

The cause of coloration in Derbyshire Blue John banded fluorite and other blue banded fluorites

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SUMMARY. The cause of coloration of Blue John fluorite from Castleton, Derbyshire, and blue banded fluorites from Ashover, Derbyshire, and Weardale, Co. Durham, has been investigated by a number of techniques, including mass spectrometry, optical spectroscopy, and paramagnetic resonance measurements on natural and irradiated samples. In all respects Blue John is indistinguishable from the other blue banded fluorites. Although traces of hydrocarbons were found in all the natural fluorites including Blue John, they are shown not to be the cause of the colouration. The optical spectra and bleaching behaviour are consistent with colouration by colloidal calcium rather than F-centres. The causes of colour banding are discussed.

BLUE JOHN is the name given to the purplish-blue striated fluorite, CaF_2 , found in the Castleton area of Derbyshire and used for ornamental purposes. A detailed description of its occurrence and mineralogy has been given by Ford (1955, 1969).

Since the earliest days of its use the cause of colour and banding in Blue John has been the cause of speculation, usually based on scant experimental evidence. Most writers have suggested, however, that the colouring agent in Blue John is unique and not related to that of the blue banded fluorites found elsewhere in Britain and abroad. Although much has been written on the coloration of fluorites in general, up to the time of the present work only the following experimental observations have been made specifically of Blue John:

It occurs in the vicinity of natural deposits of asphalt-like minerals and when destructively distilled yields hydrocarbon oils (Garnett, 1920). If extracted with an organic solvent a maximum of 0.1 % of an 'oily substance' is recovered, but no decoloration of the mineral occurs (Blount and Sequira, 1919), except when treated with boiling carbon disulphide (Mueller, 1954). Gas analysis by chemical methods showed a gas content of CO_2 , CO , H_2 , N_2 , and Ar (Blount and Sequira, 1919). When Blue John is ground or heated a pungent odour is given off (Ford, 1955), but opinions differ as to whether this is a 'bituminous' or fluorine-like smell. Analyses of organic matter by Barnes and Holdroyd (1896) indicate 0.12 % carbon in both blue and white bands.

Chemical analyses have shown that the blue bands contain marginally more Al_2O_3 and Fe_2O_3 than the white and that no Mn is present (Blount and Sequira, 1919), while spectroscopic analyses revealed a deficiency of radioactive elements and rare earths, the sample containing only 0.02 % yttrium and a trace of strontium

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(McClelland, in Dunham, 1952). Radioactivity was unsuccessfully sought by autoradiography (Garnett, 1920).

When gently heated Blue John becomes lighter in colour, changing from purple through dark red and pale pink to colourless (Mueller, 1954). An instantaneous bleaching is effected by shocking the crystal, particularly by the use of explosives during mining operations or when turning an ornamental article on a lathe (Ollershaw *et al.*, *c.* 1960) or by tapping a crystal on its cubic apex (Barnes and Holdroyd, 1896).

On exposure to radium the dark bands become darker while the lighter parts become blue (Blount and Sequira, 1919). A thermally bleached sample became blue on exposure to radium but exposure to X-rays produced a purple colour (Blount and Sequira, 1919). All of the samples coloured by irradiation faded within a week or two.

The main theories of coloration to date can be summarized in three categories:

Hydrocarbon theories. Great stress has been laid on the coexistence of Blue John and bituminous shales, and the carbon content of Blue John (Ford, 1955; Mueller, 1954). However, none of the variations of this idea, first advanced by Mawe (1802), have been able to explain convincingly in crystallochemical terms how any form of carbonaceous matter can produce a blue or red colour. Blount and Sequira (1919) and Garnett (1920) seem to imply an organic dyestuff (containing a charge-transfer chromophore?) while Mueller (1954) suggests that the colour-producing hydrocarbons are 'highly oxygenated and carbonized bitumens of the albertite and elaterite group yielding aromatic fractions' but gives no details of the action of the supposed chromophores. More recently, Kranz (1969) in a mass-spectroscopic study of blue fluorites (but not Blue John) detected the presence of fluorohydrocarbons in uranium-bearing samples. This author does not, however, make it clear whether he considers the colour to be due to the fluorohydrocarbons, radiation damage by the uranium component, replacement of $(\text{CaF}_6)^{6-}$ groups in the lattice by $(\text{UO}_4\text{F}_4)^{6-}$ and $(\text{UO}_2\text{F}_6)^{6-}$, or a combination of all three effects. No discussion of the chromophore is given.

