

THE PARAGENESIS AND COLOR OF FLUORITE IN THE ENGLISH PENNINES

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INTRODUCTION

The beautiful violet crystals of fluorite from the English Pennines are known to mineral collectors the world over, being among the finest specimens of the mineral obtainable. There are few mineralogical museums in which examples bearing the labels "Cumberland," "Durham," "Weardale" or "Boltsburn" are not to be found. "Blue John," the deep purple and yellow banded fibrous variety of the mineral, which was first used by the Romans for the making of ornaments, also comes from this region. The details of mode of occurrence of fluorite in the Pennines are not as familiar to the mineralogist as are the specimens. Encouraged, therefore, by a suggestion made by Professor Palache some years ago, the present paper has been prepared. Boltsburn mine, for many years the source of some of the finest specimens, closed down in 1931 and is now flooded. It seems desirable to place on record an account of its cavities. The results of a study of the distribution of colored varieties of fluorite in the Northern Pennines, demonstrating the existence of regional color-zones, are also presented for the first time.

OUTLINE OF THE GEOLOGY OF THE PENNINES

The Pennine Range extends from the valley of the South Tyne, west of Newcastle, to Central Derbyshire. It is made up of flat-lying or gently folded Carboniferous sedimentary rocks, pierced in places by minor intrusions, resting on a basement of strongly folded Lower Palaeozoics. The northern part of the area, between the Tyne and the Craven district of West Yorkshire, is a structural block bounded on the west, north and south by major faults. Lower Carboniferous rocks outcrop over the high western part of the block, and in general dip to the east, disappear-

ing eventually beneath the coalfields of Durham and Yorkshire. The general easterly dip seems to have been superimposed on two gentle domes, occupying respectively the northern and southern halves of the block, separated by a sharp east-west syncline at Stainmoor. The Lower Carboniferous succession here is made up of massive limestones, overlain by alternating thin limestones, sandstones and shales (the Yoredale series). The limestone bands in the latter series are persistent, but the

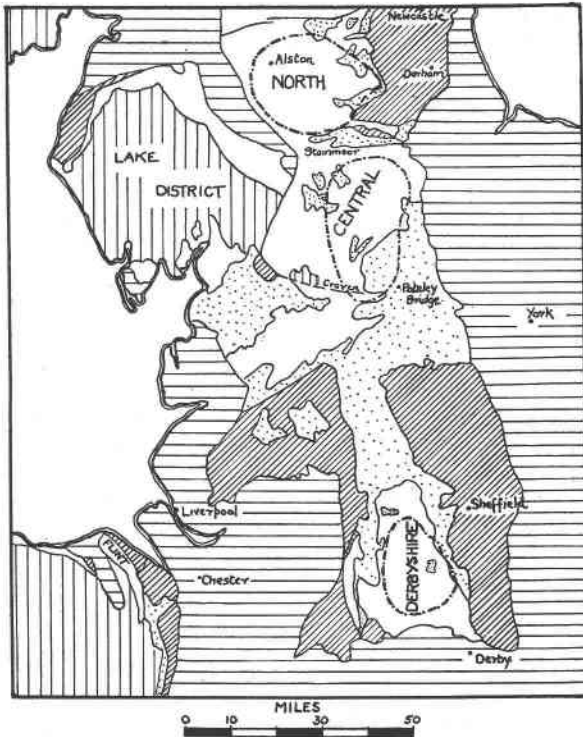


FIG. 1. Sketch map of Northern England. Unshaded areas, Lower Carboniferous; Stipple, Millstone Grit. Diagonal shading, Coal Measures. Vertical shading, Pre-Carboniferous rocks. Horizontal shading, Post-Carboniferous rocks. Heavy broken lines show the limits of the mineralised areas of the Pennines. Geological boundaries from Teall's Geological Map of the British Isles (2nd ed. 1912).

shales and sandstones are subject to considerable variation. The Great limestone, 60 feet thick, which is the thickest of the Yoredale limestones in the northern part of the block, is important because it has proved a very favourable horizon for mineralisation.

South of the Craven faults the Lower Carboniferous rocks are covered by Millstone Grit. They re-appear, however, in the High Peak district

of Derbyshire, where a broad anticline brings to the surface shale and sandstone equivalent to the Yoredale series of the northern districts, and underlying massive limestone 1500 feet thick.

