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The Blue coloration in banded fluorite (Blue John) from Castleton, Derbyshire, England

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SUMMARY. From the microscopic examination of lightly etched, cleaved (111) surfaces of banded blue fluorite (Blue John, from Castleton, Derbyshire) it is concluded that the coloured lamellae are not necessarily or exclusively associated with lattice-line imperfections. Elemental analyses, by electron dispersive methods, of fresh cleavage (111) surfaces in the immediate vicinity of small inclusions (*c.* 10 μm diameter) possessing associated coloured haloes detected no appreciable concentrations of impurities. From the evidence available, it is suggested that the zones of blue colour consist of colloidal calcium resulting from radiation damage caused by the intermittent deposition of radioactive material on the surfaces of fluorite during crystal development. The dispersion of colloidal calcium produced is particularly stable as a consequence of the close correspondence between lattice spacings in calcium fluoride and in calcium metal.

THE unusual and aesthetically pleasing banded fluorite, often referred to as 'Blue John', occurring near Castleton in Derbyshire has been the subject of long and continuing investigations of the reasons for the striking blue coloration. Comparisons have been made with the properties of colourless material from the same location and, or, banded or colourless fluorites from other widely scattered sources. However, despite many investigations no general agreement concerning the identity of the chromophore has yet been reached perhaps partly because much of the experimental evidence has been negative in character. More possible explanations have been eliminated than proposals positively proved.

MacKenzie and Green (1971) summarize the earlier literature concerned with Blue John and related fluorites and identify the three general types of chromophore that have been proposed to explain the blue coloration. These are incorporated hydrocarbon, inorganic impurities, and lattice imperfections or damage produced mechanically or by radiation. These workers applied the usual complementary chemical and physical techniques and conclude that the chief colouring material is colloidal Ca, banded as a consequence of changing conditions during mineralization. Braithwaite *et al.* (1973) find no correlations between the distributions of colour and of either inorganic or organic impurities in Blue John and related minerals. They conclude that physical rather than chemical factors are responsible for the coloration and suggest that colloidal particles of Ca have been formed by the aggregation of Ca atoms preferentially within the more defective regions of the crystal. These atoms are believed to have been released from the lattice during long-term irradiation by radioactive elements, which are known to have been available by their continued presence in associated uraniferous deposits (collophane).

Calas (1972) concluded that colloidal Ca is not necessarily the colouring matter in all banded fluorites and discusses the possible existence of alternative light-absorbing centres containing inorganic impurities, notably yttrium. Holgate (1973), from consideration of the dichroism of coloured fluorites, believes that the most probable chromophore in Blue John is a hydrocarbon, though the particular compound or molecular grouping is not identified. Thus, from these and other recent reports, we must conclude that the light-absorbing centres in coloured fluorite have not been positively and finally characterized and that the nature of the chromophores present remains a matter for active discussion.

The present article reports a study of two aspects of the structure and composition of Blue John. Firstly, we have investigated the relationship between the distribution of lattice-line imperfections (dislocations) now present, as revealed by etching of cleaved surfaces, and the distribution of the blue coloration. This was intended to determine whether direct support could be obtained for the theory that dispersed Ca in the bulk crystal was precipitated or aggregated in the form of a stable colloid preferentially within defective zones. Although deformation and annealing under natural conditions could be expected to cause continuing variations in lattice imperfection distribution, it was thought probable that extensive precipitation of colloidal material within dislocations would stabilize them against further movement. It seems inherently more likely that progressive dispersal of single Ca atoms would occur more readily than the annihilation of the dislocation networks within which such atoms were preferentially accommodated in the first place. Secondly, we have attempted to establish the composition of features having the appearance of inclusions and which characteristically occurred in irregular groups comprised of numerous individual members, each possessing an associated zone of blue coloration. We have been unable to identify any foreign constituent and conclude that there are no appreciable local concentrations of any included non-volatile impurity.

In this article we also make brief reference to certain other of our measurements. These report no new information but are entirely consistent with and serve to confirm earlier observations by others. The nature of the colour centres resulting in the blue banding and the manner of its production under natural conditions are discussed.

