

Conclusion. It appears that the initial tholeiitic magma, after the early precipitation and settling of olivine, was intruded in a dyke fissure. Strong undercooling, due probably to some loss of fugitives or also to the comparatively cool walls of the fissure, led to the nucleation of high-calcic pigeonite, the release of heat of crystallization keeping pace with the undercooling, so that its crystallization continued, promoting the growth of large elongate crystals in a melt that became supersaturated.

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[Manuscript received 6 December 1971].

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MINERALOGICAL MAGAZINE, DECEMBER 1972, VOL. 38, pp. 977-79

On the blue colour of natural banded fluorites

K. J. D. MACKENZIE and J. M. Green propose, in a recent article (this vol., p. 459), an explanation of the blue colour of natural fluorites based upon the presence of colloidal calcium particles. It seems, however, that this explanation—from studies on specimens gathered in two places (Ashover, Derbyshire, and Weardale, Co. Durham)—cannot be generalized and should be received with the greatest prudence. It is surprising, in fact, not to see recent studies on natural (Bill *et al.*, 1967) or synthetic (Staebler and Schnatterly, 1971) fluorites, to explain this blue colour.

Firstly, it is necessary to remind the reader that the classic 'four-band spectrum', first found by Smakula in X-irradiated fluorites, is constituted by bands at 224, 335, 400, and 580 nm. O'Connor and Chen (1963) have shown the action of yttrium concentration on this spectrum; from studies of Staebler and Schnatterly (1971) on synthetic fluorites doped with yttrium and some rare earths (La, Ce, Gd, Tb, and Lu)

and X- or γ -irradiated it appears that the responsible colour centre is orientated along [111] and consists of two electrons trapped by a fluorine vacancy and a nearest trivalent rare-earth ion (in the case of the classic spectrum seen above, it is an Yt^{3+} ion). This result was confirmed by E. P. R. studies (Anderson and Sabisky, 1971). This spectrum is very different from the Mollwo spectrum, obtained by additive coloration and constituted by two bands at 375 and 520 nm. This latter spectrum reveals the presence, near a single F-centre (an electron trapped in an anion vacancy), of F-aggregate centres (Beaumont *et al.*, 1972). The authors do not note the presence of colloidal calcium particles in either of these two cases.

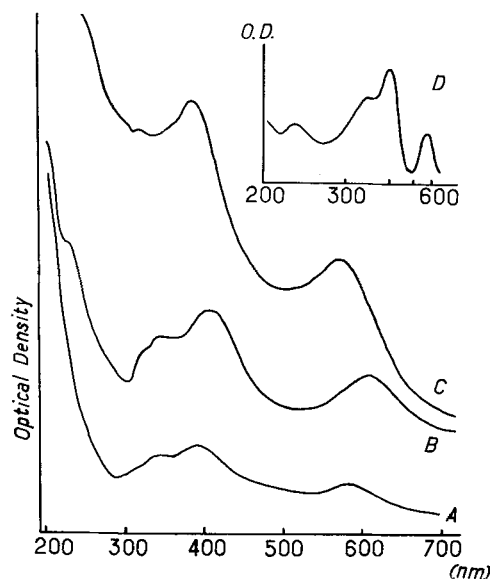


FIG. 1. Absorption spectra of some blue-zoned fluorites (at room temperature). Natural samples from: Djebel el Kohol (Tunisia), A; Valzergues (France), B; Chavaniac (France), C. Synthetic $\text{CaF}_2:\text{Yt}$, additively coloured or γ -irradiated (from Staebler and Schnatterly, 1971), D.

We have studied (Calas, 1972) the absorption spectra of cleaved blue-zoned fluorites from two French lodes (Valzergues, Aveyron, and Chavaniac, Haute Loire) and a Tunisian deposit (Djebel el Kohol) with a Cary 14 spectrophotometer: these spectra are identical to those obtained by Staebler and Schnatterly with, in addition, a very intense absorption at about 200 nm (where there are many absorptions due to OH^- , O^{2-} , and certain trivalent rare-earth ions). In this case, the coloration is not caused by colloidal calcium particles, and that shows the particularity of Derbyshire Blue-John fluorite: this latter has different optical properties and the theory of MacKenzie and Green is not valid for all blue-banded fluorites.

The presence of a band at 580 nm in Derbyshire fluorites is not a proof of the presence of colloidal calcium particles: this band is a typical feature of yttrium-doped and irradiated fluorites. However, the rest of the spectrum is very different because of the absence of the other bands in the U.V.

The colloidal theory of Allen (1952) was rejected because it was not based on experiments; it explained the diversity of colours of natural fluorites by the presence of colloidal particles of different sizes (which then diffuse light differently according to different wavelengths); we now know that these colours are due in fact to different colour centres (Bill *et al.*, 1967). In addition, results concerning the colloidal calcium presence in CaF_2 are very difficult to explain now: studies by Rao and Bose (1970) on low electron bombardment show very different results from those obtained by McLaughlan and Evans (1968), on which MacKenzie and Green rely. The role of impurities is obscure and it seems that the production of colloidal particles in X- or

γ -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 [III] 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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[Manuscript received 13 March 1972]

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MINERALOGICAL MAGAZINE, DECEMBER 1972, VOL. 38, pp. 979–81

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