North of Stainmoor there are two suites of minor intrusions. The well-known Whin Sill, actually a series of sills at different horizons in the Carboniferous limestone series, is of late Carboniferous age. The rock is a quartz dolerite. Associated dikes strike east-north-east. A series of tholeiite dikes, associated with the Tertiary igneous activity of Western Scotland, strike west-north-west across the area in linear echelons.

In Derbyshire there are basaltic lavas interbedded with the limestone, and intrusive dolerite sills and agglomerate and basaltic necks.

Lead, zinc and copper ores, barite and witherite as well as fluorite have been mined in the Pennines. The deposits are confined for all practical purposes to the Lower Carboniferous rocks. There are three mineralised districts (Fig. 1); the North Pennine field, the Central Pennine field, and the Derbyshire field. The deposits occur as veins along fault-fissures of small displacement; along mineralised joints; in caverns, pipes, and metasomatic replacements ("flats"). The veins are very numerous, some 584 being known in the Northern field alone.

PARAGENESIS OF FLUORITE

The quantitatively important primary minerals in the deposits include galena, sphalerite, fluorite, barite, witherite and calcite. Any one of these may constitute the bulk of an individual deposit. In addition, the following minerals occur in subordinate amounts: chalcopyrite, jamesonite, marcasite, pyrite, niccolite, ullmannite, quartz, chalcedony, aragonite, siderite, dolomite, alstonite, baryto-calcite, strontianite. In the North Pennine field, where the necessary detailed study has been made, it has been shown (1934) that the minerals are distributed in a rational manner, in concentric regional zones. Here a fluorite zone occupying the veins of the central part of the area is surrounded by an outer zone of barium minerals (Fig. 2). There is a corresponding arrangement of sulphides, and in the central area, the fluorite occurs as gangue in veins belonging to the copper and lead-zinc zones. The quantity of fluorite greatly exceeds that of sulphides in the innermost part of the central area, and the veins are wrought for their fluorspar.

There are indications that a similar zonal arrangement exists in Derbyshire (Webb and Drabble, 1908; Sweet, 1930). Veins with fluorite occupy the eastern side of the field, and it seems likely that much of the fluorite zone is still concealed beneath the shales covering the Carboniferous limestone. To the west, the fluorite zone gives place to barite, as in the northern area. The barite zone is succeeded by a calcite zone.

