The cause of the colour of Blue John and other purple fluorites

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SUMMARY. 'Blue John' and other purple fluorites have been studied by a wide range of techniques. Hydrocarbons are not the cause of the colour of these fluorites. No significant difference in the concentrations of 73 elements between the purple and colourless zones of Blue John has been detected. The spectroscopic and thermal bleaching behaviour of the purple zones is consistent with the presence of 'colloidal' calcium as colouring agent, and coloration of fluorites with calcium vapour gives material showing similar properties. The distribution of colour suggests trapping of the calcium in lattice defects along {111} (cleavage) planes through {001} (growth) zones. The 'colloids' could be produced by aggregation of calcium atoms liberated by irradiation from sources found in the geological environment of Blue John. The banding could arise from variations in the concentration of lattice defects caused by variations in growth rates of the fluorite.

MacKenzie and Green (1971) have recently described a study of the cause of coloration of 'Blue John', the bluish-purple banded fluorite from Castleton, Derbyshire, and similar fluorites from Ashover, Derbyshire, and Weardale, Co. Durham, and conclude that the colour is due to the presence of 'colloidal' (dispersed) calcium. The present authors have independently studied Blue John and similar coloured fluorites from other localities using a wide range of experimental techniques, and present additional evidence that supports colloidal calcium as the cause of the colour.

Materials. The basic material used in our studies was intensely blue-purple fluorite, containing bands of colourless material, from Blue John Cavern, Castleton, Derbyshire (entrance at National Grid Ref. SK 132832). Whenever possible, experiments on purple material were repeated under identical conditions with material picked from a colourless band immediately adjacent to the purple sample.

Other materials studied for purposes of comparison are detailed in Table I.

No fluorite samples from Weardale of this type of deep purple colour have been seen by the authors. As Calas (1972) points out, more than one cause of colour of blue to purple fluorites exists. Relatively pale mauve to purple, as well as green and yellow fluorites, all with a strong blue fluorescence, are common in Weardale and elsewhere in the northern Pennines, the colours and fluorescence being ascribed to the presence of rare earths, in particular europium, gadolinium and samarium (Dunham, 1952; Bill, Sierro, and Lacroix, 1967). The Blue John–'antozonite' type of purple colour is normally much more intense than these rare earth colours, and is easily seen in thin section. The only fluorite sample of those studied that displays fluorescence is

RSWB 63–280 from Treak Cliff, in which a pale reddish purple band sandwiched between purple and colourless zones fluoresces bright red in ultra-violet radiation of wavelength 365 nm but not with that of wavelength 254 nm. No compositional reason for this fluorescence could be found in a mass spectrographic analysis (see below). This is the first record of fluorescence in Derbyshire fluorite.

TABLE I. *Specimens of fluorite studied*

Fluorite sample studied	Accession number (RSWB)	Locality
Purple and white banded Blue John with red fluorescent zone.	63–280	Exposure at SK 13408345 in Treak Cliff, near Odin mine, Castleton, Derbyshire.
Large blue-purple Blue John cubes with complex curved faces.	67–146	Vein in roof of 'Witches' Cave', Treak Cliff Cavern, Castleton, Derbyshire. (Collected by Dr. F. M. Broadhurst)
Purple cubes on massive.	63–329	Ladywash mine, Eyam, Derbyshire.
Deep purple cubes on massive.	59–3	Dirty Rake, Stony Middleton, Derbyshire.
	60–32	Cobbler mine, Bonsall, Derbyshire.
Purple cubes in white baryte.	62–416	Raygill Delph, Lothersdale, Yorkshire.
Small blue zoned cubes (purple in tungsten-filament light) on limestone.	70–220	Swinden Limeworks Quarry, Linton, Yorkshire.
Cluster of purple cubes.	66–337	Cave-in-Rock, Illinois, U.S.A.
Deep purple massive 'antozonite'.	66–13	Uranium vein, Wilberforce, Ontario.
	70–348	Bauzot uranium mine, Issy l'Évêque, Saône-et-Loire, France.
Colourless cubes.	—	Elbolton Hill, Thorpe, Yorkshire.
Precipitated calcium fluoride.	—	

As MacKenzie and Green (1971) have pointed out, the theories of coloration that have been proposed fall into three main classes: Organic impurity theories; inorganic impurity theories; and colour centre theories.

