Changes in habit during the growth of baryte crystals from the north of England.

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SOME specimens of baryte, recently obtained from Westmorland, show up to six changes of habit during growth. This was elucidated with the aid of the colour-zoning and fluorescent zones. A change of habit is also recorded in one specimen from County Durham.

Occurrence.

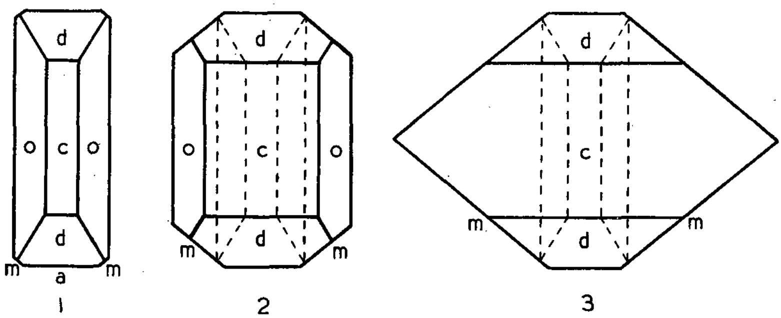
Silverband mine, near Knock, Westmorland.—The coloured crystals, which show numerous habit-changes, were found in a small unnamed vein running obliquely between the Dunfell and Henrake veins, two of the chief veins in the mine. The deposit occupies a considerable replacement area at the base of the Great Limestone. Bands of limonite and psilomelane occur in the vein, the former being abundant. The lower bands of limonite have druses containing clear, colourless, tabular crystals of baryte. Coloured baryte crystals are found in the higher oxide bands, but are mainly confined to the uppermost band, while occasionally they are found for a distance of a few feet in the limestone above. The doubly-terminated crystals are found mainly on the roofs of the druses, while those which are singly-terminated occur on the floors and the lower parts of the sides. Druses containing small, clear fluorite crystals are found. Galena is also present.

Cowgreen mine, Harwood-in-Teesdale, County Durham.—A number of specimens from this mine show groups of thin rectangular crystals, with no visible change of habit; they are tabular on *c*, and bounded mainly by *d*, *o*, *a*, *b*, and *m*, the last three forms being subordinate in size. Elongation is in the direction [100]. The crystals, although colourless and transparent, possess a finely 'frosted' appearance, due to etching.

A single specimen, discovered recently, has a yellow overgrowth on *o*, and presumably on *b*, tending to complete the prism laterally, as in stage 3 of the baryte from Silverband mine. The yellow overgrowth is not fluorescent. This specimen was found at the 106-feet level in the Greenhush vein in the Melmerby Scar Limestone. This east–west baryte vein carries some ankerite and calcite, as well as small quantities of chalcopyrite, galena, and blende.

CRYSTALLOGRAPHY OF BARYTE FROM SILVERBAND MINE.

Stage 1.—The forms are represented by the conventional letters: *a*{100}, *b*{010}, *c*{001}, *m*{110}, *d*{102}, and *o*{011}. The earlier-formed



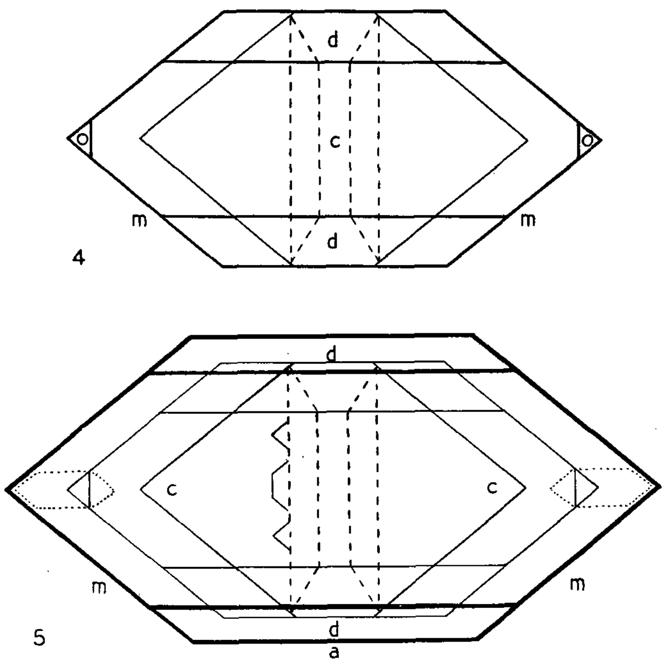
FIGS. 1–3. Baryte crystals from Silverband mine, Westmorland, showing successive stages of growth.