Scattering by colloidal carbon seems never to have been specifically invoked as a cause of coloration in Blue John; it appears to be the most reasonable of all possibilities involving carbon but the measured carbon concentrations are always much lower than would be necessary to produce such a dark coloration.

The hydrocarbon theory has been used to explain the banding in Blue John by assuming that distillation processes occur during pulsatory deposition from mineralizing solutions (Ford, 1955; Mueller, 1954). Apart from providing no plausible chromophore, the theory does not satisfactorily explain the shock-bleaching properties, the colour change from blue to red on heating, or the effect of radiation. Neither does it explain why coexisting regions of the same crystal having the same carbon content should occur in both white and blue varieties.

Inorganic contamination theories. A commonly held theory that manganese is the colouring agent in Blue John was discounted by Blount and Sequira (1919) who were

unable to detect manganese in Blue John. The spectrographic analyses of McClelland (in Dunham, 1952) have shown that Blue John is extremely free of rare earths; similar conclusions were reached regarding a number of other natural blue and violet fluorites examined spectroscopically by Allen (1952), who thus ruled out coloration by rare earths.

Radiation and mechanical damage theories. Radiation has been briefly considered by Ford (1955) as a possible cause of coloration in Blue John, but discounted because the blue or purple irradiation colours tend to fade on exposure to light. Irradiation of crystals containing traces of rare earths produces coloration (Przibram, 1954); irradiation of a mechanically stressed crystal also produces striations of colour similar to the striations in natural Blue John (Przibram, 1954; Feltham and Ghosh, 1968). Radiation can cause natural coloration by providing the electrons for F-centre formation, or more drastically, by partial destruction of the fluorite structure, leading to the formation of colloidal calcium (Gobel, 1930; McLaughlan and Evans, 1968), either by omission of fluorine ions or neutralization of excess calcium ions caught in structural holes (Allen, 1952). Although never specifically mentioned in connection with Blue John, evidence for the operation of this colouring mechanism in other fluorites is considerable (Allen, 1952). A blue coloration due to excess calcium is also produced by exposing white fluorite to calcium vapour (Doelter and Leitmeir, 1931), irradiation (Gobel, 1931), electron bombardment (McLaughlan and Evans, 1968), or by the presence of small amounts of variable valence cations (Allen, 1952). The colloidal particles form aggregates, the size of which determines the natural colour (Gobel, 1930, 1931); small particles give green while an increase in aggregate size produces blue, violet, and colourless crystals (Allen, 1952). The u.v. and visible spectra of coloured fluorites show two absorption maxima; one, at 380 to 405 nm, has been attributed to F-centre activity (Mollwo, 1934; Arends, 1964), but the other, at 575–650 nm, has been associated with colloidal calcium aggregates (Allen, 1952; McLaughlan and Evans, 1968).

On the basis of experiments with CaCO_3 and HF heated together in closed steel tubes Barnes and Holdroyd (1896) concluded that fluorite can be coloured by mechanical damage alone and suggested that this is the colouring mechanism in Blue John; their experiments have, however, been criticized for the high impurity concentrations thus introduced into the crystals.

Colour-centre theories, whether radiation, pressure, or chemically induced, provide explanations for thermal and shock bleaching in terms of defect annihilation or changes in colloidal aggregation, while the banding in fluorites might be interpreted in terms of a periodic fluctuation of either the radioactive or the variable-valence cation content of the original mineralizing solution.

