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Cleavage and Etching of Prism Faces of Apatite

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A large number of (10$\bar{1}$0) perfect cleavages have been obtained by cleaving natural apatite crystals parallel to the prism faces. The (10$\bar{1}$0) faces have been studied by multiple-beam interferometry and it is observed for the first time that they are perfect, having regions as large as 10 mm^2 quite flat. The cleavages have been etched in citric acid successively for different periods and it is established that the pits indicate the sites of dislocations in the crystal. This is also confirmed by studies made on the etch patterns on matched cleavage faces. The nature of the dislocation is revealed by the structure of the pits. Along with the normal etch pattern, a stratigraphical etch pattern is also produced on some cleavage faces and it is observed that the stratigraphical pattern is displaced while crossing large cleavage steps. From the measurements made on the step height and the corresponding displacements in the stratigraphical pattern it is conjectured that the stratigraphical pattern reveals the edges of some weak growth layers deposited on the (10$\bar{1}$1) dome faces. It is thus conjectured that the crystals must have grown by deposition of layers on the dome faces. By etching a thin flake of thickness 1·8 mm it is shown that the stratigraphical sheets run right through the body of the crystal. The implications are discussed.

Introduction

Mineralogists and crystallographers have made extensive use of etching techniques to explore defects in solids (Patel & Tolansky, 1957; Keith & Gilman, 1960; Amelinckx, 1956, *etc.*). Gilman & Johnston (1956) on lithium fluoride, Patel & Ramanathan (1962) on mica, Patel & Goswami (1964) on topaz and Patel & Desai (1964) on calcium fluoride have shown that etch pits nucleate at dislocations and other surface defects.

Little work has been done on the etching of the apatite crystals. Honess (1927) used the etch figures produced on the natural basal and prism faces for indexing them. Lovell (1958) has reported etch beaks in apatite. She carried out etching on polished basal (0001) planes and found that, within the limits of her model, each pit corresponded to one dislocation. Price, Symes & Fleischer (1964) have reported the origin of anomalous etch pits in these crystals.

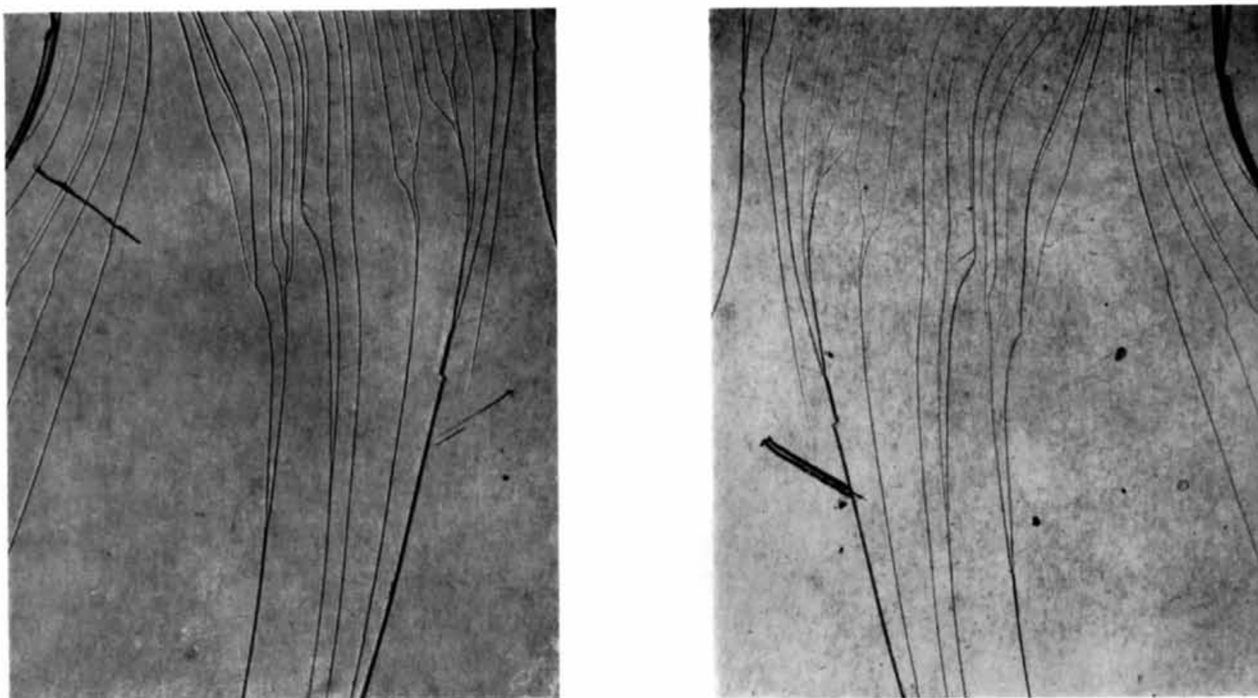
Apatite displays an imperfect basal (0001) cleavage, and a prism (10$\bar{1}$0) cleavage which is still more imperfect (Dana, 1963; Palache, Berman & Frondel, 1963). In studies of the distribution of dislocations on the basal cleavages of these crystals, attempts were made to produce basal cleavages by cleaving across basal planes. These operations produced chips cleaved along planes parallel to the prism faces which had very smooth and perfect cleavage faces. It is indeed surprising to find smooth cleavages parallel to the prism faces which are generally reported to show very imperfect cleavage. That these were (10$\bar{1}$0) cleavages was confirmed by etching. Since no work has so far been reported on these cleavages we have made an attempt in this paper to study their nature and the nature of their etch patterns.

