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# The use of proton irradiation to reveal growth and deformation features in fluorite

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**Abstract**

It has long been known that natural fluorite, exposed to X-ray, $\gamma$-ray, or electron radiation develops diffuse purple-pink color banding. However, irradiation from 2.5 MeV protons or $\alpha$-particles with doses of from 5 to 50 $\mu C/mm^2$ develops color banding in extraordinary detail. This color banding is crossed by colored lines which are shown to be decorated growth dislocations. Deformation-induced dislocations decorated in the same manner are difficult to resolve by optical microscopy; nevertheless the effects of both brittle and plastic deformation are revealed by proton irradiation. Healed fracture surfaces, subgrain boundaries, kink- and deformation-band boundaries are all colored by the irradiation treatment. Although proton irradiation of fluorite provides the same type of information as that obtainable by X-ray topography, the technique is direct, rapid, has high resolution, and is applicable to samples with any degree of deformation.

## Introduction

During the past twenty years, application of dislocation etching techniques in studies of materials with the rock-salt structure, especially MgO and LiF, has resulted in notable advances to the understanding of detailed mechanisms of deformation (Stokes, 1972; Kingery *et al.*, 1976). Many results are applicable to other materials of simple structure such as metals and substances belonging to the fluorite structure type.

Fluorite is highly favored for fluid inclusion research of the genesis of ore deposits, and it is desirable to know the growth and deformation history in some detail for unequivocal interpretation of results. Moreover, fluorite is isostructural with $UO_2$ and $ThO_2$ and may serve as a model for such nuclear reactor materials. Despite this, few studies of natural or experimentally-deformed fluorite have been carried out. One reason for this is that fluorite is optically isotropic, so that features of deformation and recovery involving lattice rotation, which have an optical expression in anisotropic materials, cannot be observed easily with the polarizing microscope.

Fluorite is readily colored by X-rays, $\gamma$-rays, and electrons (Przibram, 1956). Ionizing radiation can often be used to develop color banding along growth layers in natural crystals and is useful in determining growth histories, but the bands are typically diffuse. Kubo (1966) noted the appearance of colored lines in a synthetic $CaF_2$ crystal following irradiation with 1.5 MeV protons. He attributed the effect to the decoration, with colloid particles, of dislocations introduced during irradiation. Natural fluorite crystals have been observed to rapidly develop a general coloration under proton irradiation (Lisitsyna, 1965), but no proton-induced decoration was reported in that study. Recently we have found that decoration can be produced by irradiation with 2.5 MeV protons or $\alpha$-particles with exposures of a few minutes (Wilkins *et al.*, 1978). By this simple irradiation technique, growth and deformation features are revealed in extraordinary detail.

## Method

Growth features are best observed on polished sections of a few millimeters thickness cut normal to crystal faces, if present. Deformed specimens can be

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cut in any convenient orientation. Selected areas are irradiated with protons or $\alpha$-particles from a van de Graaff accelerator until a light purple-pink coloration develops. This requires a total dose of 5–50 $\mu$C/mm$^2$. Typical beam conditions are 2.5 MeV ions, 150 nA, beam diameter 3 mm, exposure time a few minutes. Samples of much larger diameter can be irradiated using scanning techniques. There is a risk of bursting fluid inclusions and even cracking the specimen with heat developed by the use of higher beam currents. Penetration to 50 $\mu$m is achieved by 2.5 MeV protons, and 7 $\mu$m by 2.5 MeV $\alpha$-particles. Within the colored layer, inclusions and radiation induced features can be directly correlated by microscopic examination in transmitted light.

Samples with a range of natural color, developed growth forms, and degree of deformation were selected from the mineral collection of the Australian Museum, Sydney, and supplemented by fluorites in the CSIRO collection from a number of Australian ore deposits.

## Observations

### *Growth features*

Although protons and $\alpha$-particles are equally effective in revealing growth features, proton radiation has the distinct advantage of greater penetration, enabling surface scratches to be defocused during microscopic examination. This is illustrated by irradiations of different parts of a polished slab of fluorite with protons and $\alpha$-particles (Figs. 1a and 1b). A wealth of growth information is revealed by either radiation.