The purpose of the present work was to determine whether or not Blue John is a unique mineral and to ascertain which of the above coloration mechanisms is most feasible, by applying a number of experimental techniques to Blue John and, for comparison, several other British blue banded fluorites. Pure synthetic CaF_2 was also used in a series of control experiments.

Experimental

Materials. Six fluorites were examined in this work. These were a natural Blue John picked from a surface outcrop above Treak Cliff Cavern, Castleton, a natural white sample collected from the same outcrop, a sample of Blue John from the Bull Beef vein, Castleton (so called because of the dark blood red colour produced by gentle heating), and blue banded specimens from Ashover, Derbyshire, and Weardale, Co. Durham. The sixth sample was a high purity CaF_2 single-crystal chip supplied by Koch Light Pure Chemicals Division. Irradiated samples of all these fluorites were prepared both by exposure to a ^{60}Co γ -source and to 20 to 80 kV X-rays at room temperature. Other natural blue samples were thermally bleached by very slow heating to about 375°C in a muffle furnace.

Experimental techniques. Thin slices were cut and polished by diamond saw and lap and examined by u.v., visible, and i.r. transmission spectroscopy on a Carey 14 spectrometer (200 to 720 nm.) and Perkin Elmer 337 spectrometer (4000 to 400 cm^{-1}). Similar samples were examined in an A.E.I. electron-probe microanalyser in which point counts of carbon, calcium, and fluorine were made on both blue and white areas of the sample. The presence of other selected elements was also sought.

Powdered samples were semi-quantitatively analysed in a Philips X-ray fluorescence spectrometer and were also examined by D.T.A. and thermogravimetry in both static air and nitrogen atmospheres at heating rates of 5 and $4^\circ/\text{min}$. Powdered samples were also used for room temperature e.p.r. and n.m.r. measurements using a Hilger and Watts E.S.R.3 spectrometer in the X and Q bands and a JEOL JNM 3H-60 n.m.r. spectrometer operating at 23.3 M Hz (fluorine resonance). The composition of the evolved gases from powdered samples was recorded as a function of temperature up to 900°C in vacuo by an A.E.I. MS10 mass spectrometer as described elsewhere (MacKenzie, 1970). Flame-photometric analyses for Na and K were made on solutions prepared by digestion of powdered samples with concentrated H_2SO_4 .

Results

X-ray fluorescence analyses. These results, which give an order-of-magnitude only, are shown in table I, which also contains the flame-photometric analyses of Na and K. Some Blue John specimens contained a trace of manganese, which was not, however, found in other specimens. All the natural blue fluorites were low in rare earths, as previously found (McClelland, in Dunham, 1952), but most contained traces of other transition metals (iron and chromium). The Bull Beef Blue John, which is the darkest in colour, was also one of the purest samples with respect to rare earths. All the natural fluorites contained comparatively large concentrations of alkalis, particularly sodium, which was present in greatest amount in the dark Bull Beef sample. There is, however, no significant difference between the alkali contents of blue or white Blue John, suggesting that alkali ions are not by themselves responsible for the coloration. All the natural fluorites contained strontium, probably in the cation sites of the fluorite lattice.

TABLE I. *Impurities present in the natural fluorites*

Sample	Fe	Cr	Sr	Mn	Yt	Cu	Na (ppm)	K (ppm)
White Blue John	e	b	e	a	d	b	250	10
Blue John	d	b	e	a, c*	d	b	200	10
Bull Beef Blue John	e	b	e	a	b	b	270	30
Ashover Blue	d	b	e	a	a	b	260	30
Weardale Blue	b	b	d	a	e	b	170	20

Key: a = undetected, b = 0-5 ppm, c = 5-10 ppm, d = 10-20 ppm, e = 20-50 ppm.

* Mn only detected in some of the Blue John samples.

The X-ray fluorescence results are semi-quantitative and give orders of magnitude only. The alkali metal figures were obtained by flame photometry.

Mass spectrometry. The gases evolved from all the natural fluorites during heating contained very slight traces of hydrocarbons, the Weardale sample being slightly richer in hydrocarbons than the other fluorites examined. The mass spectra for several natural fluorites at 800 °C are shown in fig. 1.