crystals, which compose the cores of those showing changes of habit, are of the type usually found at this mine, and shown as stage 1 (fig. 1). The habit is not absolutely constant and the degree of elongation in the direction [100] is somewhat variable. The form *a* is fairly common, while *b* is less so, and {*hkl*} forms are rare. Sometimes the crystals show morphological hemimorphism. One exceptional crystal is elongated in the direction [110]. Such variations are not common and the normal habit is well represented by stage 1. The constancy of the habit during growth in this stage is attested by the presence of a fine, grey, powdery deposit on *d* in some crystals, giving closely-spaced ghost-zoning. Apart from inclusions the crystals are colourless, with a high degree of transparency. Liquid inclusions are not evident. A very minor habit-change sometimes occurs, whereby *a* is partly and *b* completely eliminated by a semi-opaque white overgrowth.

In this stage the most rapid growth takes place on *m* and *d*, as shown by the direction of elongation. Most of the colourless ghost crystals are between 2 and 8 cm. in length.

Stage 2.—At this stage the first major habit-change occurs. Growth stops on *m*, *d*, and *c*, but proceeds on *o*. This initial overgrowth is yellowish-brown, sometimes with a tinge of green. When viewed through *c* parallel to *o* the overgrowth is seen to consist of closely-spaced yellowish-brown and colourless zones. An occasional very thin blue zone accounts for the greenish tinge. When viewed normal to *c* the colour of the crystal appears homogeneous. If *a* was originally present it is eliminated at this stage.

Stage 3.—The further growth on *o* is pale blue in colour, and again shows zoning. This is continued until *o* finally disappears. Since stage 1



FIGS. 4 and 5. Baryte crystals from Silverband mine, Westmorland, showing later and final stages of growth.

there has been a considerable extension of *c*, *d*, and *m* at the expense of *o*, but no growth, or virtually none, has taken place on the first three of these forms. The cessation of growth on *c*, *d*, and *m* can be seen from the distribution of the coloured overgrowth, and is indicated with even greater clarity for the latter form by the transitional ghosts outlined within the crystal by fine particles of an impurity. In one such series of ghosts a bipyramid can be seen.

There are occasional exceptions to the uniform blue overgrowth on *o*.

In some cases it is so pale that the colour is barely perceptible, in others reversion to a yellowish-brown colour marks the final growth on *o*, while one specimen shows a clear green succeeding blue in the closing phase of stage 3.

Most of the crystals are singly-terminated, the width of the crystal, as measured from the centre of the colourless ghost to the tip of the blue zone, ranging from about 1·5 to 6 cm., depending on the length of the ghost crystal.

Stage 4.—After the cessation of growth on *o*, following its elimination, deposition starts on *m*. This takes place in such a way that *o* reappears. The overgrowth on *m* is very closely zoned, showing a succession of thin layers with differences of colour, hue, or transparency. The earliest zones, which are very pale blue, are followed by an alternating series of yellow and colourless zones, yellow predominating in the later zones. Minute solid inclusions also form a number of ghost zones in this stage. The thickness of the very pale blue zone is about 4 mm. and that of the yellow and colourless zones together is about 5 mm.