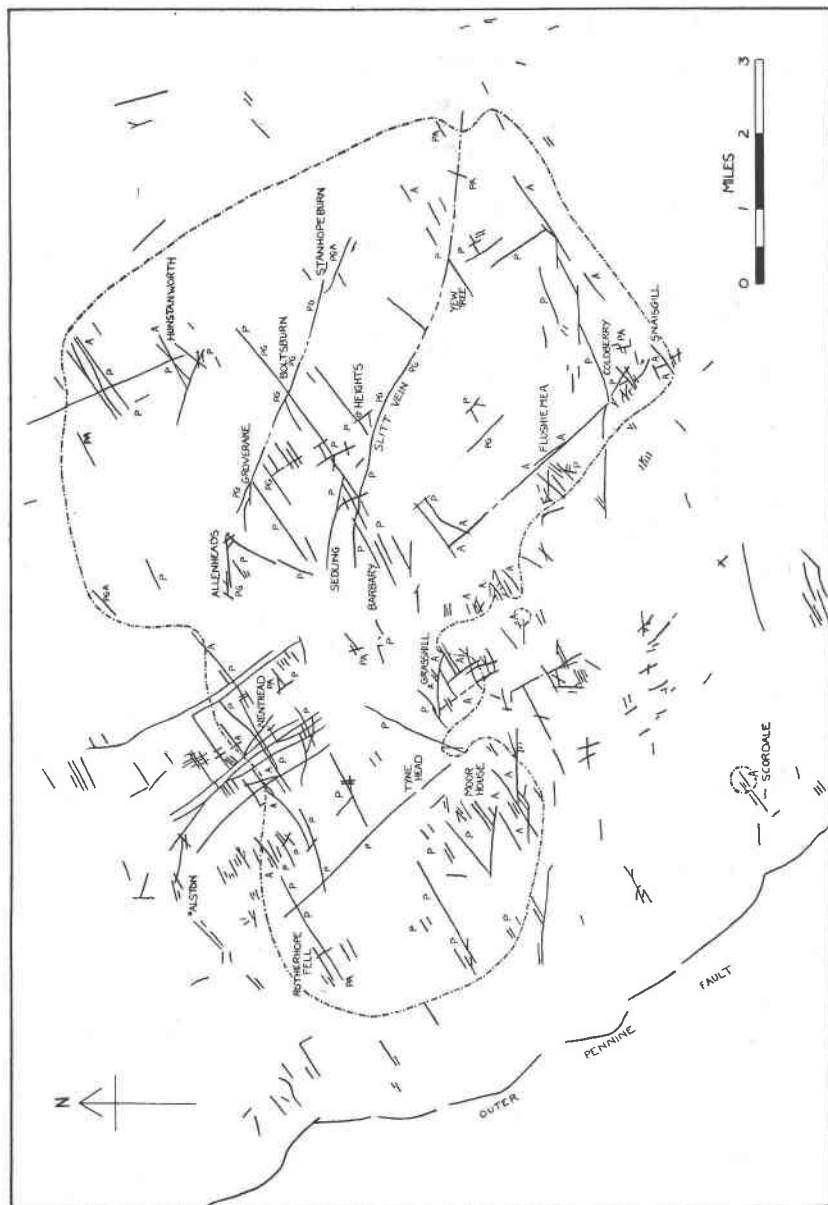


FIG. 2. Distribution of colored fluoroite in the North Pennine area. Continuous lines, veins and faults. The broken line indicates the margin of the fluoroite zone, which is surrounded by the barite zone. P, purple; G, green; A, amber.

Fluorite also occurs in the Central Pennine field, but the details of its distribution have not yet been worked out.

The mineralogy of the fluorite from the Pennines is so well known that it is only necessary to mention that isometric penetration twins are the only important morphological type. The edges of the cube faces are often beveled by a tetrahedron, probably {310}, and vicinal faces, indicated by stria, are almost always present on the cube faces through which the penetration twins emerge. The octahedral variety is very rare and I have never had the good fortune to find an example.

The relations between fluorite and its associated minerals will be considered according to the two chief modes of occurrence of deposits.

In Banded Veins. Banded structure, sometimes rudimentary, sometimes very well developed with many repetitions, is characteristic of the veins of the region. The bands seldom exhibit a simple sequence of minerals, for each mineral present in the vein may be repeated several times. It follows that there is no such thing as a simple "order of deposition."

The remarkable fact about the banding is that it shows that the veins were filled by successive incrustations of pure minerals, both walls of the vein being covered simultaneously. The symmetrical development of bands indicates that they are due in general to simple deposition, not to re-fracturing and replacement; and evidence of reopening is rare and of little importance. Individual pure bands may vary from less than an inch to several feet in width. The bands themselves are not always continuous; sulphides in fluorite veins frequently occur as a series of isolated masses within the gangue. Inspection usually reveals however that these are aligned parallel to the banding, and joined up by a discontinuity in the fluorite. Such isolated masses must therefore be regarded as incompletely developed bands.

Crystal faces may or may not occur on the inward-facing surface of a band. Some typical examples will illustrate this point. The vein at Sedling mine showed, from wall to centre, bands as follows: sphalerite—massive mauve fluorite—quartz—fluorite—galena—fluorite—cavities with quartz and green fluorite crystals. Here crystal faces were to be found in the centre of the vein only. A narrow vein at Groverake showed: purple fluorite—chalcedony—galena—chalcedony—green fluorite with good faces—quartz with good faces. A vein at Whiteheaps mine, Hunstanworth, showed six alternations of fluorite and quartz, good faces being developed on the inward surface of each fluorite band. It is easier to picture the conditions obtaining when crystal faces are developed than those which inhibit their free growth. In any case, the details of the process are not yet understood.

