

$\gamma$ -irradiated fluorites is very difficult except with very special dopings, e.g. with hydrogen in large concentration (W. Hayes, *pers. comm.*).

Lastly, one should not forget the crystallization processes of hydrothermal fluorites at low temperatures (100 to 150 °C), which exclude processes studied by electron-bombardment for production of colloidal particles, and in a saline solution (up to 30 % NaCl). One finds, in fact, fluid inclusions, which distort total chemical analyses; the absence of such inclusions in the fluorites studied by MacKenzie and Green is not clearly shown.

As a conclusion, it seems difficult to accept the generalization of MacKenzie and Green's results, from the analysis of six specimens coming from two places only, to all blue-banded fluorites. It is not certain that the reasons why the Derbyshire fluorites are blue are the same as for those we have studied. Furthermore, while we have shown the similarity of the colour of the latter with the absorption of a [111] orientated complex centre associated with yttrium, there is, up to now, no evidence for the existence of colloidal calcium particles as the origin of the blue colour of Derbyshire fluorites.

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## The possible role of sulphur in the coloration of Blue John fluorite

IN a recent paper (MacKenzie and Green, 1971) a number of different theories concerning the coloration of Blue John fluorite were examined in the light of experimental evidence. The purity of this and similar fluorites precludes coloration by most

of the well-known chromophores (transition metals, rare earths, etc.). It has recently been suggested (H. O'Daniel, personal communication) that an alternative explanation to that advanced in the previous paper might be provided by the presence of sulphur, which could act as a chromophore in two possible ways, either by its occurrence as colloidal sulphide inclusions (Steinmetz, 1925; Steinmetz and Brull, 1967), or as the blue  $S_2^-$  ion (Giggenbach, 1971).

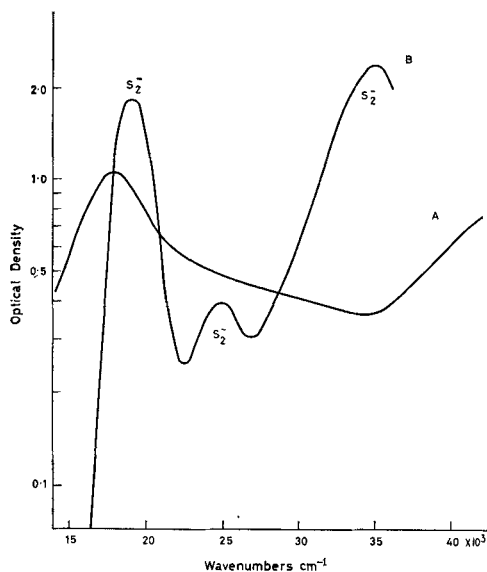


FIG. 1. Optical transmission spectra. A. Blue John fluorite, Castleton. B.  $S_2^-$  ion in dimethylformamide solution.

Analyses for sulphur were performed on both the blue and white material from the banded Blue John samples previously described (MacKenzie and Green, 1971). A preliminary semi-quantitative X-ray fluorescence analysis confirmed the presence of sulphur in both the white and blue material at a level of  $< 100$  ppm; this was in good agreement with subsequent wet-chemical analyses by gravimetric determination as  $BaSO_4$  which showed that the blue material contains 50 ppm and the white contains 85 ppm of sulphur.

The fact that the colourless bands contain higher sulphur concentrations does not automatically rule out the feasibility of a sulphur-containing chromophore since oxidation to sulphate might have occurred in the colourless regions. Nevertheless, the possibility of coloration by colloidal sulphide is ruled out by the extremely

low total sulphur concentrations since the physical scattering of light requires a higher sulphide concentration than would be present even if the total sulphur in the blue bands occurred exclusively as sulphide. Moreover, the presence of sulphide argues the presence of cationic metal impurities, of which Blue John is particularly free.

On the other hand, the presence of even 50–80 ppm of sulphur as the intensely coloured  $S_2^-$  ion could provide an explanation of the observed colour consistent with the sulphur analysis figures for the blue material (oxidation must again be invoked in explanation of the colourless regions). However, the optical spectrum of  $S_2^-$  is well known (Giggenbach, 1971) and when compared with that of Blue John (fig. 1) the latter is seen to lack two characteristic absorption bands, viz the weak band at  $\sim 2.5 \times 10^4$   $cm^{-1}$  and the very strong band at  $\sim 3.5 \times 10^4$   $cm^{-1}$ . Moreover, the thermal bleaching behaviour of Blue John at  $\sim 375$   $^\circ C$  militates against the possibility that  $S_2^-$  is the chromophore since the latter is stable even above 900  $^\circ C$ ; the spectra of borate glasses containing blue  $S_2^-$  have been measured up to 950  $^\circ C$  (Giggenbach, 1971). Thus coloration by  $S_2^-$  must be ruled out on the basis of both optical and

thermal evidence; the previously proposed coloration mechanism (MacKenzie and Green, 1971) still appears to be the most promising yet advanced.

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