Stage 5.—This is the final stage in the growth of the baryte crystals from Silverband mine. Growth continues on *m* and *o*, but as *o* is now growing fast relative to *m* (the converse of stage 4) this results in the second and ultimate disappearance of *o*. Growth now starts on *d*, leading to the reappearance of *a*. For the majority of crystals this is the first time that growth has taken place on *d* since stage 1, although a few crystals show a thin yellowish-brown layer which was deposited at the beginning of stage 2. The whole of this new growth is white and semi-opaque, but the last millimetre of it is least translucent of all, and forms a white layer on the surface of *m*, *d*, and *a*. Variations in the degree of translucency give rise to banding parallel to *m*. The semi-opaque white overgrowth on *m* and *d* is about 7 mm. thick. The total width of a doubly-terminated crystal at the end of stage 5 varies from about 8 to 20 cm. No new growth has taken place on *c*.

Stoppage of growth.

A few crystals have passed successively through all the stages from 1 to 5, some only reached stage 4, others only stage 3, while the rest did not grow beyond stages 1 or 2. Apart from two exceptions, to be described below, no specimens show the omission of one or more stages during growth from stage 1 to stage *n*, although *n* may have any value up to 5 for different specimens. Thus, while some specimens were passing through the whole series of changes from stages 1 to 5, others had their growth terminated at earlier points in the series.

It is interesting to consider what may have caused the cessation of growth at different times. It is known from the experiments of Bunn[1] and Humphreys-Owen[2] that crystal faces may stop growing while in contact with a solution of sufficient supersaturation to cause growth. In such cases the stoppage depends on some property of the face, and not of its environment. After an interval of time the faces may be observed to start growing again. That this is not the explanation in the case of the baryte crystals here described seems clear from the fact that the pauses in growth observed by Bunn and Humphreys-Owen (loc. cit.) were of relatively short duration, and therefore would not explain the long periods involved here. It appears that crystals in different places were cut off from contact with the solution at different times, so that the habits of stages 1 to 4 represent final habits for some crystals, but only transitional habits for others, while stage 5, the end of the series, is only reached by a few crystals.

In the course of this work over thirty specimens have been examined, and only two of them show the omission of a stage or stages during growth. One shows the habit of stage 2, the other of stage 3. Both have a fluorescent overgrowth which is thickest on *o*, thinner on *d*, and a mere film on *m*. It is completely absent from *c*. This distribution of the fluorescent overgrowth, and particularly its appearance on *d*, strongly suggests that it was formed during stage 5. Thus, although all the crystals were probably cut off from the solution at different times, it appears that in a few cases contact was re-established at a later period.

Inclusions in stages 2 to 5.

All stages of the overgrowths show long, cloudy, linear inclusions. Microscopic examination shows them to be trains of liquid inclusions. In stages 2 and 3 the inclusions seem to be parallel to (100), but, as they can only be seen through *c*, it is difficult to be certain whether they are parallel to the *b*-axis or normal to *o*. They do not appear to be sufficiently inclined to be normal to *o*. Microscopic observation, using the calibrated fine adjustment, does not solve the problem, as the trains of

[1] C. W. Bunn, Discussions of the Faraday Society, 1949, no. 5, p. 136 et seq. [M.A. **11**–337.]

[2] S. P. F. Humphreys-Owen, Discussions of the Faraday Society, 1949, no. 5, pp. 145 and 148. [M.A. **11**–337.]

inclusions have too great a depth and too ill-defined an outline on the upper and lower surfaces to make measurement possible.

In stages 4 and 5 the inclusions seem to be normal to *m*, that is, they are parallel to the direction of growth. When the colour in stage 3 is faint, such as that at the beginning of stage 4, so that the boundary between the two stages is not definable with certainty, the orientation of the inclusions provides the necessary evidence.

Where a large train of inclusions reaches the surface in stage 3 it can often be seen that a similar train in stage 4 starts from the same point. It is interesting that such a series of inclusions should be continued, although changed in direction by some 51°.

When one of the trains of inclusions in stages 2 and 3 reaches the surface of *c* it tends to form a line of low vicinal pyramids. When etching has been extensive the trains of inclusions also form directions of preferential solution, which lead to the development of channels parallel to the *b*-axis. Etching is much less common, and when present it is less extensive on *c* of the colourless ghost than on the coloured overgrowth, suggesting greater structural perfection in the former.