Organic impurity theories. These are based on the observed close association of hydrocarbons with Blue John and some other purple fluorites. No explanation has been offered of how hydrocarbons or other organic impurities could cause the purple coloration. To cause the purple colour, the organic material would have to be a conjugated system of fairly high molecular weight, or a charge transfer complex, and would have to be present in appreciable concentration.

We have carefully examined both purple and colourless zones of Blue John for the presence of organic material, and have repeated the work of early authors who claim positive results. Bituminous minerals occur associated with Blue John, and to eliminate contamination by these, all samples were crushed and thoroughly washed in turn with

dilute hydrochloric acid, water, benzene, ethanol, acetone, and water before examination. The washing process caused no observable change in colour of the crushed purple material.

Samples of Blue John were combusted in oxygen in a standard organic micro-analysis train. Traces of gas were evolved, which if assumed to be carbon dioxide were equivalent to less than 0·01 % carbon content, which could have originated from CO_2-containing vacuoles or organic matter. Blount and Sequeira (1919) reported < 0·046 % CO_2, and Garnett (1920) reported 0·27 % CO_2 using similar techniques.

Five purple and five colourless samples of Blue John were heated to red heat in air, the purple samples being decolorized (and used as 'thermally bleached Blue John' in subsequent experiments). The samples lost 0·16–0·33 % weight, with no significant difference between purple and colourless samples.

Garnett (1920) obtained an oil by dry distillation of Blue John. Evans et al. (1964) report the pyrolysis of Blue John at 1000 °C, gas–liquid chromatographic analysis of the products giving ten peaks representing volatile products.

In our work no organic compounds were detected in the products of dry distillation of large samples of Blue John at up to red heat, at atmospheric pressure, and in vacuo. In one experiment Blue John (327 g) heated in a platinum tube for 3 hr at a pressure of a few mm of Hg gave 11·2 cm³ of gas measured at room temperature and atmospheric pressure, mass spectrometric analysis of which showed only air, water, and carbon dioxide.

Samples of fluorite were crushed in vacuo at room temperature in a steel cylinder, and any gases evolved examined by high-resolution mass spectrometry. Blue John (210 g) gave 4·6 cm³ of gas containing air, water, and CO_2, but giving small peaks due to hydrocarbons similar to those recorded by MacKenzie and Green (1971) in the mass spectra of pyrolysed fluorites. In another experiment traces of sulphuryl fluoride were detected, as found by Krantz (1968) in purple fluorite ('antozonite') from Wölsendorf, Bavaria. Although blank experiments using the same apparatus also yielded traces of all these peaks their intensity was considerably greater when the sample was present. A dark purple fluorite ('antozonite') from Bauzot uranium mine, France (RSWB 70–348), which evolves a strong halogen-like odour on being struck, also gave trace amounts of sulphuryl fluoride as detected by accurate mass measurement and by comparison of the low-resolution fragmentation pattern with the literature (Cornu and Massot); sulphur dioxide and some organic compounds were also detected.

Blount and Sequeira (1919), Garnett (1920), and Mueller (1954) reported obtaining organic materials from Blue John by extraction with covalent solvents. In particular Mueller claimed decolorization of a sample of Blue John by extraction with carbon disulphide, evaporation of the solvent yielding a brown substance. Blue John samples, powdered both before extraction and under the solvents used, were extracted at room temperature and at boiling point with a number of solvents including carbon disulphide. In one experiment, Blue John (50 g) was treated in a Soxhlet extractor with refluxing carbon disulphide (100 cm³) for 24 hr. In no case was any fading of colour observed in the Blue John, or any difference in solvent composition before and after extraction found on analysis by gas–liquid chromatography.