Experimental

Natural transparent apatite crystals used in the present work were obtained from Dr P. B. Price, General Electric Research Laboratories, U.S.A. The (10$\bar{1}$0) cleavages were obtained in the manner described above. Different acids *e.g.* tartaric acid, citric acid, gaseous hydrogen chloride, nitric acid, and sulphuric acid at different concentrations were tried as chemical etchants. The best results were obtained by using citric acid of 50% concentration. In the etching experiments freshly cleaved faces of apatite were dipped in the etchant for the required period. They were then cleaned with distilled water, dried and examined under a metallurgical microscope after first depositing a thin silver film (reflectivity >95%) on them to enhance the contrast. They were then examined by multiple beam interferometry (Tolansky, 1948), phase contrast microscopy (Osterburg, Bennet, Jupnik & Richards, 1951), and light profile microscopy (Tolansky, 1952).

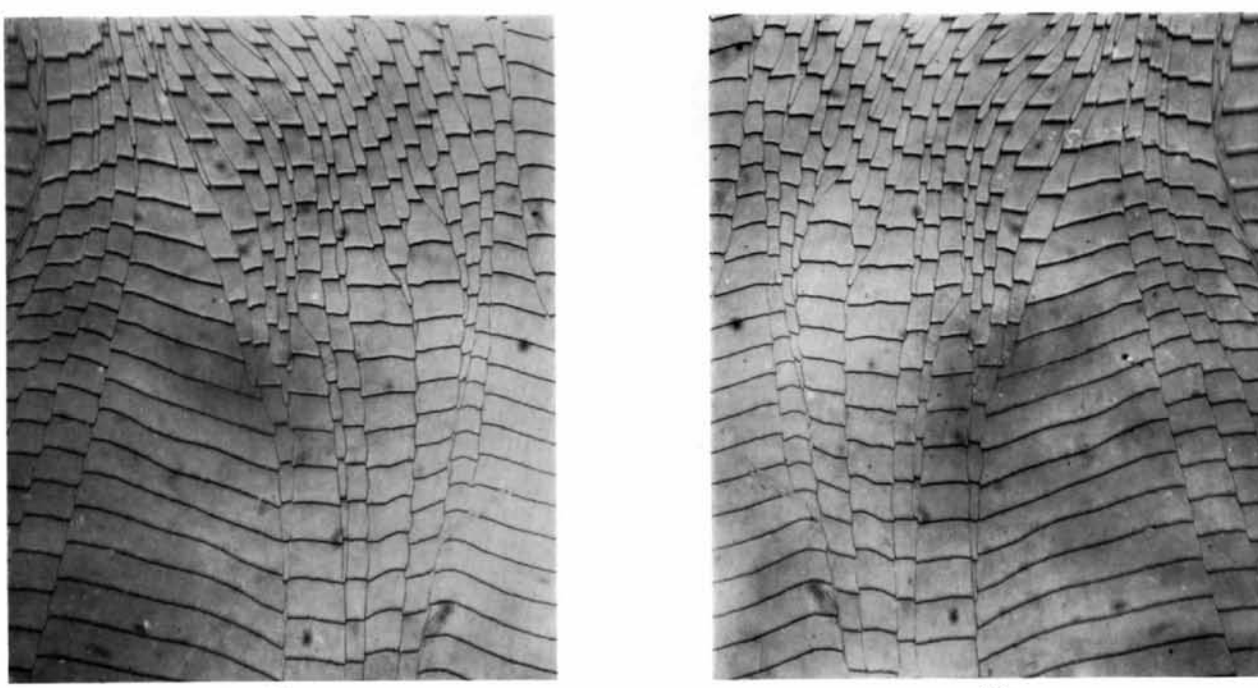
Observations

Fig. 1(*a*) and (*b*) represents one of the matched cleavage pairs obtained during our experiments on cleaving along planes parallel to the (10$\bar{1}$0) prism faces. From the nature of the cleavage lines in the picture it appears that it is a perfect cleavage. The nature of these faces is revealed in Fig. 2(*a*) and (*b*), which are multiple beam interferograms taken over the regions of Fig. 1(*a*) and (*b*) respectively. The topography of the faces is clearly revealed by the interferograms. It is very interesting to note from the nature of the fringes that the cleavage facets are quite flat and smooth. Some of the cleavage faces were selected and etched in citric acid



(a) (b)

Fig. 1. A matched pair of (10$\bar{1}$0) cleavage faces obtained by cleaving natural apatite (× 55).



(a) (b)

Fig. 2. (a) and (b). Multiple beam interferograms corresponding to Fig. 1 (a) and (b). (× 55).