Vicinal pyramids on *c* are much more numerous on the areas of coloured overgrowth than on the colourless ghost. This provides a sensitive test for the absence of appreciable further growth on *c* of the ghost. The facts just mentioned, together with the inclusions in stages 2 to 5, suggest a much more rapid growth in these stages than in stage 1.

Interesting solution effects are seen in one crystal, representing an early phase of stage 5, in which there is an overgrowth about one millimetre thick on *d* and *c* (the latter being exceptional in these crystals, in which growth usually stops on *c* at the end of stage 1). It shows marked solution-channels internally on *c* of the blue crystal at the earlier part of stage 3, which are made visible by the presence of minute particles of impurity, although the later clear green growth of that stage in this atypic crystal appears unaffected.

The drawing (fig. 5) of the crystal in stage 5 shows a closed area, marked by dotted lines, near the lateral extremities of the crystal. These areas have been likened to a candle flame in shape and are dark yellow in colour. The figure unavoidably gives the impression of a well-defined outline, which is by no means true in white light. The 'flame' was not easy to interpret, as the distribution of its colour seemed to bear no relation to the forms on which the crystal had grown. The solution of this problem, described below, was only found by the use of ultra-violet light, in which certain zones are fluorescent.

Fluorescence and phosphorescence.

The ultra-violet lamp used in these investigations is specified to emit 95% of its total radiation at 3650 Å. The fine, yellow zones deposited on *m* towards the end of stage 4 show a strong cream fluorescence. The whole of the overgrowth in stage 5 on *m*, *a*, and *d* fluoresces white, except the outermost 1 mm. layer of least translucent baryte, which appears to be non-fluorescent.

The 'flame' fluoresces strongly with the same cream colour as the yellow zones on *m*. The outline of the 'flame' is now sharply defined, as shown in the drawing of stage 5, and in some specimens can be seen to consist of alternations of strongly and weakly fluorescent zones on *o*. In ordinary light these strongly fluorescent zones are yellow, and it is the overlapping of the yellow zones on *o* and *m*, when the crystal is viewed through *c*, which produces the 'flame', and gives it such an ill-defined outline. The 'flame' is the trace of *o*, and it shows how *o* reappears during stage 4, maintains a constant size for some time and ultimately disappears again immediately before the end of stage 5.

On some crystals, in which development stops early in stage 4, a minute fluorescent spot appears just below *o*-faces, while no fluorescence appears on *m*-faces. This shows that the earliest fluorescent layers are deposited on *o*, just prior to the first fluorescent zones on *m*.

The yellowish-brown zone, sometimes found succeeding the blue zone at the very end of stage 3, is fluorescent. Only a few crystals show the yellowish-brown 'tip'. The simplest explanation of its appearance is that solutions bearing this coloured impurity arrive towards the close of stage 3, in which the crystals are growing only on *o*. This solution causes the same habit, so growth from it only occurs on those crystals in which *o* has not yet vanished. On the other crystals, mainly the smaller ones, no deposition of yellowish-brown baryte takes place at this stage, as *o* is absent.

One specimen has been seen of crystals which are tabular on *c* and elongated in the direction [010], and bounded by *c*, *d*, *m*, and *o*. They are yellowish-white and semi-opaque in the centre and transparent at the ends, except for internal semi-opaque white patches in similar positions to the 'flame' in crystals of stage 5. They show no sign of colourless ghosts or of colour-zoning. The specimen exhibits a cream-coloured fluorescence throughout, except for the semi-opaque patches, which are a brilliant white, representing zoning on *o*. This appears to be a new generation of crystals formed simultaneously with the later part of stage 4. There growth is restricted to *o* and *m*, which agrees well with the elongation on [010] in the specimen just described.

In all the Silverband baryte those parts of the crystals which are fluorescent are also phosphorescent, with an afterglow of about four seconds for the brighter zones.

A number of specimens of baryte from Felsőbánya, Romania, were examined. Some showed faint colour-zoning, by no means comparable in depth of colour with the present specimens, and none showed fluorescence.

The mechanism of habit-changes.