Samples of washed and crushed purple and colourless Blue John from neighbouring bands were submitted to Lord Energlyn of the University of Nottingham who had these analysed by 'pyrochromatography', in which samples were heated to 1000 °C and the gases evolved analysed by gas–liquid chromatography using carbon-packed columns. Carbon monoxide, air, hydrogen, and traces of methane were detected, the last only in a colourless sample. Two peaks that could represent organic compounds were also present in the chromatograms from a control sample of a Swedish mica. No other peaks were present.

A possible criticism of all this work is that the fluorite crystal lattice is not completely broken down (m.p. 1360 °C). Calcium fluoride is soluble in boiling aqueous aluminium chloride and samples of powdered Blue John were treated at room temperature and under reflux with aqueous aluminium chloride solutions covered with layers of benzene and toluene to trap organic compounds. Gas–liquid chromatographic analysis of the solvents before and after the experiments showed no changes in composition.

No carbon or organic compounds were detected in Blue John by MacKenzie and Green (1971) using DTA, TGA, infrared spectroscopy, and electron-probe microanalysis.

Small traces of organic compounds may occur in both colourless and purple zones of Blue John but cannot be the cause of the colour.

Inorganic impurity theories. These are based on the presence of ions that can cause absorption of light by electronic transitions involving charge transfer, or crystal field splitting effects. Crystal field absorptions are weak, particularly in rare-earth ions and ions with one electron in each d or f orbital, e.g. Mn^{2+}, and a high concentration of the absorbing ions would have to be present to produce the intense colour of some Blue John. A much smaller concentration of the absorbing species could produce such a colour intensity by a charge-transfer mechanism, which, however, would not explain the thermal and shock bleaching behaviour of Blue John.

MacKenzie (1972) has shown that the blue S^{2-} ion is not responsible for the colour of Blue John.

Electron spin resonance spectra of Blue John at room temperature showed no evidence of the presence of ions with unpaired electrons, and are discussed below.

X-ray fluorescence, emission arc spectrography, and spark-source mass spectrometry showed our samples of Blue John to be surprisingly pure, some containing less impurity than 'Analar' calcium fluoride. Six samples of Blue John were analysed for 73 elements by spark-source mass spectrometry at the Centre for Materials Science, Birmingham University, and no significant difference in impurity concentration between deep purple and colourless zones was observed. Those impurity concentrations cannot therefore be the cause of the colour or the banding. Table II shows the range of highest concentrations of homogeneously distributed impurities detected in the samples.

Colour centre theories. Colour centres at lattice defects can be produced by irradiation or chemical mechanisms. These range from the F-centre, well known in alkali halides, which consists of an electron trapped in an anion vacancy, through various

types of combined vacancy centres to neutral centres approaching colloidal size which are thought to consist of metal. These can absorb light by electronic transitions, and in the case of the larger colloidal particles, colour can also be produced by scattering, in which case the colour will depend on particle size, and a Tyndall effect will be observed.

The u.v. and visible absorption spectra of our intensely coloured fluorites were obtained by a reflectance technique using powdered samples, the range 200 to 700 nm being scanned using a Beckmann DK-2a spectrometer. The spectra obtained from coloured materials show a broad band with a maximum near 580 nm, similar to those reported by MacKenzie and Green (1971), and in addition a weaker band, often

TABLE II. *Analyses of Blue John by mass spectrometry*

Concentration	Elements
> 100 p.p.m.	Al, Fe, K, Na, P.
10–100	Cl, Cr, K, Mg, Ni, S, Si, Sr, Ti.
1–10	Ba, Cu, I, Mn, V, Y, Zn.
< 1, or not detected	Ag, As, Au, B, Be, Bi, Br, Cd, Ce, Co, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, La, Li, Lu, Mo, Nb, Nd, Os, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Ta, Tb, Te, Th, Tl, Tm, U, W, Yb, Zr.