Of more fundamental interest is the problem of the cause of the banding. The explanation probably lies in the nature and flow of the mineralising solutions. If these were electrolytic solutions, then their composition must have been subject to repeated change, and they must in general have been saturated with respect to only one solute at once. If colloidal, then some process must be imagined whereby only one disperse phase is caused to coagulate at any one time. A possible mechanism is the "plating-out" process, applied to these veins a century ago by Leithart (1838). The essential points are summarised in the following quotation:

Suppose the rocks forming the walls of a vein be electrified negatively, in this case they will attract to them the electro-positive elements of matter, as the metals, etc.; but when these electropositive elements are accumulated on the walls to some certain thickness, the action of the wall-rock will become null, and the positively polarising substance plating the walls will act as electro-positive surfaces, and attract to them . . . the electro-negative elements, as oxygen, fluorine, etc.; or the substances in which they predominate, as quartz, fluate of lime etc.; these alternations being repeated until the vein is filled up, if the electrical action continue (1838, pp. 49, 50).

A similar mechanism has been advocated for the coagulation of disperse phases in colloidal solution by Boydell (1927). Colloidal solutions may have been developed during the formation of the veins here under discussion, and cryptocrystalline varieties of silica may have been deposited from them; but in the main, the massive vein deposits were probably deposited from electrolytic solutions. Perhaps a combination of changing composition and "plating-out" is the explanation of the banded texture.

Certain minerals tend to appear only in the outer bands in the veins. These include chalcopyrite, marcasite and usually sphalerite. In complex veins, barite and calcite often occur in the inner bands only. In the North Pennine area, examination of a large number of specimens failed to reveal a single case in which barite had crystallised earlier than fluorite; but interbanding of fluorite and barite has been observed at the Odin and Crich mines in Derbyshire.

In "Flats" and Cavities. The crystal-lined cavities found in replacement deposits, cavern deposits and pipes in limestone are the source of the finest fluorite crystals. Compact replacement deposits are rare in the Pennines and in general, limestone dissolved has exceeded new material deposited in amount. Indeed, in certain deposits the first effect of the mineralising solutions seems to have been the wholesale solution of limestone, forming caverns; minerals were later deposited on the floor, walls and roof. Cavern deposits are found in Derbyshire and the Central field. In the thin limestones of the northern area, deposition more nearly kept pace with solution and the cavities are smaller.

At the Boltsburn mine, cavities were found in "flat" deposits which occurred on both sides of a fissure vein. Immediately adjacent to the vein was a belt of compact limestone, recrystallised and replaced by siderite and dolomite. Beyond this lay mineralised ground rich in galena, with fluorite, quartz and siderite as the principal gangue minerals. Irregular cavities up to 50 feet long and only a few feet high were encountered in this belt, completely lined with crystals. Fluorite in partly developed cubes as much as 15 inches on the side were observed, but inspection showed these to be composed of many smaller cubes in polysynthetic growth. Complete cubes up to 6 inches side with penetration twinning were not uncommon, and were picked out for use in optical work.

Detailed examination showed that in these cavities crustification for more complex than that in the banded veins was present. A typical example of the sequence of crusts is as follows: green fluorite—sphalerite—colorless fluorite—chalcedony—colorless fluorite—dolomite—galena—quartz—calcite. In the cavities, it is the general rule that crystal faces have developed at each incrustation. Examination of a large number of cavities failed to reveal any consistent order of deposition of minerals, or even any consistent repetition in the sequence. Why should the minerals separate in pure crusts, instead of in a thoroughly mixed granular mass? Only laboratory investigation of precipitation from complex solutions is likely to solve this problem.

Stalactites composed of the primary minerals of the deposits were observed in the cavities at Boltsburn and elsewhere. Such occurrences are sufficiently rare among mineral deposits to make them worthy of special mention. Interesting examples composed of siderite covered with crystals of fluorite and galena, which were found in West level, Boltsburn, had apparently grown upwards. As they have a central tubular hole through which the solutions passed they must be classed as stalactites and not stalagmites. Beautiful stalactites made up of crystals of purple fluorite and quartz, sometimes in several layers, were formerly obtainable at Boltsburn. Slender stalactites composed of "nail head" calcite crystals were also found here. Sphalerite stalactites, composed of radiating crystals, were obtainable from a vein at Hunstanworth.

EPIMORPHS AFTER FLUORITE

Casts of fluorite crystals preserved in minerals which formerly covered them are occasionally found in the deposits. The term "epimorph" seems to be a suitable one to apply to such "negative crystals," preserving as they do surface impressions of minerals no longer present. Fluorite epimorphs originated in three different ways in the present area.