Distribution of coloration in Blue John

The present study was exclusively concerned with samples of natural banded fluorite (Blue John) collected from a surface exposure directly above the entrance to Treak Cliff Cavern, near Castleton, Derbyshire (Nat. Grid Ref. SK 135 831). From relatively perfect single crystals (*c.* 10–30 mm linear dimensions) selected specimens were cleaved, by a sharp blow with a knife edge, into thin plates suitable for microscopic examination. Coloration in banded fluorite occurred in two characteristic distributions: in the form of planar lamellae and in the immediate vicinity of individual members of features having the appearance of irregular groups of inclusions. There were significant variations of hue, even within a single crystal fragment; perceived colours varied from pink-magenta to dark blue. In addition to these readily recognizable patterns of colour distribution, with which we are particularly concerned here, there were also zones of less regular tinting, ranging from what appeared to be lamellae of restricted extent to regions of ill-defined outline containing no recognizable structure. It should be remembered that any explanation of the coloration, based on consideration of the properties of representative lamellae and the most concentrated groups of point features with associated haloes, must also be capable of accounting for the existence of the ill-defined and more diffuse regions of tinting.

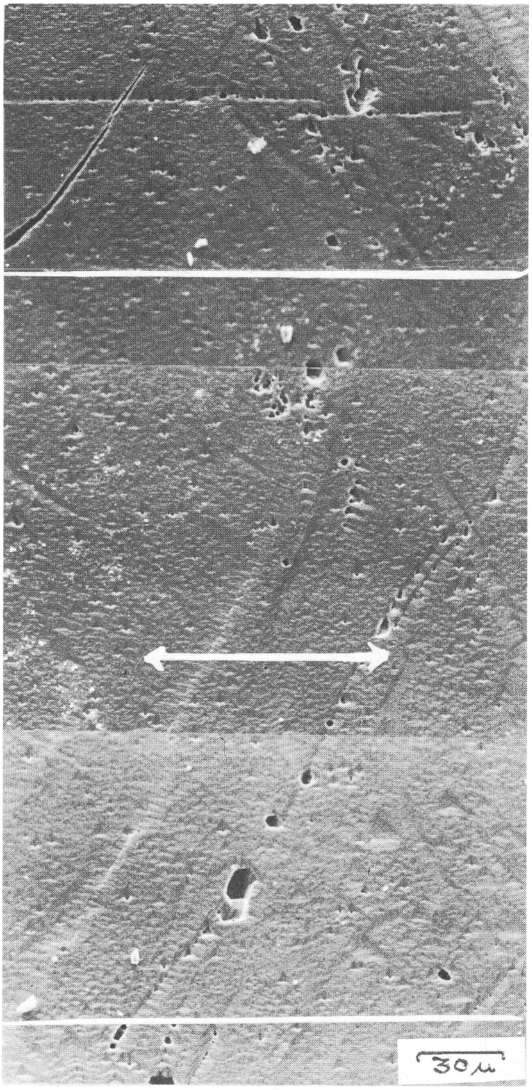
Lamellae of coloration. Planar lamellae of coloration, many being *c.* 0.1 mm thickness, obliquely traverse the thin plates (0.2–1.0 mm) of fluorite prepared for examination by parallel cleavages at the (111) plane. This appearance is consistent with the production of the thin coloured lamellae at crystal planes parallel to cubic growth faces, during or following addition of CaF_2 in mineralization: natural deposits of fluorite are often produced in the form of assemblages of intergrown cubes, for which the (100) faces predominate. Growth directions, and their relict structures, therefore, appear as planes orientated at 54° 44′ to the strongly preferred (111) fracture direction of the fluorite crystal.