Six samples studied: three deep purple, two from adjacent colourless material, one from pale reddish purple band showing red fluorescence.

present as a shoulder, at 335 nm. The 580 nm band is, of course, absent in the spectra of colourless and of thermally bleached Blue John, but the 335 nm band is shown by colourless Blue John, colourless fluorite from Elbolton Hill, Yorkshire, and precipitated calcium fluoride, but not by thermally bleached Blue John. This band is bleached below 300 °C (see below), is found in irradiated and additively coloured fluorites (Smakula, 1950; Lüty, 1953; Bontinck, 1958; Lisitsyna, 1965), and is due to some kind of lattice defect centre not specific to Blue John or any coloured fluorite.

The 580 nm band is characteristic of many purple fluorites, including Blue John, and was detected in all purple fluorite samples examined, including specimens from various localities in Derbyshire and Yorkshire, from Cave-in-Rock, Illinois, and intensely coloured specimens from uranium deposits in Ontario and central France. This band is also well known in fluorites coloured additively or by irradiation (Mollwo, 1934; Smakula, 1950; Lüty, 1953; Bontinck, 1958; Scouler and Smakula, 1960; Messner and Smakula, 1960; Fong and Yokom, 1964; Lisitsyna, 1965), and has been ascribed to colloidal calcium (Gobel, 1930, 1931; Przibram, 1938; Allen, 1952; Mueller *et al.*, 1961; McLaughlan and Evans, 1968; MacKenzie and Green, 1971) first proposed as a colouring agent by Doelter (1925). The wavelength of this absorption maximum varies somewhat from sample to sample, and probably depends on the thermal history of the sample after coloration, as shown by thermal bleaching experiments described below.

Smakula (1953) and McLaughlan and Evans (1968) showed that the 580 nm band

in irradiated fluorites is not optically bleached by radiation of the absorbed wave-length, in contrast with F-centre bands, which are optically bleached. We find that Blue John is not optically bleached when illuminated for 24 hr by light of wavelength 573 nm or 335 nm, no change in absorption spectrum being observed.

That Blue John is decolorized by heating is well known (Blount and Sequeira, 1919, and later authors). The 335 nm band in Blue John is thermally bleached below 300 °C but the 580 nm band requires a higher temperature for bleaching.

Thermal bleaching experiments were performed with powdered samples of dark Blue using a DuPont 900 differential thermal analyser as an accurate furnace with constant heating rate, the position of maximum absorption of the products being measured by reflectance as described above, intensity of absorption not being measure-able using this technique.

At constant heating rate the position of maximum absorption (initially 573 nm) moves to shorter wavelength with increasing temperature, and the intensity of absorp-tion correspondingly decreases. This shift and bleaching are slow up to 350 °C after which they increase rapidly, the samples being completely bleached by 500 °C; imme-diately prior to complete bleaching the weak absorption maximum was near 500 nm.

The shift in absorption maximum with increasing time at constant temperature was also studied; the shift is initially rapid but levels off, with little further change after about 1 hr. Thus after 1 hr the 573 nm maximum had shifted to 510 nm at 375 °C, and to 502 nm at 400 °C, with complete bleaching at 425 °C. A shift of absorption maximum to shorter wavelength with increasing temperature is normally attributed to colloidal colour centres, and was observed by McLaughlan and Evans (1968) for the 580 nm band in electron-bombarded fluorites showing the low-temperature electron spin resonance spectrum of colloidal calcium. An alternative explanation of this shift could be that this very broad and featureless absorption band is composed of two or more overlapping bands, which bleach at different rates at about 400–500 °C.