Evidence has been obtained from the baryte here described of two distinct morphological mechanisms of habit-change.

1. *The mechanism of gradual habit-change.*

This seems to be the mechanism of many changes of habit, and the one operating throughout in stages 1 to 5, apart from one exception to be mentioned below. Some variation in the environment induces a change in the relative growth-velocities of the forms concerned. A face with a high growth-velocity relative to its neighbours, and to which it is not normal, will decrease in size as growth proceeds, and may ultimately disappear, while the neighbouring faces encroach upon it and grow larger at its expense An example is provided by *o* in stages 2 and 3. Because of its relatively rapid growth this form disappears by the end of stage 3, and thereby much increases the size of the neighbouring faces of *c* and *m*.

2. *The mechanism of abrupt habit-change.*

Inside several crystals from Silverband mine fine serrations, like saw-teeth, may be seen on the edge (011) $(01\bar{1})$ of the colourless ghost, as represented by continuous lines on the ghost drawn in stage 5 (fig. 5). Some are pointed and others are elongated. They are bounded, vertically, by *m*. The other surfaces cannot easily be determined. It is not always possible to say whether the 'teeth' are actually growing on (010), or from the common edge between $(0\bar{1}1)$ and $(0\bar{1}\bar{1})$, or very near it. If the former is the case, they are probably bounded by *m* and *o*. If they are growing on *o* the bounding surfaces are probably vicinal $\{hhl\}$ forms.

The morphological result of this type of growth is the very rapid elimination of a particular form, which was presumably unstable under the new conditions prevailing in the solution at that time. By further growth, and coalescence of the 'teeth', a normal crystal would develop, without re-entrant angles, but of a new habit.

In the Cowgreen mine specimen the apparent basal pinakoid of the yellow overgrowth consists of a number of steep intergrown vicinal forms of the type $\{hhl\}$, which produce shallow serrations on the surface. Similar markings on crystals in stage 5 from Silverband mine suggest that it was through the development of these vicinal forms that *o* was finally eliminated.

Other examples of this phenomenon are not hard to find. One of us (A. F. S.) has noticed a slight roughness on the basal pinakoid of certain wulfenite specimens, consisting of an overgrowth of a large number of minute pyramidal forms. Among the Yugoslavian wulfenite specimens in the Mineral Department of the British Museum (Natural History) were found examples of the expected habit-change. Specimens from Mežica (= Mies) and Črna (= Schwarzenbach) in Slovenia show simple tabular crystals, transitional habits with numerous minute pyramidal projections, and the final form a bipyramid. In one specimen the tabular, transitional, and bipyramidal habits are found together. The bipyramidal crystals disclose their origin by the difference in colour of the dark orange-red tabular crystal and the paler overgrowth.

Zircon also affords good examples. J. A. Butterfield[1] and F. Smithson[2] record overgrowths on detrital zircon which have formed in situ in sedimentary rocks. The original grains, whether nearly euhedral or much rounded, show elongation in the direction [001]. The habit is long or short prismatic with bipyramidal terminations. The overgrowth is almost entirely bipyramidal, forming minute serrations on the original prism. The prism appears to be less stable in the new environment, and is replaced by numerous small elements of the bipyramid.

Calcite seems to be peculiarly susceptible to changes of habit. One of the authors (A. F. S.) has a number of specimens of calcite showing marked changes of habit. Most of them belong to the gradual type of habit-change, but there are three examples of the abrupt type. One shows a scalenohedron completely overgrown by obtuse negative rhombohedra; another consists of a large positive unit rhombohedron covered by numerous crystals of nailhead habit. The last specimen, from Bleiberg, Carinthia, began as a positive unit rhombohedron of which the lateral edges were bevelled by a scalenohedron, and was later over-

[1] J. A. Butterfield, Geol. Mag., 1936, vol. 73, p. 511. [M.A. **6**–432.]

[2] F. Smithson, 1937. Geol. Mag., vol. 74, p. 281.

grown by crystals bounded mainly by the same scalenohedron and an acute negative rhombohedron.

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