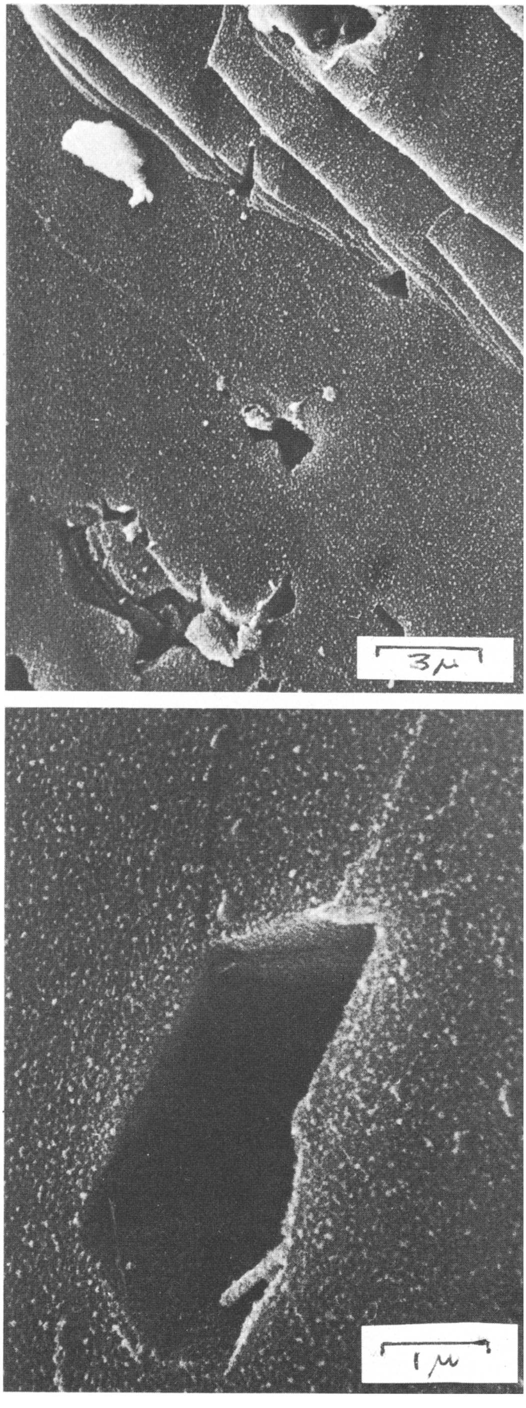
Assemblages of inclusions. Slivers of fluorite, obtained on cleavage, occasionally contained zones of irregular dispositions of large numbers of small features provisionally identified as inclusions. The individual members of these assemblages were too small (diameters *c.* 10 μm) to permit the resolution of detail by optical microscopy. In some places each opaque zone was surrounded by an indistinct blue halo.

Line dislocations in Blue John

The preferential dissolution of crystal surfaces initiated in the vicinity of imperfections has been widely used as a method of locating points of intersection of line dislocations with surfaces. Preliminary work with the present mineral showed that triangular etch pits were developed after *c.* 2 min dissolution in 10% aqueous hydrochloric acid at *c.* 350 K. An unidentified deposit produced in this treatment was removed from etched surfaces by washing with hot distilled water before microscopic examination or analysis.

About twenty different thin cleaved (111) plates of Blue John, each specimen having been selected to include at least one strongly coloured lamella, were individually etched under an appropriate range of conditions (of severities greater than and also less than the optimum) and the treated surfaces examined in detail in a scanning electron microscope. This technique has the disadvantage that the precise position of the coloured zone does not appear on the image, but it was possible to prepare overlapping sequences of photographs of areas of interest for comparison with features identified and located in a previous optical examination. A representative composite photograph of an etched surface is shown in fig. 1, for which it was independently known that a blue lamella





FIGS. 1 and 2: FIG. 1 (*above*). Texture of (111) cleavage surface of Blue John etched briefly with 10% aqueous hydrochloric acid at *c.* 350 K. A blue lamella, aligned in the direction shown by the arrow, intersected the surface somewhere between the limits given by the horizontal white lines. None of the several aligned etch features could be positively ascribed to the presence of the coloured zone. SEM photograph. FIG. 2 (*right*). Typical inclusions found on (111) cleavage surfaces of Blue John: both examples occurred on faces exposed by the vigorous disruption of the mineral on heating at 750 K. SEM photograph.

intersected the surface as a horizontal band (of unknown width) somewhere between the limits shown (as horizontal lines). No feature of the etched surface could be correlated with the zone of blue coloration.