The mass spectra of white and blue Blue John are identical, both showing traces of hydrocarbons, which appear gradually as a function of temperature with no sudden occurrence at the thermal bleaching temperature (about 375 °C). Even at 800 °C the hydrocarbon content from all samples was extremely small, corresponding to a partial pressure of about 1.3×10^{-10} mmHg.

No trace of fluorine was observed in any of the mass spectra, nor any peaks that could unambiguously be ascribed to fluorocarbons such as were found by Kranz (1969).

Electron-probe analysis. Within the limits of error for the electron microprobe (about 0.1 % for C) no detectable difference was recorded between the carbon content of the blue and white regions of the same Blue John crystal. A similar result was obtained for fluorine but the comparatively large scatter in the calcium intensity readings from point to point in the sample made it impossible to tell whether the observed differences between the blue and white areas were significant. No other impurity elements were detected by the electron microprobe.

D.T.A. and thermogravimetry. Neither technique showed any signs of reaction at the temperature of thermal bleaching as would be expected if such bleaching was associated with the burning-off of hydrocarbons. The resulting D.T.A. exotherm and weight loss would have been observed in air but not in nitrogen, but was not detected in either atmosphere between 20 and 800 °C.

Spectroscopy. The i.r. transmission spectra of all the natural fluorite samples showed small amounts of adsorbed water but no traces of the absorption bands in the characteristic C-H, C-O, or C-N regions. Since this technique is very sensitive it supports the mass-spectrometric result that such hydrocarbons as were found were present in extremely small amounts.

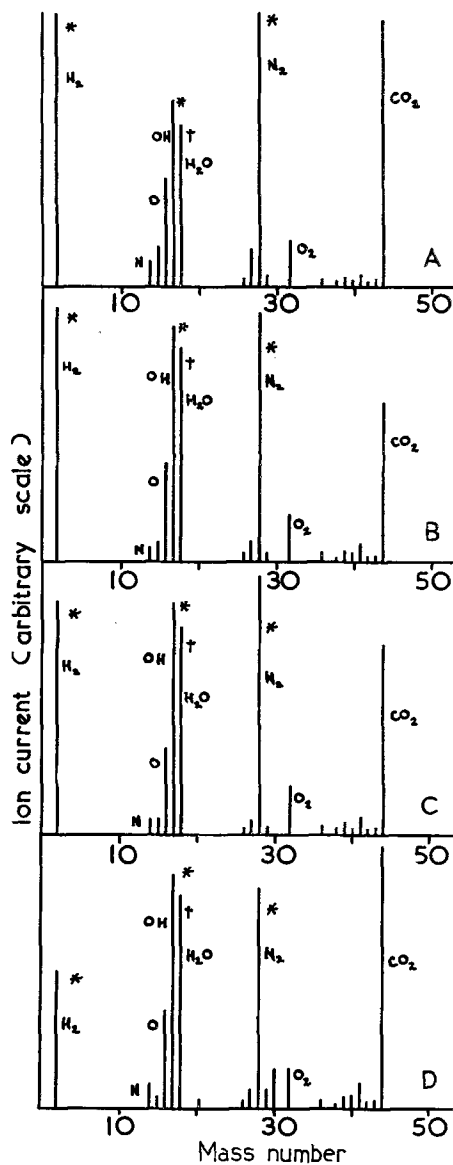


FIG. 1. Schematic representation of mass spectra from natural fluorites. * denotes scale reduction by 2.5. † denotes scale reduction by 10. Peak 28 (marked N_2) also contains CO. Unmarked peaks are taken to be hydrocarbons.