In the Oxidation Zone. Epimorphs often occur in the outcrops of the deposits. Here they are due to the removal of fluorite mechanically and chemically, leaving impressions in such stable minerals as quartz and chalcedony. That chemical solution of fluorite occurs in the oxidation zone is evident from an examination of natural surfaces of fluorite crystals from this zone under the reflecting microscope, which reveals innumerable tiny etch pits. Such etching is everywhere to be seen in the oxidation zone, but it is very rare below this zone. It should be noted that the solution of fluorite is a much slower process than the other chemical processes in the oxidation zone, so that substantial quantities of the mineral persist in this zone.

Dr. J. A. Smythe undertook a laboratory investigation of the etching of fluorite collected during the present study, and the following results are quoted by his kind permission:

The surface were deeply etched by immersion in 5% HCl and 5% H₂SO₄ on the water bath for 10 hours, at about 83°C. 5% Na₂CO₃ and 5% KOH under similar conditions produced very much less notable results. In the cold, the same acids produced etching after immersion of the surface in them for three days; slight etching was produced by Na₂CO₃. HF had no effect.

These results are of interest because they suggest that the etching in the oxidation zone is due more to the presence of sulphuric acid than to the action of carbonates in solution. Natural and artificial etch pits are square in shape, oriented at 45° to the edges of the cube.

In Primary Deposits. In deposits beyond the reach of the circulating waters of the oxidation zone, epimorphs after fluorite are also occasionally found. The origin of some of these appears to be purely mechanical. Crusts of other minerals, which have covered fluorite crystals on the roofs of cavities, have fallen down, perhaps shaken by slight earth tremors. Some shaking-down of crystals from the roofs of cavities at Boltsburn seems to have occurred during the late stages of the mineralisation there, and a generation of huge calcite crystals followed the event, cementing together the fragments on the floor. No other primary minerals were deposited after the fall.

This explanation is, however, inadequate to cover all the observed cases. Professor Palache has pointed out to me specimens from this area in the Harvard collection which from their shape and from the presence of epimorphs on both sides could not have been formed in this way. These, therefore, imply a primary resorption of fluorite during the mineralisation process. Evidence of primary resorption of marcasite was found at the Nentsberry mine, near Nenthead, where epimorphs after marcasite occur.

DISTRIBUTION OF COLORED FLUORITE IN THE
NORTHERN PENNINES

During the investigation of the distribution of primary minerals in the North Pennine area, which led to the establishment of the zonal arrangement (Dunham, 1934), note was made of the color of the fluorite whenever that mineral was recorded. Plotting of the results on a map showed that just as there is a systematic distribution of minerals in the area, there is also a systematic distribution of colored varieties of fluorite.

Massive fluorite in the veins is generally white and opaque, or slightly tinted with mauve or green. Crystals, however, show a variety of beautiful tints, among which purple and amber are the commonest, green somewhat less common. In the central part of the fluorite zone, the crystals are purple or occasionally green. In the outer part of the zone, these give place to amber varieties (Fig. 2). The approaching transition from fluorite to barite in the veins is thus heralded by the appearance of amber fluorite. It was noteworthy that in every locality where barite and fluorite were found together, the color of the fluorite was amber. Scordale, Flus-hiemea, Snaigsill and Grasshill are the most notable of these localities.

However, the cause of the color cannot be chemically related to barite, for elsewhere purple and green fluorite are found in intimate association with barite, as in Derbyshire. Thus the only conclusion that can justifiably be drawn is that the purple and green varieties crystallised at a higher temperature than the amber variety. Any conclusion about the cause of the color of fluorite based on chemical evidence must account for this relation, established with surprising clearness in the present area.

It should be noted that Smythe (1927) had observed the association of amber fluorite and barite some years before the present work.

Some interesting specimens from the Rotherhope Fell mine show that the amber variety crystallised later than the purple; individual crystals here have purple coloration inside, and amber margins. At the Blue John mine in Derbyshire, the upper and under surfaces of flat "veins" are coated with deep blue or purple fluorite, while the space between these is filled with clay, yellow fluorite crystals, and nodular barite (Carruthers and Pocock, 1922).

