APPENDIX

APPENDIX - A

CLEAVAGE AND ETCHING OF PRISM FACES OF APATITE

A - 1 Introduction

Little work has so far 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 (0001) planes and found that, within the limits of her model, each etch pit corresponded to one dislocation. Price, Symes and Fleischer (1964) have reported the origin of anomalous etch pits in these crystals.

The crystal form of apatite $[Ca_5(Cl,F)(PO_4)_3]$ is hexagonal bipyramidal of the class 6/m, and it varies in habit from long prismatic to short prismatic and tabular as shown in figures 124(a), 124(b) and 124(c). Apatite displays an imperfect basal (0001) cleavage, and a prism $(10\bar{1}0)$ cleavage which is still more imperfect (Dana 1963; Palache, Berman and Frondel, 1963). In studies of the distribution of dislocations on 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. In fact it was seen for the first time that in some of the experiments, a perfect cleavage along the prism faces over an area as large as ten sq. mm. could be obtained. That the cleavages were $(10\bar{1}0)$ cleavages was confirmed by etching. Since no work has so far been reported on these cleavages an attempt has been made in this appendix to study their nature and the nature of their etch patterns.

A - 2 Experimental

Prismatic yellow transparent natural single crystals of apatite 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, sulphuric acid at different concentrations were tried as chemical etchants. The best results were obtained by using citric acid of 50 % concentration, because it was a weak etchant and so the crystals could be etched slowly yielding greater control over the development of pits. 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 contrast. They were then examined by multiple beam interferometry and phase contrast microscopy.

A - 3 $(10\bar{1}0)$ cleavages and their etch patterns

Figures 125(a) (X 55) and 125(b) (X 55) represent one of the matched cleavage pairs obtained during the experiments on cleaving along planes parallel to the $(10\bar{1}0)$ 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 figures 126(a) (X 55) and 126(b) (X 55) which are multiple beam interferograms taken over the regions of figures 125(a) and 125(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 at room temperature for 45 minutes after examination by multiple beam interferometry. Thus figures 127(a) (X 55) and 127(b) (X 55) represent the cleavage face and its multiple beam interferogram respectively whilst figure 127(c) (X 55) represents the etch pattern produced on the face. The individual isolated pits are clearly seen in figure 127(c). It may be mentioned that the shape and orientation of the pits in figure 127(c) are the same as those produced on natural $(10\bar{1}0)$ faces as shown in figures 128 (X 250) and 129 (X 250). Here figure 128 (X 250) is a magnified photograph of a region of figure 127(c) (X 55) and figure 129 (X 250) represents the etch pattern on the natural $(10\bar{1}0)$ face of apatite. Thus it is confirmed that the cleavage studied above is $(10\bar{1}0)$. The nature of the surface after etching is revealed by the multiple beam interferogram of figure 130 (X 55) taken over the region of figure 127(c). Comparison of the interferograms of figure 127(b) and figure 130 reveals a striking contrast. The structure of the fringes in figure 130 reveals that not only are individual isolated pits produced on the surface but that general dissolution also 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 figures 131(a) (X 300), 131(b) (X 300) and 131(c) (X 300) 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 the 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 figure 131 (b) (X 300).

(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.

A - 4 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 figures 132(a) (X 300) and 132(b) (X 300) represent 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 and Johnston (1956) in lithium fluoride, Mendelson (1961) in sodium chloride and Patel and 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 considerable amount of 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.

A - 5 <u>Rectilinear etch patterns</u>

(a) <u>Calculation of angle</u>

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 by Patel and Tolansky (1957) on diamond. Thus figure 133 (X 125) represents an etch pattern produced on the $(10\bar{1}0)$ cleavage face of apatite. The dark lines running across the picture are large cleavage steps. It is clearly seen that the linear patterns are displaced where they cross the large cleavage steps. The shift in the pattern and the corresponding depth of the step ware measured at a magnification (m) of 70 at a number of places along the cleavage steps. The observations are given in Table No. A - 1.

TABLE A - 1

DISPLACEMENT OF RECTILINEAR ETCH PATTERNS ACROSS CLEAVAGE STEPS

Obs. No.	Step height, h (Microns)	Shift in the Pattern, d cm.	Angle Calculated $\theta = \tan^{-1}(\alpha m \times \frac{h}{d})$
1.	10	0.060	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'

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 and Tolansky (loc cit) and is given in the last column of the Table A- 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 A- 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.

(b) <u>Matching of etch patterns on the opposite sides of a cleavage plate</u>

To investigate how far in the body of the crystal the stratigraphical pattern extends, a cleaved 1.8 mm thick plate of apatite was etched in nitric acid. The patterns on the two opposite sides were then examined. Figures 134(a) (X 200) and 134(b) (X 200) represent 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.

A - 6 Conclusions

Although $(10\bar{1}0)$ cleavage on apatite is generally somewhat imperfect, the interferograms taken on the cleavage faces discussed in this appendix 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 two fold.

(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 of 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.