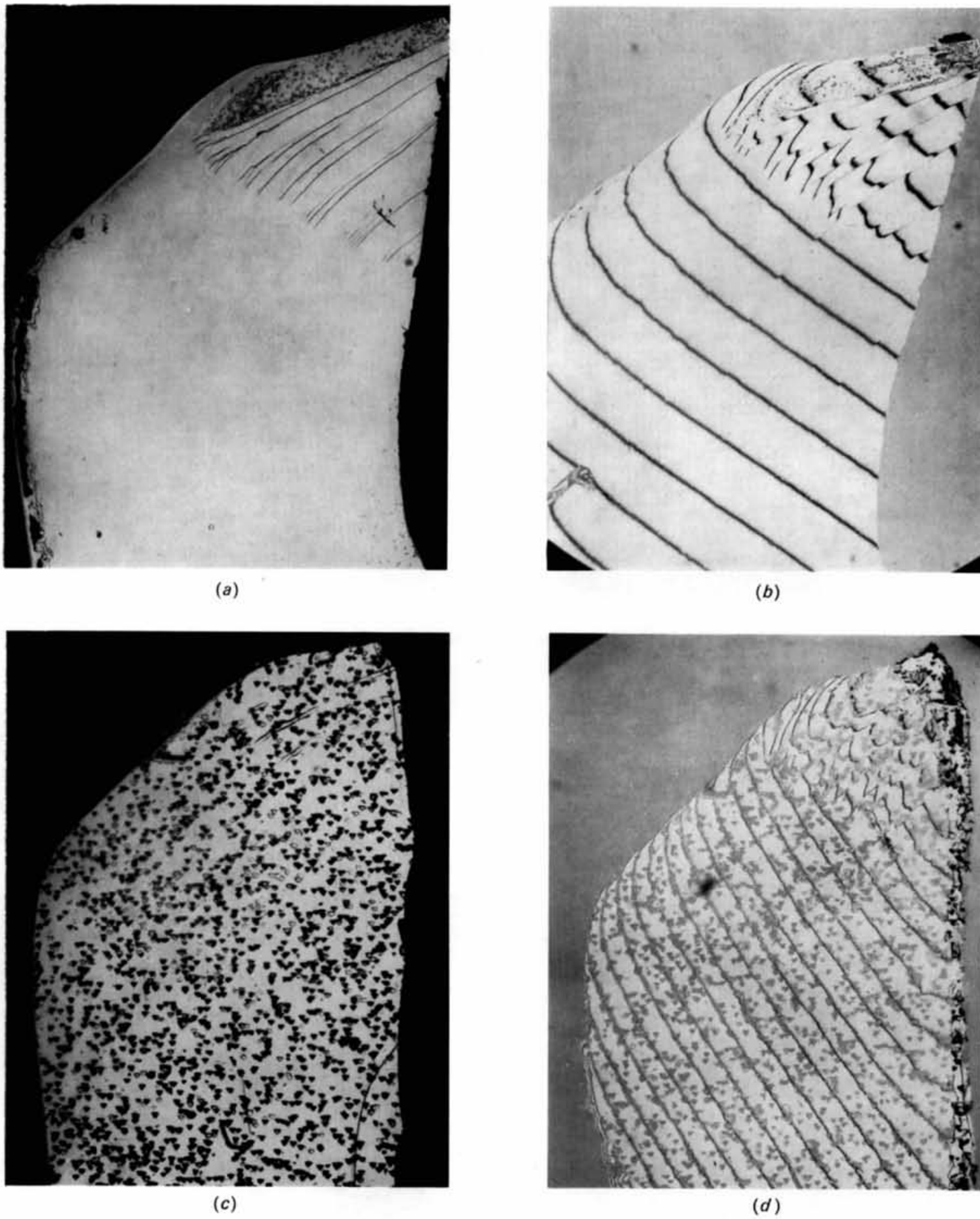
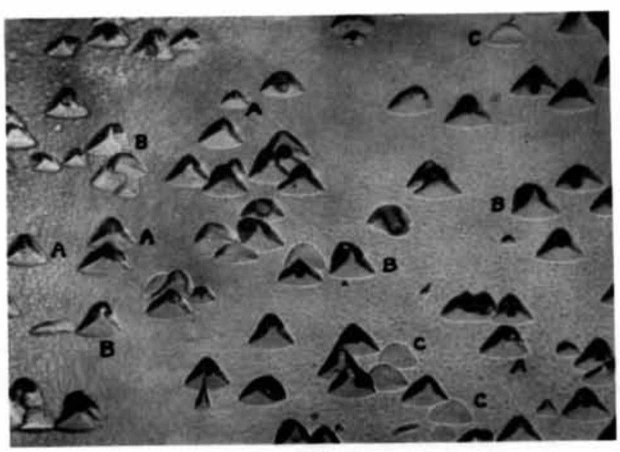


Fig. 3. (*a*) A (10$\bar{1}$0) cleavage face of apatite and (*b*) its multiple beam interferogram. (*c*) The etch