The electron spin resonance spectra of purple and colourless zones of Blue John (from Blue John Cavern) at room temperature were found to be identical, consisting of a single small narrow peak. The same spectrum was obtained from purple fluorites from Cobbler mine, Derbyshire, Dirty Rake, Derbyshire, and Raygill, Yorkshire, and from colourless fluorite from Elbolton Hill, Yorkshire, and appears to be an intrinsic property of the fluorite lattice, not connected with colour. This peak can be thermally bleached, beginning to disappear at 150 to 200 °C, and is absent in purple or colourless Blue John which has been heated to 500 °C. MacKenzie and Green (1971) obtained a similar, but not thermally bleachable, spectrum from some Blue John samples. McLaughlan and Evans (1968) irradiated fluorite with electrons, producing purple material with absorption spectral properties similar to those of Blue John, including thermal bleaching with hypsochromic absorption maximum shift, and the spectra of electron irradiated fluorites figured in Rao and Bose (1970) show very similar effects. According to McLaughlan and Evans (1968), the e.s.r. spectrum of most of this material at cryogenic temperatures shows a narrow isotropic band at $g = 2·006$, observed at 1·4 to 12 °K, but not at 77 °K or above, and which is ascribed to conduc-tion electron spin resonance in calcium particles of colloidal size. Particle size seems

to be critical for observation of this e.s.r. signal, as it was not seen from some samples with the same optical absorption characteristics.

Dr. D. J. Edge of this department has measured this region of the e.s.r. spectra of two purple and two colourless samples of Blue John at temperatures down to 1·6 °K using a Varian V4500–10A unit with a super-heterodyne detection system at the Physics Department, University of Keele. No absorption corresponding to that observed by McLaughlan and Evans (1968) was detected. In Blue John the colour centres may be more dispersed than in the electron-irradiated material and concentrations may not be high enough for detection by the method used, and the particle size and perhaps shape may be such that this e.s.r. absorption is broadened beyond detection.

Several authors have pointed out that coloration of calcium fluoride by laboratory X-ray bombardment is difficult in the absence of special dopings. Natural irradiation by γ-rays over long geological time periods is in no way equivalent to short-period laboratory irradiation by X-rays, both in the time factors involved and in the relative energies of the radiation. Secondary β-(electron)emission from materials irradiated by γ-rays is well known, and is utilized for the detection and measurement of γ-ray intensities, whereas the lower-energy X-rays liberate electrons from materials only with difficulty. γ-ray irradiation could produce coloration either directly or by the action of these secondary electrons. The stabilities of the various types of colour centre are of prime importance when considering the effects of long-period low-intensity irradiation, the more stable centres building up in concentration relative to the less stable centres, even if the latter are formed preferentially.

The various types of defect centres are annealed at characteristic temperature ranges. As annealing takes place, the energy is released as light (thermoluminescence, TL). A curve of light emission against temperature—the TL glow curve—can be obtained (Hill and Aron, 1953; Bettinali, 1959; Blanchard, 1966, 1967; Kittel, 1968), and can, in an ideal case, reveal the number of types of electron traps present, their concentrations, and their stabilities.

Samples of purple and colourless Blue John from adjacent bands in the material from Blue John Cavern were sent to Dr. M. J. Aitken at the Archaeology Department, Oxford University, who measured their TL glow curves before and after thermal bleaching and subsequent irradiation with β-rays from ^{90}Sr. The purple material gave peaks at 500° and 600 °C, and the colourless at 240°, 340°, 500°, and 600 °C. In both cases the bleached irradiated material gave peaks at 140°, 240°, and 330 °C and thus contains the same three types of electron trap, the 500° and 600 °C traps being absent. It was hoped to bleach out each TL peak thermally in turn and identify them by optical and e.s.r. spectroscopy. Unfortunately, overlap of peaks and time limitations prevented this, but the more separated 240 °C peak was bleached out by heating Blue John to 300 °C, and subsequent optical spectroscopy showed the 335 nm band to be missing. Thus this absorption band is probably related to the 240 °C TL emission and the room temperature e.s.r. peak described above, but it is present in both purple and colourless Blue John, and in other fluorites and it is not specific to Blue John. The overlapping 500° and 600 °C peaks are present in both purple and colourless Blue John, and are

therefore not directly related to colour though they may be related to the defects in which calcium may be trapped, and are reminiscent of the possibility that the shift of optical absorption maximum on thermal bleaching might be due to differential bleaching of two bands.