In certain parts of fluorite crystals, color banding along growth zones may be developed in considerable detail (Fig. 1c). Many of the color bands are only a few $\mu$m wide. Horizontal color bands are crossed by colored lines oriented to within 10° of normal to the growth banding. That they are linear, and not sections of planar features, is demonstrated in Figure 1d. The linear structures which cross the growth banding in the (100) growth sector in the lower part of that figure are seen in cross-section as points in the (001) growth sector in the upper part of the same figure. They are arranged in curved surfaces which merge together to form a sort of dendritic pattern (Figs. 1a and 1b). The nature of these linear features can be seen even more clearly on irradiated {111} cleavage surfaces of a crystal from Marion, Kentucky (Fig. 1e), which has a relatively low dislocation density ($\sim 10^4 cm^{-2}$). The lines intersect the cleavage surface at angles between 25° and 45° as expected for lines making small angles with $\langle 001 \rangle$, as $\langle 001 \rangle \wedge (111) = 35.3°$.

Two lines of evidence indicate that these linear features represent growth dislocations. Firstly, they are identical in appearance to growth dislocation images in X-ray topographs of fluorite (Beswick and Lang, 1972; Tanner, 1972), especially in the slight change of direction they make at certain growth boundaries. Secondly, concentrations of these lines in planes or bundles can be correlated with regions of enhanced contrast observed in strain birefringence patterns. In diamond, an analogous case, concentrations of strain birefringence have been shown to correlate with radiating bundles of growth dislocations observed in X-ray topographs (Lang, 1967).

### *Primary inclusion sites*

Primary fluid inclusions are observed to be situated in distinctive positions in relation to the growth features revealed by irradiation. In crystals grown on {100}, the primary inclusions are within cavities partially filled with successive layers of fluorite (Figs. 1f, 2a). Dislocation lines are visible approximately normal to the layering. Fluid inclusions are located at the junctions of growth sector boundaries within these partially filled cavities. It is clear that they correspond to the cavities commonly formed between mosaic blocks on fluorite crystal surfaces. As the crystal continues to grow, deposition of layers of secondary fluorite reduces the size of the cavity and its opening until it is finally sealed off, trapping some fluid.

In crystals which have grown with a simple {111} form, recorded by natural color bands parallel to the {111} cleavage, sections cut normal to the crystal faces may show a complex growth structure formed by small mosaic blocks, in which growth has occurred on a variety of crystallographic planes (Fig. 2b). The relative perfection of cleavage, however, shows that individual blocks are only slightly misoriented. All fluid inclusions in this green fluorite from Karibib, Namibia are of primary origin formed by the trapping of fluid along lineage boundaries. Inclusions, approximately tetrahedral in shape, are characteristic of such fluorites (Fig. 2c).

### *Deformation features*

Not only are growth features revealed by proton irradiation, but deformation features also become visible. Boundaries and sub-boundaries of all types are color-decorated. Healed fracture surfaces, the