Etching invariably revealed the presence of alignments of crystallographic imperfections, which appeared as linear troughs apparently composed of closely spaced, overlapping triangular etch pits. Dimensions of such troughs were significantly less than the thicknesses of the coloured lamellae. While, in some instances, etch pit alignments coincided with known positions of blue zones, in other examples no such correlation was evident and elsewhere, again, linear patterns of etch pits were present in places remote from any coloration. Thus, blue lamellae cannot be identified with the presence of line imperfections, lattice disorder, or increased surface reactivity resulting in any significant enhancement of the local rate of salt dissolution.

While it is possible that extensive redistribution and perhaps removal of dislocations may have occurred during the post-depositional interval, it was none the less unexpected that there was no evidence of an enhanced, or even changed reactivity of the crystal in the vicinity of blue zones. This would appear to suggest that the crystal lattice within the lamellae does not now contain high concentrations of line imperfections or impurities. If it is believed (Braithwaite *et al.*, 1973) that the colour banding arose as a consequence of the dislocation net providing sites for the preferential aggregation of Ca particles of colloidal dimensions from atoms released by radiation damage within the crystal bulk, it is difficult to explain how such an impurity-laden and locked network could have been reorganized without achieving conditions of sufficient severity to either redisperse the Ca as atoms or permit its continued aggregation within the imperfect zones. It is also necessary, on this model, to make the additional assumption that the trapped colloid has particular stability, since coloured fluorites from several distinct sources give (MacKenzie and Green, 1971) rather similar spectra, presumably attributable to the presence of particles within the same size range.

From this evidence, therefore, we conclude that, since the imperfection structure assumed to have been present during colloidal particle development is not now detectable, the maintained colour distribution in bands cannot be ascribed to the formation of a colloidal dispersion of Ca metal in a preferred size range resulting from Ca atom aggregation exclusively within a pre-existing and, in places, highly inhomogeneous, distribution of lattice imperfections.

Assemblages of inclusions in Blue John

Representative small opaque zones, each with an associated blue halo, were examined in an attempt to identify any included material, since this could give evidence of the composition of substances present during hydrothermal deposition of the mineral. Optical microscopy yielded no useful information and it was difficult to ascertain whether the very small opaque spots ($< 10\ \mu$m) of interest were exposed at the *surfaces* of samples cleaved for stereoscan examination, even for crystals containing locally dense concentrations of these features. Accordingly, numerous comparisons were made between stereoscan pictures of cleavage surfaces traversing inclusion-rich regions and those from clear fluorite. The only general conclusion to emerge from this comparison was that there was an enhanced incidence of pitting in areas from the inclusion-rich material. Some representative pits are shown in fig. 2. We believe, therefore, that the opaque spots were holes within the crystal filled with a gas or volatile liquid. The interiors, edges, and immediate vicinities of upwards of 100 of these holes, and, in addition, such rare atypical surface features as were noted, were analysed by the EDAX method (Energy Dispersive Analysis of Xrays: Edax International). The only element (of atomic number > 15) present was Ca, though one or two instances of the presence of Fe in trace amounts and at the lower limits of detection were indicated. There was no evidence, therefore, that elements, held in any solution that was contained within these inclusions, were deposited on solvent evaporation. We cannot be certain from our observations that included minerals containing Al, O, Si (etc.) were entirely absent. We can be sure, however, from detailed consideration of data for both typical and atypical areas of representative cleaved surfaces that all analytical results were entirely consistent with the view that the mineral was pure calcium fluoride. Again, within the very few zones of exceptional texture found, it was apparent from EDAX analyses that calcium was the preponderant, possibly exclusive, cation.

Crystals heated to *c.* 700–800 K (below the temperature at which colour is completely lost: some aspects of thermal bleaching are discussed by Braithwaite *et al.*, 1973) disrupted violently with preferred cleavage at (111) planes. Stereoscan examination showed that the surfaces exposed were rich in pits and EDAX analysis again confirmed that calcium was apparently the exclusive surface cation. Surface pits were not invariably associated with colour and the exposure of such features on heating suggests that disruption of the crystal may be a consequence of pressure developed by fluid within the inclusion at elevated temperature.