A. Natural dark Blue John.
C. Ashover blue fluorite.

B. Natural white Blue John.
D. Weardale blue fluorite.

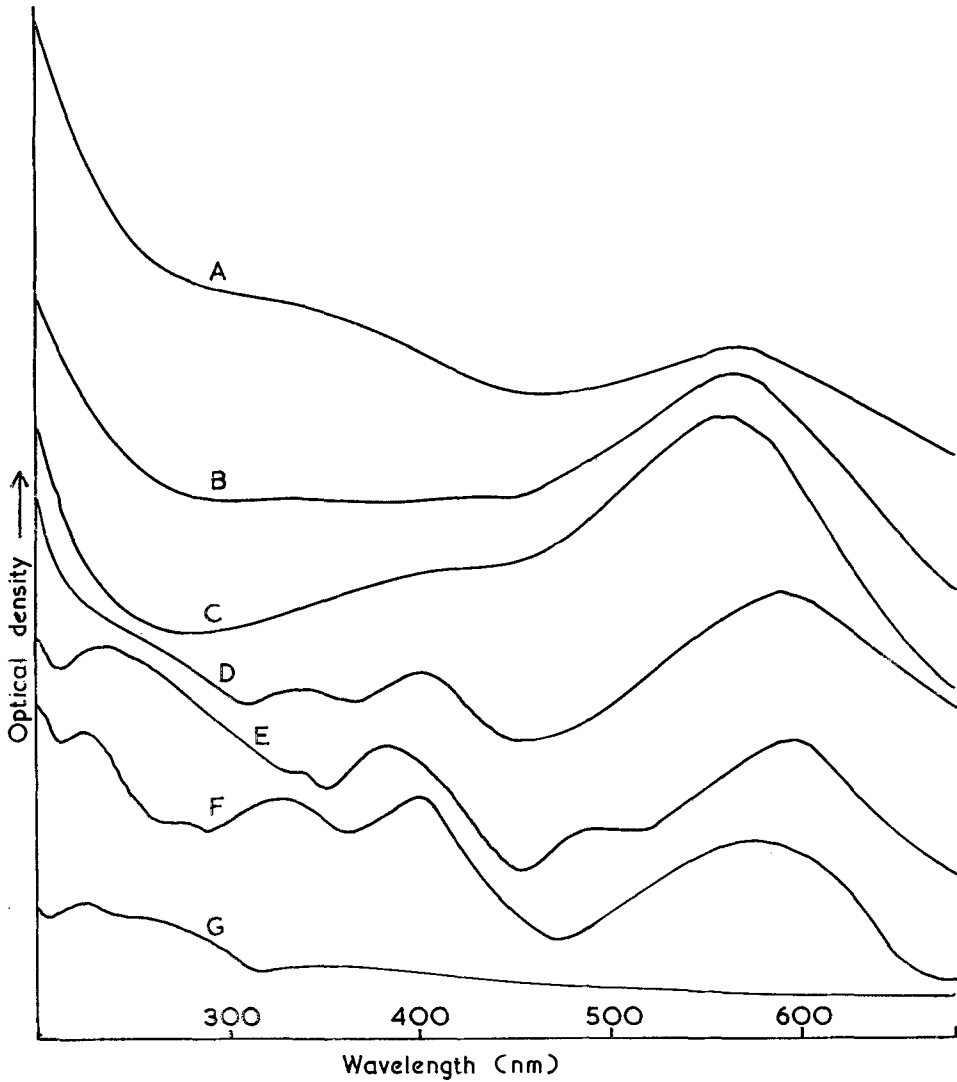


FIG. 2. Optical transmission spectra of various fluorites.

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| A. Natural dark Blue John. | B. Ashover blue fluorite. |
| C. Weardale blue fluorite. | D. Irradiated dark Blue John. |
| E. Irradiated white Blue John. | F. Irradiated synthetic CaF_2 . |
| G. Unirradiated synthetic CaF_2 . | |

The u.v. and visible spectra of several natural and irradiated fluorites are shown in fig. 2 from which it is clear that the three natural blue fluorites have indistinguishable absorption spectra with a maximum at about 550 nm and a slight inflexion at 300 to 400 nm. The deep colour of the natural samples made it impossible to obtain better

spectra and for the same reason it was impossible to obtain a spectrum of the very dark Bull Beef sample. The spectra of the irradiated samples, both natural and synthetic, all show a maximum at about 580 nm but contain extra bands in the region 200 to 400 nm. The 500 nm bands of the irradiated spectra are clearly related to the natural spectra but the former have an added complexity due to the presence of additional absorption bands.