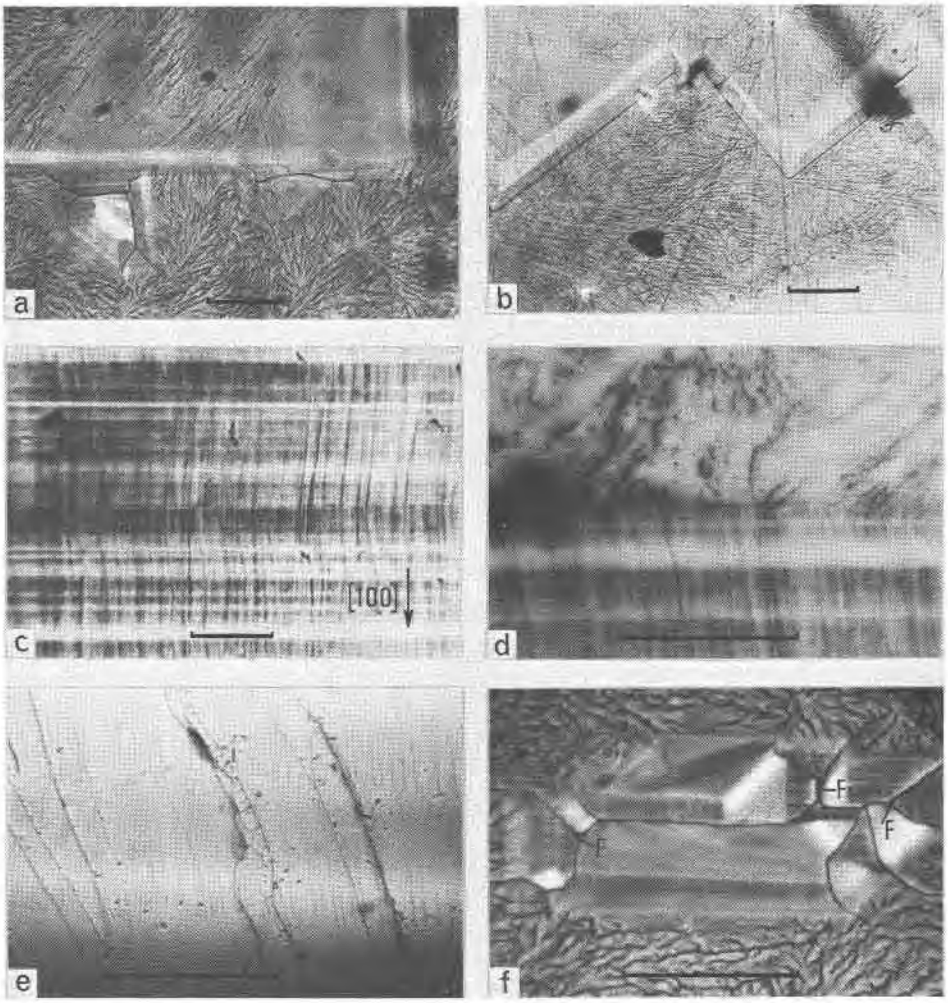


Fig. 1. Growth features revealed by proton or α-particle irradiation of natural fluorite. Only surface markings and fluid inclusions could be seen before irradiation. Bars represent 100 μm. All except (e) are purple fluorite from Rosiclare, Illinois. With the exception of (b) all specimens were proton-irradiated. (a) Fluorite crystal cut and polished parallel to (001), showing the region of a lineage boundary. Surface scratches defocussed. (b) α-particle irradiated lineage boundary region. Same surface as (a) but because of the thinness of the colored layer, scratches cannot be defocussed. (c) Section normal to cube face showing growth banding parallel to (100), and growth dislocations making small angles with [100]. (d) Growth dislocations observed as lines in the (100) growth sector in the lower part of the figure appear in section as points in the (001) growth sector in the upper part of the figure. The dislocations are arranged on curved surfaces which merge together to form a dendritic pattern, seen in 1a, b, and f. (e) (111) cleavage surface showing faint and relatively broad growth bands induced by radiation, and surfaces containing parallel dislocations making small angles with [001]. Yellow fluorite, Marion, Kentucky, Australian Museum D39504. (f) Section cut parallel to (001) shows partly filled cavities lined with fluorite layers parallel to the cavity walls. Note faint images of growth dislocations crossing the growth layering. Primary fluid inclusions (F) are situated within these partly filled cavities at the junctions of growth sector boundaries.

sites of origin of secondary fluid inclusions, become clearly marked (Fig. 2d). Some are simple but others have an unexpected complexity (Wilkins and Bird, 1979).

Microstructures in intensely and heterogeneously deformed fluorite are revealed in detail (Figs. 2e, f). The figured specimen from Woolgarlo, New South Wales, contains mildly deformed augen within fluorite which has the appearance of cataclastic microstructure. Within the augen, what appear to be deformation- or kink-band boundaries are visible in places. Intact fluid inclusions in the least deformed parts of the specimen are smeared out in zones of intermediate deformation and are absent in the adjacent highly deformed layers (Fig. 2f). The 'smearing' of inclusions shows that plastic deformation has occurred, and the microstructural characteristics of the material can best be explained if deformation oc-