A more precise application of the same general approach to the chemical identification of included material was made by selecting for examination a single relatively large, separate, and distinct inclusion, *c.* 10 μm diameter, surrounded by a coloured halo, *c.* 8 μm thickness. The fluorite overlaying this structure was gently removed by systematically finer polishing until the dark spot was adjudged by optical microscopic examination to be at the mineral surface. This crystal was then mounted in an electron microprobe and the beam (accurately located by the intentional production of a blue spot on the surface at a point somewhat removed from the feature of interest) was focused on the centre of the selected inclusion prepared for examination. Analytical scans were made extending across the complete spectrum available (30–130°) for three crystal analysers: lithium fluoride, quartz, and KAP. In addition, specific impurities were sought. No perceptable concentration of any element other than Ca was detected, from which it is concluded that the local concentrations of impurities (atomic number > 10) were all $< 0.1\%$. The same result was obtained for two further selected inclusions, similarly exposed on the surface and analysed.

Electron microprobe analyses at each of a linear sequence of surface points extending across the zone of intersection of a blue band with a cleavage face gave no evidence of the presence of any detectable quantities of the following possible impurities: Fe, K, Mn, P, S, Si, Sr, U, or Y. The only major response was (again) for Ca and, indeed, the indications were that the concentration of this element was perhaps marginally *greater* (by $< 0.5\%$) within the blue band. While this apparent local enhancement of concentration is too small to be accepted as reliable, it does confirm that there is not a diminished concentration of Ca^{2+} within the coloured zone; this is, perhaps, the most probable consequence of the presence of cationic impurities.

Other measurements

Other of our measurements agree with, and serve to confirm, conclusions published elsewhere; relevant experimental data which we have obtained may be briefly mentioned:

The coloration was not removed on boiling crushed Blue John with organic or inorganic (aqueous NaOH, HCl, or H_2SO_4) solvents. Lattice spacings, measured by X-ray diffraction, for blue and for colourless material were indistinguishable. The absorption spectrum (MacKenzie and Green, 1971) included a broad band between 550–600 nm, but no useful information could be obtained from electron spin resonance and proton spin resonance spectra.

X-ray fluorescence spectral analysis of powdered samples revealed no detectable difference in impurity concentrations between coloured and colourless Blue John; approximate amounts detected were Sr 25, Fe 15, Y 10, and Mn 25 ppm. Combustion analyses gave H 0.15 and C 0.35%. Mass spectral analysis, using an AEI MS902 instrument, for the immediate analyses of the volatile products obtained on vacuum heating of Blue John to 700–50 °K, identified only H_2O, CO, and CO_2. Although the background response of the instrument within the mass range 100–40 was generally increased during sample heating, no significant quantity of any identifiable product was detected within the mass range 100–250. Helium, a possible product of radioactive decay, was sought, but not found, in the gases released on heating the mineral to 800 °K. There was no indication of the formation of any detectable (i.e. $< 10^{-9}$ mol g^{-1} or 0.00001%) quantity of organic products in the C_4–C_{10} hydrocarbon boiling range by the thermal desorption method (Galwey, 1965), on heating various samples of Blue John to the temperature at which the colour was lost, *c.* 770 °K.

DISCUSSION

Previous studies, together with limited observations within the present work, have shown that the bulk composition of the coloured fluorite zones is indistinguishable from that of the colourless mineral. Our attempts here to identify any highly localized compositional changes that might be associated with microstructural anomalies or inclusions (dimensions *c.* 5 μm upwards) have been unable to detect the existence of any variations in composition, or impurity aggregation, capable of accounting for the coloration. Ca was virtually the only element detected by the techniques employed.

These analytical investigations were conducted in conjunction with etching studies of cleaved surfaces, which revealed, from the pattern of etch pit development, that line imperfections were distributed throughout the crystal and dislocations were not associated with either lamellae of coloration or assemblages of inclusions. From this we conclude that structures within tinted zones were generally similar to those elsewhere and that the chromophores are accommodated within a zone of relatively perfect crystal, containing no recognizable lattice distortion features.