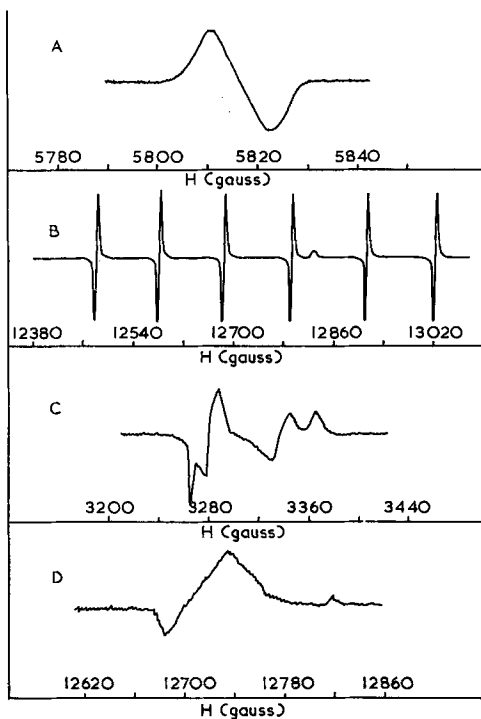


FIG. 3. Paramagnetic resonance spectra of various fluorites.

- A. Typical ^{19}F NMR spectrum of natural fluorites.
- B. Typical Q-band EPR spectrum of Blue John containing manganese. Gain = $0.5 \times$ maximum.
- C. Typical X-band EPR spectrum of Blue John and coloured fluorites not containing manganese. Gain = $2.3 \times$ maximum.
- D. Typical Q-band EPR spectrum of Bull Beef Blue John. Gain = $5 \times$ maximum.

Typical e.p.r. and n.m.r. spectra are shown in fig. 3. All the samples gave the same broad fluorine magnetic resonance spectrum (fig. 3A) which is characteristic of the fluoride lattice (Pake and Purcell, 1948). Irregularities such as neutral fluorine atoms, which would have given extra spectral lines, were not present in any of the samples in concentrations detectable by n.m.r. Relaxation time measurements such as those of Rollin and Hatton (1948) on irradiated CaF_2 could not be made because of the unavailability of low-temperature facilities.

The e.p.r. spectra fall into three types. The six-line spectrum (fig. 3B) is characteristic of manganese although its sharpness is unusual in systems of this type (J. F. Baugher, personal communication). The manganese spectrum was found only in those specimens in which manganese was detected by X-ray fluorescence. It could be destroyed neither by thermal bleaching nor by irradiation. A second type of e.p.r. spectrum was recorded for those natural Blue John samples that did not contain manganese (fig. 3C); this

was much broader and weaker than the manganese spectrum but was detectable even in the manganese-containing samples. This spectrum was not destroyed by thermal bleaching or irradiation and occurred also in the natural white Blue John and Wear-dale fluorite. A similar but very much less intense spectrum was obtained from the Bull Beef sample (fig. 3D), but no e.p.r. signal could be detected from the Ashover sample under the present experimental conditions. The e.p.r. spectra reveal no striking

differences that may be attributed to the sample colour, but these room temperature measurements were probably not adequate to detect and identify the colour centres responsible since no e.p.r. signal could be detected from an irradiated sample of synthetic CaF_2 . It seems likely that the relaxation times of the relevant species may be such that measurements at low temperatures would be necessary to detect resonance and such facilities were not available at the time of this work. The e.p.r. signal from colour centres in fluorite is of low sensitivity and subject to broadening due to hyperfine coupling to the F-nuclei (Arends, 1964).

