

# Etch pits on basal cleavage faces of apophyllite crystals

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## Abstract

Basal cleavage faces of apophyllite crystals were etched in the base etchant (dil HF) containing different concentrations of ammonium fluoride as a poisoning salt. At low concentrations, square pyramidal pits formed with their sides parallel to the  $\langle 100 \rangle$  direction. At higher concentrations, pits with their sides parallel to the  $\langle 110 \rangle$  direction were formed. The lateral growth of a pit is dependent on pH value of the etching solution. Activation energy for dissolution at a pit (active site) was found to decrease with increasing concentration of poison in the base etchant. The change in orientation of the pit is attributed to adsorption of aqueous complexes having different chemical constitutions which have different directional adsorption sites in apophyllite.

KEYWORDS: apophyllite, etch pits, cleavage.

## Introduction

CONSIDERABLE interest has recently been shown in experimental studies of the dissolution kinetics and mass transfer rate during weathering of silicates (Lasaga, 1983; Helgeson, 1984). It has

been observed that in silicates and aluminosilicates immersed in a solvent, dissolution at the site of a dislocation is greater than that on the remaining exposed surface (Joshi and Ittyachen, 1967*a, b* and *c*; Kotru *et al.*, 1979; Grandstaff, 1978; Gupta and Kotru, 1981; Lasaga and Blum,

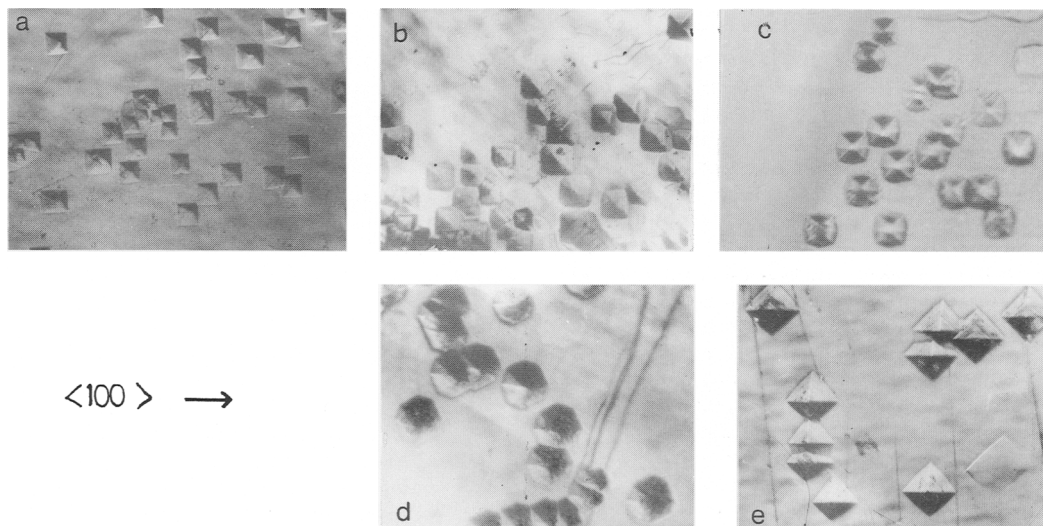


Fig. 1. (001) face of apophyllite crystal etched in the base etchant containing (a) 0.6 moles of NH<sub>4</sub>F (etching time 15 sec); (b) 2.0 moles of NH<sub>4</sub>F (for 30 sec); (c) 3.0 moles of NH<sub>4</sub>F (for 45 sec); (d) 4.0 moles of NH<sub>4</sub>F (for 75 secs); (e) 6.0 moles of NH<sub>4</sub>F (for 120 secs). All  $\times 300$ .

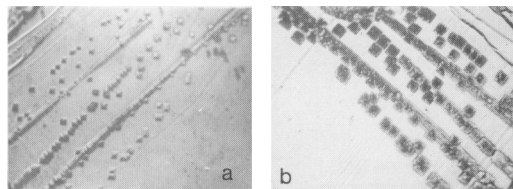


FIG. 2. Matched faces of apophyllite crystals etched in the base etchant containing (a) 0.6 moles and (b) 6.0 moles of  $\text{NH}_4\text{F}$ . Note the orientation of pits. ( $\times 230$ , etching time 10 sec (a), 30 sec (b)).

1986). This preferential dissolution causes formation of a pit on the surface at the site of a defect. For a pit to be readily visible, the ratio of lateral dissolution rate,  $V_s$ , to normal dissolution rate,  $V_n$ , should be less than 10 (Gilman *et al.*, 1958).  $V_s$  can be increased or  $V_n$  decreased by adding poisoning salt in the solvent. Mostly inorganic salts dissolved in the solvent have been used as a poisoning salt.