Colloidal particles produce colour by absorption and by scattering, the latter becoming more and more important as particle size increases above about 30 nm, when Tyndall effects may be observed. Mayerl (1951), using the Mie theory, calculated the positions of absorption maxima for colloidal calcium in the fluorite lattice; the 540–580 nm maxima corresponds to particle sizes of 50–80 nm, increasing with particle size. McLaughlan and Evans (1968) quote a maximum diameter of 30 nm for the colloidal calcium particles producing the 580 nm absorption in electron irradiated fluorite, since the particles were invisible in an electron microscope of 30 nm resolution, and no Tyndall effect could be observed.

The absorption profiles of the 580 nm band for Blue John observed by MacKenzie and Green (1971) by transmission are very similar to those observed by the present authors using a reflectance method, with no Tyndall effect evident.

Some evidence of scattering was obtained by dark-field microscopy with a Carl Zeiss phase-contrast microscope using an annular diaphragm technique in which only light scattered by the specimen (a 0·3 mm thick section of Blue John) could be observed. The intensity of the scattered light did not depend on the angle of illumination of the specimen and thus did not involve scattering by oriented inclusions or crevices, but the colour was observed to be the same as that seen by transmitted light. The lack of observable Tyndall effect suggests that the colour of Blue John is caused largely by absorption by particles of average diameter < 30 nm rather than by scattering.

The additive colouring of fluorite with calcium vapour is well known (Wohler and Kasarnowski, 1905; Mollwo, 1934; Lüty, 1953; Scouler and Smakula, 1960; Van Doorn, 1961–2; Fong and Yokom, 1964; Hayes, Lambourn, and Smith, 1970). Powdered samples of colourless and thermally bleached fluorites were heated in the presence of calcium in vacuo in glass tubes at 450°, 670°, and 760 °C for from 1 hr to 18 hr. The tubes were allowed to cool in the furnace before opening, and the products washed with very dilute hydrochloric acid to remove any surface calcium. The visible results bore no relationship to the temperature or time of heating, but depended on the sample used. Naturally colourless Blue John became deep purple, and colourless fluorite from Elbolton Hill, Yorkshire, became a very deep blue-purple colour, whereas thermally bleached Blue John and thermally bleached fluorites from Cave-in Rock, Illinois, and Wilberforce, Ontario developed much paler shades of purple. The absorption spectra of these products were very similar to those of naturally purple Blue John, but the absorption maxima were shifted to shorter wavelength (540–560 nm), probably due to partial thermal bleaching during the cooling period. This absorption could not be optically bleached, and thermal bleaching followed the same pattern as that of naturally purple Blue John. The additively coloured material from Elbolton Hill, Yorkshire, was exceptional in that thermal bleaching reduced its maximum absorption at 570 nm in intensity but did not change the position of absorption maximum. Unlike natural purple or colourless Blue John, additively coloured

Blue John and Elbolton Hill material gave exothermic peaks at 230° and 240 °C respectively on differential thermal analysis, though additively-coloured thermally-bleached samples gave no clear peaks. These DTA peaks were bleached out by heating to 250 °C with no change in absorption spectra apart from the normal shift due to partial thermal bleaching, and are therefore not connected directly with the coloration.

