced to a minimum for the synthetic cap.

If we compare the growth into bar stock from the ordinary and synthetic caps there are the following differences:

(*a*) The ease of growth as reflected by the degree of control required is much greater for the synthetic cap.
(*b*) Almost invariably the ordinary caps induce a major veil at the interface and fine veils within the first 5 mm. of the new material. In part this might be explained on the basis that the ordinary cap is a smooth faced crystal while the synthetic cap has ground (hence more active) surfaces.
(*c*) Incidentally one step in the operation is eliminated. From a theoretical point of view the synthetic cap is simply the optimum choice of seed.

Veils that occur during the bar growth have been attributed to supersaturation differences across the face, poor temperature control or inadequacy of the solution circulation.[13] Concerning the origin of these veils "The temperature must be controlled with considerable precision. Throughout the growth process sudden drops of even 0.1° are likely to cause flaws from too rapid growth and a temperature rise of 0.3–0.5° is likely to cause the crystal to redissolve and leave a ghost at that point when growth is resumed."

The two veils or flaws mentioned above differ only in their relative position within the crystal—a temperature drop gives an internal veil while a temperature rise gives a veil originating at the prism edge because of the rounding of the prism—pyramid intersection through solution. Both veils are, of course, parallel to the corresponding faces of the termination.

The laboratory grown crystal previously described and illustrated (Plate 2), with repeated veils at approximate weekly intervals, re-emphasizes the cause of veiling—that of an interruption or a change in the rate of growth over a weekend. In a large laboratory plant, the daily and hourly voltage variations may change abruptly in the heating of the growth apparatus. Similar changes in the humidity delivered by air-conditioning apparatus may produce some effect on crystals grown by evaporation. If one removes a growing crystal from solution and then replaces it after a five minute exposure to air, a flaw usually results. It is the interruption or change in rate of growth that is responsible for these fine veils. The crystal material on either side of the veil interface is in optical continuity. During the act of veiling the growth is so rapid

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* Slawson, S. I., U. S. Patent No. 2,543,071 (2/27/51).

[13] Holden, A. N., *Discussion Farad. Soc.*, No. **5**, 312 (1949). Walker, A. C., *J. Franklin Inst.*, **250**, 490–492 (1950). Robinson, A. E., *Discussion Farad Soc.*, No. **5**, 319 (1949).

that only a part of the face grows over completely. Growth is completed by the coalescence of these growth tendrils with the resulting inclusion of mother liquor. A similar situation would hold if suddenly a shower of foreign particles covered the growing face. As growth, interrupted by this shower, resumed, the particles would be included on a crystal plane as a veil.

Veiling in Other Crystals

Numerous examples of veils and phantoms in natural quartz have been reported. Johnston[14] has described fluid inclusions (veils) in vein quartz. He recognizes two types of arrangement for these fluid inclusions—"(1) in parallel planes determined by the crystallographic directions of the including crystal giving zonal growth lines and (2) in roughly parallel planes which are more or less independent of crystallographic direction and extend across adjacent crystals." Johnston ascribes the origin of type (1) to inclusion during growth and type (2) to post-growth events—possibly cracking and rehealing.

Johnston and Butler[3] have described phantoms in Brazilian quartz. These phantoms are either mineral or vacuole in character. They consist of complete or incomplete, single or multiple planes of veils parallel to the various faces of the final crystal. The phantoms do not necessarily show all of the forms of the final crystal nor do they always reflect the tapering (oscillation growth) of the final crystal.

Generally the material beyond the phantom is more likely to exhibit twinning than the material within the phantom. In Plate 3 is shown a basal slice of a Brazilian quartz crystal (Minas Geraes), photographed between crossed polaroids, illustrating the above statement.* The material within the phatom has a uniform polarization color while material outside the veil envelope is badly twinned or at least shows a low degree of perfection.

The critical growth rate for a crystal (the maximum rate at which a crystal can be grown without developing flaws) is an inverse function of size; the larger the crystal the slower the critical rate.[8] The outer hull of these crystals containing phantoms presumably grew at too fast a rate.

One common observation about quartz crystals is that the crystals are cloudy at the point of attachment or base of the crystal and may get clear toward the apex end. Milky crystals may yield clear material in the rhombohedral zone.[3] These clouds of inclusions are akin to the cloudy

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[14] Johnston, W. D., Jr., The gold quartz veins of Grass Valley, California: *U.S.G.S. Prof Paper* **194** (1940), plate 21, pp. 42–43.

* From a crystal supplied by W. D. Johnston, Jr., U.S.G.S.

zone in the caps of *ADP*. In beryl it is common to find hollow tubes (negative crystals) parallel to the *c*-axis at the base of the crystals.

The case of veiling in $NaBrO_3$ is of special interest. Sodium bromate is an apparent exception to the rule that anhydrous salts have low water solubility and grow with difficulty. It is quite soluble in water and grows with ease. Commonly it exhibits a tetrahedral habit modified by the negative tetrahedron and the hexahedron. Over a period of three years using the same solution, large crystals (4″) of $NaBrO_3$ were grown, marred however, by multiple veils parallel to (—111). Attempts to eliminate the veils by change of pH were unsuccessful.

These veils could be minimized by change of seed cut from 111 to 100 (which meant displacement and confinement of the veil rather than elimination). Analysis showed that the solution contains several per cent of Ca-ion. After this Ca-ion was eliminated the crystals grew clear and unflawed. Further studies in progress should provide an explanation for the influence of this effect.

Conclusions

The occurrence of veils (oriented inclusions or defects) in natural and synthetic crystals has been described. The orientation of the veil is related to the growth process. The veil represents an interruption in the growth process or indicates discontinuity in the growth rate curve.

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