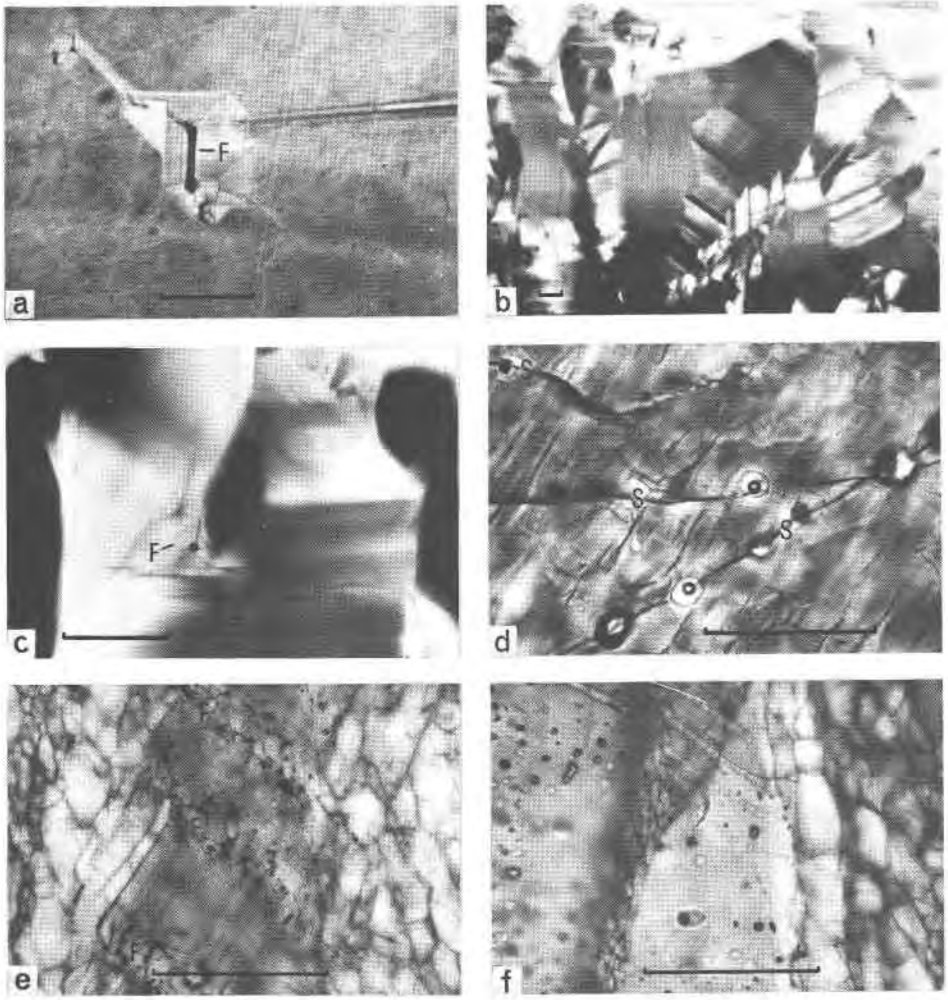


Fig. 2. Growth and deformation features revealed by proton irradiation of natural fluorite. Details as for Fig. 1. (a) Primary fluid inclusion (F), situated in a cavity which is incompletely filled with layers of fluorite. Deep surface scratches also color during irradiation. Purple fluorite, Aberfoyle Tin Mine, Tasmania. (b) Mosaic structure in a crystal which has grown mainly on {111}. Irradiation reveals that despite an almost perfect cleavage there were periods when the crystal grew as mosaic blocks on a variety of crystallographic planes. Section cut normal to (111). Green fluorite, Karibib district, Namibia. (c) Primary fluid inclusion (F), trapped between mosaic blocks in the same crystal. (d) Healed fracture surfaces (S) with fluid inclusions. The fracture surfaces were not visible before irradiation of the cleavage surface. Other lines appear to define lineage boundaries. Yellow fluorite, Marion, Kentucky. Australian Museum D39504. (e) Severely deformed white fluorite from Woolgarlo, near Yass, New South Wales. Australian Museum D21613. A less deformed central section with what appears to be deformation bands and smeared fluid inclusions (F) is surrounded on either side with fluorite having a cataclastic microstructure. (f) Little-deformed augen containing pre-deformation fluid inclusions, surrounded by intensely deformed fluorite in which fluid inclusions have been eliminated. Same specimen as (e). Boundaries could not be clearly seen before irradiation.

curred in the region of operation of restricted slip systems, below the temperature at which a general strain could be achieved. According to Pratt *et al.* (1966) this is between approximately 60° and 300°C at strain rates of $2.5 \times 10^{-3}$ and $2.5 \times 10^{-4}$/sec, but it is uncertain how appropriate these experimental data are to natural deformation conditions. Nevertheless, the range of grain size and the absence of triple junctions in the aggregate suggest that deformation occurred in the lower part of that temperature range, so that recrystallization was inhibited. 'Smeared' fluid inclusions in the material homogenize in the range 50°–200°C. The fluid was probably trapped during the waning stages of deformation, but an unknown positive correction, possibly as much as 100°C, is applicable due to pressure at the time of deformation.