Samples of naturally colourless and thermally bleached Blue John heated with calcium as above but removed from the furnace at 760 °C and quenched in liquid nitrogen showed no visible colour, though the former gave a very weak absorption with maximum near 550 nm. Quenching might be expected to trap in any F-centres produced, but these were not observed. This experiment shows that exposure to calcium vapour at temperatures well above the bleaching temperature of Blue John produces no colour, although diffusion of calcium through the lattice is favoured. At these temperatures the defects in which the calcium is trapped would probably be partly annealed, as observed in the TL glow curves, but would reappear as the lattice cools below bleaching temperature, enabling coloration to take place in the presence of calcium. The pale colours produced in the thermally bleached samples probably represent more thorough annealing of the defects at the red heat employed for bleaching, in which case fewer defect 'nuclei' would remain to reform defects on slow cooling.

More than one effect might be operative in the coloration of Blue John, perhaps a combination of calcium colloids with the more stable larger F aggregate centres, which are extremely difficult to identify (Beaumont, Harmer, Hayes, and Spray, 1972).

Holgate's (1941, 1973) observation of anisotropism in some colour bands of some Blue John fluorites suggests that orientation of the electric dipole of the transition involved in absorption can sometimes occur, with maximum absorption polarized parallel to the growth planes. Beaumont, Harmer, and Hayes (1972a, 1972b) show that small F aggregate centres with suitable symmetries can be selectively bleached by polarized light, leaving centres with anisotropic absorption, at cryogenic temperatures. These centres are optically and thermally bleached at room temperature, and can hardly be the cause of Holgate's anisotropic zones, but indicate the possibility of the existence of more stable anisotropic aggregate centres. Holgate's zones involve three orientations within each isotropic crystal, so cannot be produced by polarized optical bleaching.

Colour distribution. Microscopic examination of sections of Blue John show the colour to be distributed in irregular patches and sometimes in fir-tree like patterns along {111} (cleavage) planes within {001} (growth) zones.

The banding along growth zones suggests that the colour depends on growth conditions. The similarity in trace element distribution between purple and colourless zones suggests that impurity concentrations are unimportant, in which case physical rather than chemical conditions control the colour. The results of additive colouring experiments suggest that defect concentration is of primary importance in coloration.

Colour zoning is probably due to changes in defect concentration with growth, perhaps due to variations in growth rates, a faster growth rate producing more defects.

Microscopy suggests that the defects occur along cleavage planes {111}. This would

explain shock bleaching when struck perpendicularly to {111} (Barnes and Holroyd, 1896), which would anneal {111} defects.

The colloidal calcium trapped in these defects could be produced by aggregation of calcium atoms released from the lattice by long-term irradiation from an external source of penetrating radiation.

The source of radiation is obvious in the case of the deep purple fluorites associated with uraniferous deposits. At Castleton, Blue John is directly associated with the boulder bed of Treak Cliff (Simpson and Broadhurst, 1969) with its high concentration of uraniferous collophane (Peacock and Taylor, 1966). Uranium is also concentrated in collophane in fossiliferous bands near the base of Edale Shales, adjacent to the Blue John deposits at Castleton, and also in other parts of Derbyshire (Ponsford, 1955; Cosgrove *in* Ramsbottom, Rhys, and Smith, 1962; Stevenson and Gaunt, 1971). Bitumens, which are often associated with purple fluorites, are frequently uraniferous ('thucolite'), and this could account for the purple zones often seen surrounding hydrocarbon inclusions in fluorites (Mueller, 1954).

Dunham (1952) noted the presence of deep purple fluorite associated with bitumen at Swinden Limeworks quarry, Linton, Yorkshire (Nat. Grid Ref. SD 983 651). This is in a reef knoll of similar facies and age to Treak Cliff, and is also rich in uraniferous collophane (Peacock and Taylor, 1966). At this locality we have found fluorite cubes with deep blue-purple outer growth zones {001}.

No information is available about radioactivity at the localities of the other specimens of purple fluorite studied.

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