pattern on the same face after treatment with citric acid for 45 min at room temperature. (*d*) The multiple beam interferogram of (*c*). (× 50).

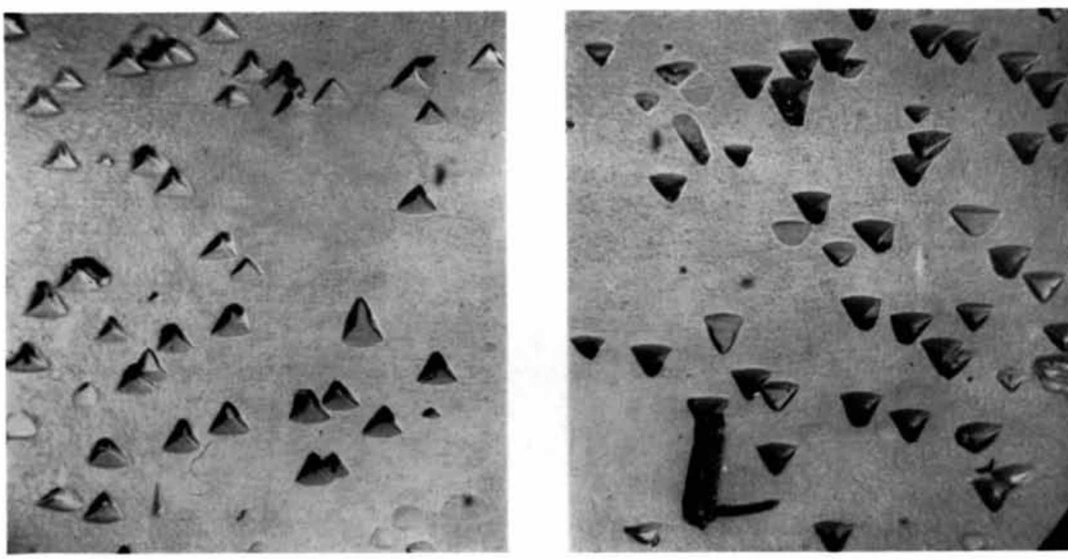
(*a*)