The available evidence, therefore, indicates that Blue John is a remarkably pure and homogeneous fluorite. Bulk and local concentrations of impurities are probably too low to account for the observed absorption spectrum. No compositional feature, local reactivity variation (etching), textural anomaly, lattice imperfection or characteristic microstructure capable of accounting for the coloration was recognized. We, therefore, conclude, with other authors (MacKenzie and Green, 1971; Braithwaite *et al.*, 1973), that the blue coloration is due to the presence of colloidal Ca, though we propose below explanations for the development of the banding and for the structure of this colloid that are somewhat different from those previously advanced.

Development of banded coloration in Blue John

Our observation that the blue coloration is not consistently correlated with the existing distribution of line dislocations within the mineral leads us to reject (see above) the suggested explanation (Braithwaite *et al.*, 1973) that banding arises because Ca atoms released in the crystal bulk (during irradiation by a radioactive material, e.g. U) segregate by aggregation as colloidal particles preferentially located within zones of imperfection, banded and oriented in the (100) direction. We prefer an explanation invoking intermittent local superficial radiation damage to the fluorite crystals during interruptions to their hydrothermal growth (Pering, 1973). Mineral development through advance of the cubic faces of the growing crystal is envisaged as proceeding by acquisition of CaF_2 from a cooling solution, also containing a soluble radioactive substance (U), which is later deposited. During this period a thin layer of the external fluorite surface suffered some radiation damage before the arrival of a further pulse of hot mineralizing solution. This rapidly redissolved the radioactive material, perhaps also some fluorite, before cooling to the point at which CaF_2 deposition, crystal growth, was resumed, covering and protecting the damaged (100) planar zone. Intermittent repetition of such cycles accounts for the irregular patterns of blue planar zones, parallel, but of varying intensity, the presence of incomplete bands (as a consequence of uneven dissolution) and the absence of retained radioactive material. On this model radiation damage is of limited thickness and crystal annealing may occur by local and limited ionic movements, which largely restore the perfection of the lattice, enveloping and protecting the incorporated crystallites of the colloidal dispersion. There is little reduction of crystal coherence along planes of blue coloration since disintegration does not preferentially propagate within the chromophore-rich laminae. This last important property of Blue John does not seem to have been adequately considered by those who identify the chromophore as large organic molecules. The required concentrations of such impurities, disposed on original growth (100) surfaces, would result in an appreciable reduction in hardness and so the crystal would more easily break in this direction, unless the impurity forms bonds with the host lattice.

The indistinct local zones of blue, apparently associated with small inclusions, are not readily accounted for on this, or, indeed, most other simple explanations. It is difficult to provide a realistic model for such inclusions, since detailed structures of the features could not be resolved by optical microscopy and no evidence of impurity retention could be obtained. The most acceptable representation that we can propose at present is that the temporary residence of particles of sediment interrupted crystal growth locally, radioactive constituents resulting in damage to the fluorite in the immediate vicinity of the resting fragment. Such deposited material was not, however, itself included within the growing mineral in analytically detectable amounts, though the temporary residence of such particles may have inhibited (or poisoned, by monolayer deposition) local surface advance sufficiently to result in the formation of some (solvent-filled?) inclusions.

This general model is consistent with the view (Stevenson and Gaunt, 1971) that Blue John was developed in its present position earlier than the main mineralization phase of the region since it tends to occur in cavities and pipe vents rather than in the veins proper.

Structure of colloidal Ca in Blue John

In the observations reported above, we have obtained no direct information concerning the sizes, shapes, relative dispositions, concentrations, or structures of the colloidal particles of Ca that we believe to be responsible for the coloration of Blue John, except that the dimensions were below the limits of resolution of the techniques available to us. The only relevant information would appear to be the absence of a Tyndall effect (Braithwaite *et al.*, 1973), indicating that the average diameter of the colloidal particles is < 30 nm.