## Mechanism of coloration

The origin of color in natural fluorite and its relationship to color introduced by radiation, or by additive coloration with calcium vapor, has proved to be a problem of considerable complexity. This is partly because a range of trace elements such as yttrium, rare earths, oxygen, and hydrogen can enhance the development of color by ionizing radiations (Hayes, 1970). In addition it seems clear that no simple correlation between color and trace-element content necessarily exists. Bill *et al.* (1967), for example, identify a rare-earth-related color center characteristic of red fluorites, but this only forms if a sufficient supply of impurity oxygen ions is available. In some cases, coloration has been attributed to the formation of metallic colloid particles. Furthermore, optical absorption spectra are in general complex, and bands having quite different origins may appear at more or less the same wavelength.

Absorption spectra of our proton-irradiated fluorites show an intense absorption band at 560–580 nm but only minor bands at 400 nm and below. This may arise from the temperature conditions associated with the irradiation. Lisitsyna (1965) has shown that the bands at 335 and 400 nm saturate rapidly, whereas the 580 nm band has both a saturating and linearly increasing component. The 335 nm band in "Blue John" fluorite is thermally bleached at 300°C, but the 580 nm band is only eliminated at 500°C (Braithwaite *et al.*, 1973). If local heating of the irradiated region of our samples produces temperatures between these two values, the predominance of the 580 nm band can be explained.

The proton-induced coloration is removed completely and uniformly from both the growth bands and the detailed decorated features by raising the specimen temperature to 550°C, and this can be attributed to either the dispersal of colloid metal or to annealing of atomic scale defects.

### *Defects*

Lisitsyna (1965) recorded an absorption spectrum of a natural fluorite which had been irradiated with 4.2 MeV protons. It showed the same four major bands at 225, 335, 400, and 580 nm as are observed for X-irradiated specimens (Smakula, 1950). These differ from the $\alpha$ and $\beta$ bands of Mollwo (1934) at 375 and 520 nm which are due to F, M and higher aggregate centers (Hayes, 1970). These simple defects cannot therefore be used to explain the effects of irradiation.

The high mass and hence momentum of protons and alpha-particles make them able to produce many defects along their path in the sample. The color-decorated features observed by Kubo (1966) in synthetic fluorite were interpreted as line defects generated during irradiation. His irradiations for 15 $\mu$A-hrs correspond to a radiation dose two orders of magnitude above that given to our natural fluorites. Using 10% $NaHSO_4$ as an etchant (Cockayne *et al.*, 1964), we established that no etchable defects are introduced at the doses used in our irradiations since identical patterns of etch pits are developed on matched cleavage surfaces, only one of which was irradiated. However, more features are etched than are revealed by coloration. Beswick and Lang (1972) also noted that some etch pits, which they supposed to have developed from dislocations introduced during cleavage, are not associated with resolved dislocation images in X-ray topographs of fluorite.

As sub-boundaries are characterized by dislocation arrays it is tempting to attribute the coloration of sub-boundaries in irradiated fluorite to that acquired by the dislocations within them. In healed fracture surfaces, etching studies (Wilkins and Bird, 1979) indicate that dislocations are 1–2 $\mu$m apart and should be readily resolved microscopically. As they are not, we conclude that, for sub-boundaries of this origin at least, color development is not due to dislocations, but is more likely associated with a different concentration of impurities in the secondary fluorite which heals the fractures. This is supported by the observation that some healed fracture surfaces are deficient in color relative to deeply colored growth zones which they intersect.

### *Impurities*

Natural fluorites have various colors (purple, green, yellow, red) which might reflect the presence of different impurity concentrations. However, irradiation with X-rays, gamma-rays, or protons all produce a characteristic violet-pink color and the classic four-band absorption spectrum. In a study of yttrium- or rare-earth doped, additively colored $CaF_2$, Staebler and Schnatterly (1971) found that in the case of yttrium dopant essentially the same bands are produced as with ionizing radiations. The 335, 400, and 580 nm bands were shown to result from a trivalent metal ion–fluorine ion vacancy complex that has trapped two electrons. For this to explain the observed effects of decoration, yttrium ions would need to be concentrated in the region of dislocations and other growth and deformation features. No detailed study has yet been made of impurity concentrations in synthetic and natural fluorites to provide confirmation. We have observed a green coloration produced by proton irradiation of a Gd-doped synthetic fluorite, suggesting that the nature of rare-earth impurities is indeed important. Proton-induced X-ray emission spectra show the presence of yttrium in some but not all of our samples, although the sensitivity of these measurements is markedly reduced by the high $\gamma$-ray production accompanying proton irradiation.