(*b*)

(*c*)

Fig. 4. Etch patterns of a (10$\bar{1}$0) cleavage face of apatite after etching at room temperature for (*a*) 20, (*b*) 40, (*c*) 60 min (× 125).



(a) (b)

Fig. 5. Matched cleavage faces after etching simultaneously in the same etchant (× 125).

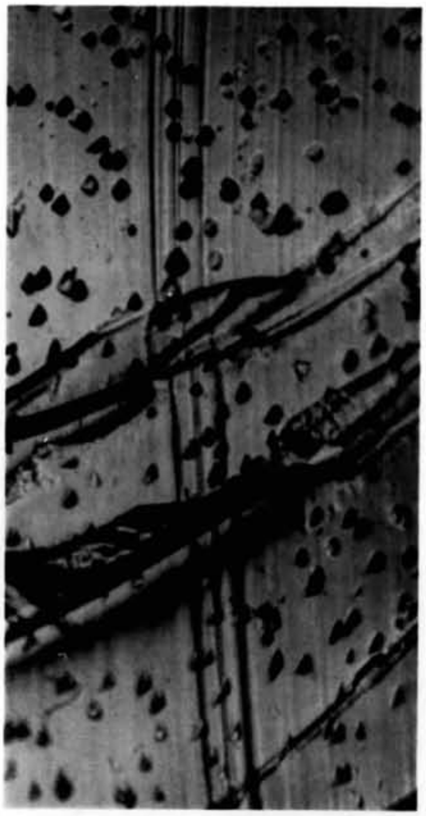
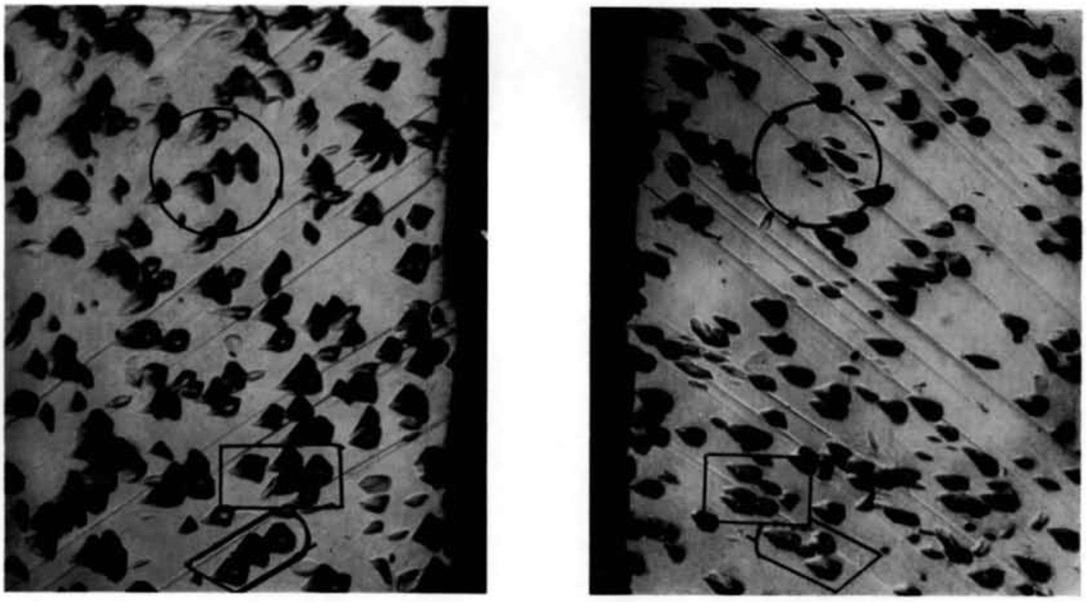