Discussion

The most striking feature of the results is the physical and chemical similarity between Blue John and the other natural blue banded fluorites studied. All these samples were comparatively free from inorganic contaminants but contained traces of hydrocarbons. All had similar spectral properties in the u.v., visible, and i.r. regions, and all had similar n.m.r. properties. The e.p.r. spectra were very similar but in some cases were obscured by the presence of intense Mn^{2+} resonances. The evidence therefore indicates that Castleton Blue John is not a unique mineral as has been previously suggested (Ford, 1955) but is similar in every way to the blue-banded fluorites found elsewhere in Britain. It is thus likely that the colouring mechanism of Blue John may be similar to that of other blue fluorites previously studied (Allen, 1952).

The evidence presented here clearly rules out several theories previously held regarding the coloration of Blue John, which will now be discussed in the light of the present results.

Hydrocarbon theories. Mass spectrometry shows the presence of hydrocarbons in all the natural samples, but these cannot be responsible for the colour because they occur equally in the white regions of Blue John. The electron microprobe also shows that the carbon content of white and blue regions of the same crystal is identical. In addition, the amounts of hydrocarbons present are so small as to be undetectable by i.r. spectroscopy, thermogravimetry, or D.T.A.; the concentration of carbon is therefore too low to provide an explanation in terms of scattering by colloidal carbon particles. No other mechanism can be envisaged whereby such small traces of organic matter can give rise to chromophores that also exhibit the shock bleaching and thermal bleaching properties of Blue John. There is likewise no evidence that the fluorocarbon-uranium theory of Kranz (1969) is applicable here since neither fluorocarbons nor uranium were identified in the present samples by mass spectrometry and X-ray fluorescence techniques respectively. Thus all the available evidence militates against the hydrocarbon theory of colouration.

Rare earth and transition metal theories. Although trace amounts of rare earths were found by X-ray fluorescence in some samples, they were undetectable in the darkest Blue John sample (Bull Beef). Thus there seems to be no correlation between rare earth content and colour. Likewise, although traces of Mn were found by X-ray fluorescence and e.p.r. measurements in some Blue John samples, this element was not detectable

in all the Blue John samples. The Mn^{2+} content of the Mn-containing samples was unaffected by thermal bleaching or irradiation, which processes markedly change the colour. The facility of the bleaching process also rules out transition metal colouration since at the bleaching temperature oxygen diffusion through the matrix would be too slow to explain the observed results. The conclusion that the natural colour of fluorites is not related to the varieties of rare earths or transition metals present is in agreement with Yoshimura (1933), Eysank (1936), and Mukherjee (1948).

Colour centre activity. The u.v. and visible spectra of natural and irradiated fluorites show similarities in the position of certain absorption maxima, and appear therefore to be related. However, irradiated specimens (including high purity synthetic CaF_2) show a number of additional spectral bands between 200 to 400 nm, the assignment of which will now be briefly discussed.

Unlike the well-understood colour centres in alkali halides, the assignment of optical bands in the alkaline earth halides has only recently been clarified, because of difficulties associated with the sensitivity of the latter to trace impurities (oxygen, water, Na^+ , K^+ , and rare earths, e.g. Yt^{3+}). Furthermore, the optical spectra of calcium fluorides depend on the method of colouration and thermal history of the sample. In all the irradiated samples studied here, the lower wavelength lines are probably due to the presence of yttrium as shown by Gorlich *et al.* (1963) and O'Connor and Chen (1963), but the band at 580 nm responsible for the blue colour in Blue John and other blue fluorites cannot be explained on this basis as it is some 50 nm higher than the longest wavelength of the yttrium spectrum and occurs in the natural materials in the absence of the other yttrium lines. Likewise the colour of the natural material is not due to F-centres since these absorb at 375 nm (Arends, 1964; Feltham and Andrews, 1965; Hayes and Stott, 1967).