Growth dislocations are believed to be surrounded by a cylindrical zone in which strain is relieved by the concentration of impurities (Friedel, 1964). If the density of coloration is a function of the concentration of certain impurities, the observed decoration of growth dislocations could thereby be explained. It is significant that where color bands are developed in natural fluorite by proton irradiation the growth dislocation images which cross them are sympathetically banded (Fig. 1c). We also observe that on {100} sections the strain birefrigence is greatest in bands most deeply colored by proton irradiation. Variations in birefringence parallel to growth surfaces follow variations in lattice parameter, consequent upon non-uniform distribution of impurities (Lang, 1967). The birefringence is present before and after irradiation and it therefore reflects some intrinsic property of the different growth layers.

*Colloid particles*

An alternative explanation of fluorite coloration is that small particles of metal develop within the specimen and preferentially at dislocations—a process which has been studied with the additive coloration in metal vapor (Bontinck and Dekeyser, 1956). Kubo (1966) reported the formation of colloid particles by heavy proton irradiation of synthetic $CaF_2$. According to the Mie theory (Schulman and Compton, 1963), absorption spectra from suspensions of colloid particles have a peak whose wavelength moves towards the red as the size of the particles increases. As a result there is a characteristic blue appearance by transmission and red in scattered light. Although the absorption spectrum of our samples could possibly be explained by the formation of colloid particles, the process of decoration would require that such particles be nucleated preferentially at dislocations. No systematic change in color has been observed with increase in proton dose or beam current density which would influence the temperature of the irradiated region.

No conclusive evidence is thus available to definitively determine the mechanism involved in proton decoration of natural fluorite. Further study will be required to resolve this problem, bearing in mind that not all fluorites—natural or synthetic—will necessarily have the same origin for their coloration (Calas, 1972).

At 5 ppm U and 50 ppm Th, which are high levels of impurity in natural fluorite (Przibram, 1956), an equivalent radiation dose from $\alpha$-particle decay would require more than $10^9$ years. Decorated dislocations in natural fluorite would therefore only be expected under unusual conditions, although a general coloration by natural $\gamma$-radiation may have developed.

**Implications for fluid inclusion research**

The origin of inclusions is the initial problem to be solved in any fluid inclusion study. This requires information on the growth and deformation history of the host mineral. Primary inclusions form at or near growth surfaces and are associated with irregularities in the growth of the crystal. As growth banding records the position of former crystal surfaces, inclusions in a zonal arangement following this pattern, or inclusions associated with any growth irregularities such as boundaries between mosaic blocks, are probably primary in origin (Roedder, 1967). Secondary inclusions of brittle-deformation origin are located along healed fracture surfaces. Growth banding and healed fracture surfaces are both revealed by proton irradiation of fluorite, enabling inclusions to be broadly classified.

More detailed information is 'stored' in the dislocations and must be retrieved by etching studies, transmission electron microscopy, X-ray topography, or decoration techniques (Patterson and Wilsdorf, 1968). A systematic study of the relationship between primary fluid inclusions and dislocation structure in any mineral has not yet been made, but the association of secondary fluid inclusions of brittle-deformation origin with certain dislocation arrays is now well established (Carstens, 1969; Wilkins and Bird, 1979). Etching of dislocations is especially useful for this purpose and should be more frequently applied. Transmission electron microscopy at 100 keV is not a useful supplement to conventional fluid inclusion research, because fields under study are very small compared to the dimensions of 20–100 $\mu$m diameter inclusions normally used for microscope heating and freezing stage studies. X-ray topography reveals dislocation structure in detail, and extinction criteria enable Burgers vectors associated with the dislocation to be determined, but in practice it is very difficult to correlate small fluid inclusions with dislocation images in the topograph. It is only applicable to essentially undeformed crystals.

Proton irradiation of fluorite crystals provides the same sort of information as that obtained by X-ray topography, but it also has the special advantage of being applicable to samples with any degree of deformation. With a resolution down to 1 $\mu$m, direct correlation can be made between small inclusions and the dislocation structure revealed by color decoration. We have found that by the application of proton irradiation, the origins of inclusions within fluorite samples can be determined with confidence, and some tacit assumptions which often weaken the arguments used in fluid inclusion investigations can be eliminated.

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