Fig. 6. Stratigraphical etch pattern on a (10$\bar{1}$0) cleavage face of apatite (× 80).



(a) (b)

Fig. 7. Etch patterns on opposite sides of a plate of apatite (× 120).

at room temperature for 45 minutes after examination by multiple beam interferometry. Thus in Fig. 3, (*a*) and (*b*) represent the cleavage face and its multiple beam interferogram respectively whilst (*c*) represents the etch pattern produced on the face. The individual isolated pits produced are clearly seen in (*c*). It may be mentioned that the shape and orientation of the pits in (*c*) are the same as those produced on natural $(10\bar{1}0)$ faces, thus confirming that the cleavage is $(10\bar{1}0)$. The nature of the surface after etching is revealed by the multiple beam interferogram of Fig. 3(*d*). Comparison of the interferograms of Fig. 3(*b*) and (*d*) reveals a striking contrast. The structure of the fringes in (*d*) reveals that not only are individual isolated pits produced on the surface but that general dissolution has taken place.

In order to test whether the individual isolated pits reveal the sites of dislocations in the prism cleavages, a $(10\bar{1}0)$ cleavage was successively etched for three different periods. Thus in Fig. 4, (*a*), (*b*) and (*c*) represent the etch patterns produced after 20, 40 and 60 minutes respectively at room temperature.

Attention is drawn to the following:

1. The shape of the etch pits resembles the shape of the pits on natural prism faces.
2. Successive etching does not produce any new pits, but the original pits grow in extension and in depth.
3. Most of the pits are point bottomed, curl bottomed and flat bottomed, as shown at A, B and C respectively in Fig. 4(*b*).
4. A point bottomed pit continues to be point bottomed and a curl bottomed pit continues to remain the same, *i.e.* the structure of the etch pits does not change on continued etching.
5. The pits of smaller size continue to be relatively smaller at all stages of etching.
6. The flat bottomed pits disappear on continued etching.

Etch patterns on matched cleavage faces

That the pits are formed at the sites of dislocations was further confirmed by etching $(10\bar{1}0)$ matched faces simultaneously in the same etchant. Thus Fig. 5(*a*) and (*b*) represents the etch patterns produced on the matched cleavage faces of the crystal. The correspondence in the number, positioning, size and the orientation of the pits is in accordance with those described by Gilman & Johnston (1956) in lithium fluoride, Mendelson (1961) in sodium chloride and Patel & Desai (1965) in calcium fluoride. Careful examination of the etch patterns on the matched faces reveals the following features:

1. The individual isolated pits have opposite orientations.
2. There is a one to one correspondence in the number and position of individual isolated point bottomed pits.
3. A pit of smaller size corresponds to a pit of smaller size on the matched face.
4. Some of the small and shallow pits observed on one face have no corresponding pits on the matched face.

The stratigraphy of the cleaved plates

In addition to etch patterns described above, linear etch patterns, *i.e.* stratigraphical etch patterns, are formed on some crystal cleavages. These are similar to those reported earlier by Patel & Tolansky (1957) on diamond, Patel & Goswami (1964) on topaz and Patel & Desai (1965) on calcium fluoride cleavages. Thus Fig. 6 represents such an etch pattern produced on the $(10\bar{1}0)$ cleavage face of apatite. The dark lines running across the picture are the large cleavage steps. It is clearly seen that the linear patterns are displaced where they cross the large cleavage steps. The displacement of the linear pattern is different at different cleavage steps. The shift in the pattern and the corresponding depth of the step were measured at a magnification (*m*) of 70 at a number of places along the cleavage steps. The observations are given in Table 1. From these observations, the inclination of the plane which may give rise to the stratigraphical pattern is calculated from the depth and the corresponding shift as reported by Patel & Tolansky (1957) and is given in the last column of Table 1. Now in apatite the angle that one prism face makes with an adjacent dome face is 49°41′ which is nearly the same as the calculated values of θ mentioned in the last column of Table 1. It may therefore be conjectured that the stratigraphy reveals the edges of some weak layers deposited on the dome $(10\bar{1}1)$ faces during growth which are revealed by preferential etching.