A strong band at 580 nm has recently been observed in impure CaF_2 bombarded with 75 KeV electrons; this was attributed to the formation of colloidal calcium particles (McLaughlan and Evans, 1968). The resulting violet colouration was thermally stable up to 500 °C and showed a broad low-temperature e.p.r. band at about $g = 2$ with a superimposed sharp line at $g = 2.006$, characteristic of colloidal calcium. Thermal bleaching caused changes in particle size and aggregation as shown by changes in the e.p.r. spectrum and a wave-length shift in the optical band. This identification of the 580 nm band with colloidal calcium is in agreement with Allen (1952) and Gobel (1930, 1931) and is reasonably supported by scattering theory calculations (Mayerl, 1951), which show that for colloidal particles of the estimated size ($< 300\text{\AA}$) the absorption maximum is at about 550 nm.

The striking similarity in optical and thermal bleaching behaviour between the natural blue fluorites of the present study and the electron-irradiated samples of McLaughlan and Evans (1968) suggests that the same colloidal colouring mechanism may be operating in both cases. The presence of colloidal calcium in Blue John and related blue fluorites could not be confirmed by e.p.r. measurements since although several broad peaks were observed at about $g = 2$, low-temperature measurements would be necessary to detect the sharp resonance due to colloidal particles. The

colloidal resonance is also extremely sensitive to particle size (McLaughlan and Evans, 1968).

The mechanism of formation of colloidal calcium in CaF_2 is not clear, but was thought by McLaughlan and Evans (1968) to be caused by intense surface heating during electron bombardment. Contaminants such as Na^+ , K^+ , and oxygen are also thought to be necessary since they create the anion vacancies required by the aggregation process. Since the natural fluorites of this study contained monovalent impurities and their mode of formation ensures oxygen contamination the necessary anion vacancies will almost certainly be present (especially in the dark, alkali-rich Bull Beef and Ashover samples). The actual mode of colloid formation in nature may not necessarily involve electron bombardment; slow cooling from elevated temperatures gives colloidal particles in preference to F-centres (Kamikawa *et al.*, 1966), while a redox mechanism involving slow cooling of variable-valence impurities has also been suggested (Allen, 1952). There is also some evidence that pressure-induced colour is colloidal; pyramidal indentations in Mn-doped CaF_2 turned a stable violet colour on room-temperature X-irradiation but the coloured volume was too small to detect an e.p.r. signal (Feltham and Ghosh, 1968). The absence of a characteristic four-band irradiation spectrum in the present natural fluorites does not rule out radiation damage since the four-line spectrum is optically unstable and would have long disappeared from natural fluorites leaving only the more stable colloidal band (which was also present in all the irradiated samples).

The suggestion that the colouration in Blue John and other blue-violet fluorites is colloidal is therefore in agreement with all the known experimental facts, explaining the optical spectrum, bleaching behaviour, and comparative stability of colour.

The possible causes of colour banding

In the light of the foregoing, the colour striations must have been caused by periodic fluctuations in either the anion-vacancy-producing agent or the colloid-aggregating conditions or both.

In the first case, the anion vacancies could have been produced by radiation, presence of Na^+ , K^+ , or oxygen, oxidation of variable valence impurities, pressure-induced damage, or a combination of all four. The geological mode of formation makes pressure-induced damage the least likely possibility but periodic fluctuations in the radioactivity, oxygen content, and monovalent and variable valency impurity contents of the mineralizing solution are quite feasible.

Since the aggregation of colloidal calcium is probably affected by both the impurity content of the original mineralizing solution and the temperature and conditions of crystallization, the actual occurrence of banding may depend on a complex balance of several of the above factors.

Conclusions

The physical and chemical characteristics of Blue John are indistinguishable from those of other blue-banded fluorites. Although traces of hydrocarbons were present in all the natural blue fluorites studied, they were not responsible for the colour since

they occurred in similar amount in the white regions of the crystal. Traces of Mn found in some samples were likewise not the cause of the colour. Comparison of the optical spectra of natural and irradiated fluorites suggests that colloidal calcium is the chief colouring material. These colloids apparently aggregate in natural fluorites during formation but can be dispersed by thermal treatment.

The colour banding in blue fluorites is thought to be due to the combination of periodic fluctuations in the composition of the mineralizing solution and the physical conditions of mineralization.

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