The possible structure of colloidal Ca in fluorite is appropriately discussed with reference to recent observations and conclusions concerning radiation damage in CaF_2 by Chadderton *et al.* (1976*a*, *b*). These workers have subjected calcium fluoride crystals to a very high flux electron bombardment and found that instead of complete disintegration, as might have been anticipated, complicated lattice reorganizations occurred, leading to new structures of considerable stability. There was fluoride ion migration in the anionic sub-lattice and interstitials became trapped at bubbles of fluorine gas. Concurrently cations were transformed into Ca crystallites, coherent with the matrix and providing nucleation centres for the anionic voids. The significant and perhaps unique feature of this metal production process (presumably also relevant to the production of chromophores, colloidal Ca, in the coloured natural fluorite) was that the cubic lattice of Ca metal could be accommodated within the (cubic) fluorite lattice with a minimum of strain, since the unit cell edge of Ca metal is but 2.1 % greater than that of calcium fluoride.

We do not intend to suggest that the radiation damage that resulted in colour development in Blue John, or any other coloured natural fluorite, approached the severity of conditions that occurred during the electron-microscope experiments referred to above. The point relevant to the present discussion, however, is that, unlike most other substances, lattice reorganization following irradiation can generate a Ca metal dispersion of particular stability, coherently accommodated within the host CaF_2 lattice with a minimum of strain. Metal enveloped within the stable, well-crystallized, and insoluble mineral may be expected to be unreactive and protected from chemical change during geological periods of time. It is reasonable to suppose that in such a dispersion there would be a particle size range of preferred stability influenced (*inter alia*) by strain energy due to molar volume differences (lattice spacings do not constitute an exact match) and strain at the Ca–CaF_2 interface, which is insufficient to cause a marked reduction in crystal coherence within colloid-containing (coloured) zones. Properties of the stable colloid, including metal particle size, are, therefore, controlled by spacings and elastic constants of the constituent phases. This explains the occurrence of broadly similar tinting of fluorite obtained from widely differing localities, while minor differences in colloid dimensions account for variations in spectra and colours. In contrast, it is not evident that the growth of metal at zones of imperfection from atoms released in the bulk under the influence of radiation would yield particles within a preferred size interval.

Although it might be expected that coloured bands, radiation-induced by this mechanism, would reduce in intensity with distance from the source (and we are indebted to a referee for this suggestion), this possibility could not be investigated by direct measurement since the blue lamellae were too thin. It was our qualitative impression, however, that both bounding surfaces of coloured zones were relatively sharp. Moreover, we are aware of no reliable method of predicting the variation in optical density with depth of radiation penetration for the complicated physical and chemical processes involved in the production of the stable colloid. It seems to us probable that crystal damage within the coloured lamellae at distances furthest from the source must arise in an asymmetric radiation field and, if this results in the generation of asymmetric colloidal particles, an explanation of the existence of the dichroic (Holgate, 1973) effect is provided.

The model proposed above, therefore, provides an acceptable explanation of the chromophore, consistent with available information and not in conflict with previous observations reported in the literature. It is suggested that lattice reorganization following radiation damage, by annealing through relatively short-distance migrations, removes most large imperfections from the lattice and no exceptional concentration of dislocations remains at the blue zones.

CONCLUSIONS

We conclude, therefore, that the banded blue coloration in Blue John represents zones of radiation damage, produced during the intermittent but temporary deposition of radioactive material at the growing cubic faces of fluorite mineral. Local damage in a thin surface layer, during and following passage of this radiation, resulted in the aggregation of fluorine as gas bubbles and the generation of small accumulations of metal atoms coherently accommodated within reorganized crystals of fluorite. During this recrystallization, local concentrations of lattice imperfections were reduced. The colloidal particles of metal were of a preferred size range, of particular stability, and protected within a relatively unreactive matrix. This explanation is based on the properties of the fluorite lattice (since the conditions that obtained during deposition of the mineral cannot now be verified directly) and possesses the important feature that it does not require the participation of impurities and, or, structures, the presence of which it has proved so difficult to demonstrate.

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