REVIEW OF OTHER FLUORITE OCCURRENCES

A search of the literature was made in the hope of finding other cases in which the relation of purple and amber varieties of fluorite had been established. None was found, however, no doubt because the necessary detailed observations have not been made. Some brief general conclusions about the typical mineral associated of fluorite may be appropriate.

The paragenesis here described is one which is found in all parts of the world, and it is noteworthy that all the deposits which are worked commercially for that mineral show an essentially similar mineral assemblage. The deposits of Illinois and Kentucky have many features in common with those of the Pennines. Barite figures prominently in the list of minerals; galena and sphalerite also occur (Ulrich, 1901; Bain, 1905). In New Mexico quartz, calcite, barite and the simple base-metal sulphides and their oxidation products are associated with fluorite in a great variety of different country rocks (Johnston, 1928; Dunham, 1935). Green fluorite seems to be the commonest variety in this state. A similar assemblage is to be found in the commercial deposits throughout the Western United States (Burchard, 1933). The same assemblage appears in the Massif Central of France (Chermette and Sire, 1935), in the Harz, Thuringia, Saxony, the Sudetes, the Bayrische Oberpfalz, and the Schwarzwald (Medenbach, 1934). In South Africa, the deposits of the Western Transvaal are essentially similar (Kupferburger, 1928).

All these occurrences are of a relatively low temperature type. The presence of cavities indicates that they were not formed at great depths below the surface. They may be classed as leptothermal or in some cases as telethermal deposits, according to Graton's modification of the Lindgren classification (Graton, 1933).

In less important amounts, fluorite has a wide distribution among mineral deposits. It is a characteristic mineral of some epithermal deposits in volcanic rocks, as at Cripple Creek, Colo. In mesothermal assemblages it is to be found associated with copper deposits, as in Cornwall, where it generally dies out before the tin zone is reached (Dewey, 1925). Among high temperature deposits, it is restricted to those of the pyrometasomatic class, where it probably occurs as a late mineral, deposited when the temperature was falling rapidly. Finally some reference must be made to its association with "alkaline" igneous rocks, to which Lindgren (1933) attaches great importance. This association is particularly common in provinces of the "Fen" type.

REFERENCES

- BAIN, H. F. (1905): *U. S. Geol. Surv., Bull.* 255.
BOYDELL, H. C. (1927): *Inst. Min. Met., Bull.* 277, 68, 69.
BURCHARD, E. F. (1933): *Amer. Inst. Min. Met. Eng., Tech. Pub.* 500.
CARRUTHERS, R. G. and POCOCK, R. W. (1922): *Spec. Repts. Min. Res. Gt. Britain*, 4.
CHERMETTE, M. A. and SIRE, M. (1935): *Le Spath-Fluor dans le Massif Central, Mines, Carrières—Paris*.
DEWEY, H. (1925): *Proc. Geol. Assoc.*, 36, 107.
DUNHAM, K. C. (1934): *Quart. Jour. Geol. Soc. London*, 90, 689–720.
——— (1935): *New Mexico Sch. Mines, State Bur. Mines Min. Res., Bull.* 11.

- GRATON, L. C. (1933): *Econ. Geol.*, **28**, 514-551.
- JOHNSTON, W. D. (1928): *New Mexico Sch. Mines, State Bur. Mines Min. Res.*, Bull. **4**.
- KUPFERBURGER, W. (1928): *Trans. Geol. Soc. S. Africa*, **30**, 5-56.
- LEITHART J. (1838): *Practical observations on mineral veins, with the application of several new theoretical principles to the art of mining*—London.
- LINDGREN, W. (1933): *Lindgren Volume, A.I.M.E.*, 152-180.
- MEDENBACH, F. K. (1934): Vorkommen, Gewinnung, Verarbeitung und wirtschaftliche Bedeutung des Flusspates, *Diss., Techn. Hochschule*—Berlin.
- SMYTHE, J. A. (1927): *The Vasculum*, **14**, 12.
- SWEET, J. M. (1930): *Min. Mag.*, **22**, 259-270.
- ULRICH, E. O. (1901): *U. S. Geol. Surv. Prof. Paper* **36**.
- WEDD, C. B. and DRABBLE, G. C. (1908): *Trans. Inst. Min. Eng.*, **35**, 501-535.