Table 1. *Displacement of rectilinear etch patterns across cleavage steps*

Obs. No.	Step height, h (microns)	Shift in the pattern, d (cm)	Angle calculated $\theta = \tan^{-1}(\alpha m \times h/d)$
1.	10	0·060 cm	49 29′
2.	12	0·073	49 1
3.	11	0·065	49 12
4.	13	0·075	50 35
5.	9	0·055	48 51
6.	12	0·072	50 3
7.	10	0·061	48 57
8.	13	0·077	49 43
9.	16	0·097	49 12

To investigate how far in the body of the crystal the stratigraphical pattern extends, a 1·8 mm thick plate of apatite was cleaved on both sides and etched in nitric acid. The patterns on both sides were then examined. Fig. 7(*a*) and (*b*) represents the etch patterns on the opposite sides of the thick plate of apatite. A close resemblance between the etch patterns on the opposite sides of the plate is clearly seen. It is thus clear that the stratigraphical patterns run right through the body of the crystal. A careful examination of etch patterns also reveals that some of the pits as marked in the figure show a correlation between the two faces of the plate.

Conclusions

Although (10$\bar{1}$0) cleavage on apatite is generally somewhat imperfect, the interferograms taken on the cleavage faces discussed here indicate that over quite large regions on this face perfect cleavage occurs. The interferogram on the etched cleavage face reveals that the etch attack is twofold: (1) attack producing general dissolution of the surface by micro-pit formation and (2) attack at isolated places indicating the sites of dislocations. Successive etching of the same face for different periods produces no new pits, but simply enlargement of existing pits. This suggests that the pits may be dislocation etch pits. This is also supported by the observation of correlated pits on matched pairs of faces. The calculations made on the stratigraphical etch pattern from its displacement while crossing large cleavage steps and the corresponding step height indicate the deposition of some weak planes on the (10$\bar{1}$1) dome faces of the crystal during growth. When the crystal is cleaved and etched, the edges of these layers form rectilinear patterns on the (10$\bar{1}$0) faces, which are preferentially attacked during etching, thus producing the stratigraphical pattern observed. The correlation in the etch pattern on the two sides of a 1·8 mm thick plate suggests that the weak planes run right through the body of the crystal.

The authors take this opportunity to express their thanks to Dr P. B. Price of the General Electric Research Laboratory, U.S.A. for supplying apatite crystals for these investigations.

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X-Ray Diffraction Study of Cold-Worked α Ag–Cd Alloys

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The Geiger counter X-ray diffractometer has been employed for the study of line profiles from cold-worked silver–cadmium alloys in the solid solution range. Stacking fault densities α and β have been obtained from measurements of peak-shift and peak asymmetry and a linear dependence of deformation fault probability α with solute concentration has been observed. Warren & Averbach's method of Fourier analysis of line shapes has been used for the evaluation of effective particle sizes $[D_e]_{hkl}$ and root mean square strains $[\langle\varepsilon_L^2\rangle]^{\frac{1}{2}}_{hkl}$ and it has been found that both are anisotropic in nature and vary with increasing solute content. The importance of faulting in the particle size broadening is also clearly observed.

Introduction

The study of cold-worked metals and alloys by X-ray diffraction is important as it reveals a fairly detailed picture of the deformed state. According to X-ray study cold-work is known to cause broadening of X-ray powder diffraction line profiles, and it is generally agreed to-day that the broadening in f.c.c. metals and alloys results from a reduction in the size of the coherently diffracting domains, from distortion within these coherent domains and from stacking faults on (111) planes. In addition to line broadening, peak-shift and peak