The overall dissolution process at the dislocations or at active sites can be viewed (for many minerals) as a consequence of adsorption, exchange and detachment reactions. The dependence of mineral dissolution rate on the aqueous species, including the hydrogen ions, is commonly interpreted in terms of surface complexes created by reversible adsorption of these species (Furrer and Stumm, 1986; Lasaga and Blum, 1987; Gandstaff, 1977). The concentration of the surface complexes depends on the concentration of the dissolved species according to the law of mass action for adsorption equilibrium. The significance of surface complexity reactions for mineral dissolution rate has been brought out by Stumm and co-workers (Stumm *et al.*, 1983; Furrer and Stumm, 1983, 1986; Zinder *et al.*, 1986). Murphy and Helgeson (1987) have shown that during the hydrolysis of silicate in acid,  $\text{H}^+$  ions or  $\text{H}_3\text{O}^+$  ions commonly replace exchangeable surface cations which are released into a solution. Sangwal (1982a and b) has used the concept of adsorption potential to show that the substitutional reaction is the fastest at the dislocation site compared to those at a kink, on a ledge or on a surface. This mechanism explains the change in pit morphology as well as the lateral growth of a pit. In the past much work has been done to study the formation of etch pits of different morphology by changing concentration of either etchant or of the poisoning salt in the etchant.

Joshi and Ittyachen (1967c) have shown the rotation of etch pits on basal cleavage faces of an apophyllite crystal as a consequence of change

in concentration of ammonium bifluoride etching solution. They attributed the rotation to the difference in the resistivities (to etching) of the edges of growth layers on 'a' and 'p' faces which extends on the basal plane of the crystal.

Here we report the effect of  $\text{NH}_4\text{F}$  as a poisoning salt, mixed in dilute HF, on the morphology of pits formed at active sites on the basal faces of apophyllite crystals. The effect of pH (of etching solution) on lateral dissolution rate is also given. The contribution of complexes formed in the process towards directional dissolution has also been studied.

Such a study can help in understanding the reactions that lead to the formation of activated complexes responsible for controlling the dissolution rates at the active sites and the interactions between the aqueous complexes and exchangeable cations available on the mineral surface.

### Experimental

The main occurrences of apophyllite are as a secondary mineral in amygdales in basalt, where it is often accompanied by zeolites. The apophyllite crystals used in the present work were collected from the Deccan trap lavas of the Poona area (Western India, Lat  $18^\circ$ , Long  $73^\circ$ ). These crystals are often accompanied by stilbite. The sector growth in Deccan trap apophyllite has been studied by Saha and Roy (1969). Small pieces of apophyllite [ $\text{K}, \text{Ca}_4\text{F}(\text{Si}_8\text{O}_{20}) \cdot 8\text{H}_2\text{O}$ ] were cleaved on (001) (which is also a basal cleavage face) and used for etching studies.

The base etchant was prepared by mixing HF (40%) with distilled water in the volume ratio 1:100. Ammonium fluoride was used as a poisoning salt. The effect of poisoning salt on pit morphology was studied by varying the concentration of ammonium fluoride from 0.6 to 6.0 moles/litre of the base etchant.

The change in lateral dissolution velocity ( $V_s < 100 >$ ) along the  $< 100 >$  direction, with variation of concentration of poisoning salt in the base etchant was calculated from measurements of pit widths.

The pH value of the base etchant has been theoretically calculated; it was also measured for each solution containing various amounts of  $\text{NH}_4\text{F}$ , using pH strips (sensitivity 0.5). Probable error in each measured value is shown by error bars in the relevant figure (Fig. 5).

### Results

It was observed that the addition of  $\text{NH}_4\text{F}$  in the base etchant causes etch pits to be formed

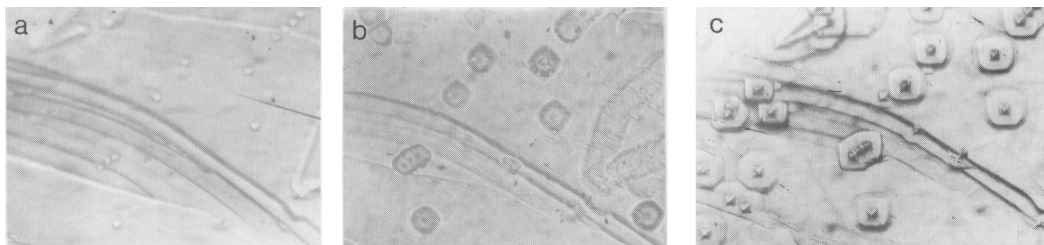


Fig. 3 (a) (001) face of apophyllite crystal etched in the base etchant containing 0.6 moles of  $\text{NH}_4\text{F}$  (etching time 5 sec). (b) Same sample pretreated as in (a) etched with the base etchant only (etching time 2 sec). (c) Sample treated as in (b) was then treated with the etchant containing 0.6 moles of  $\text{NH}_4\text{F}$  in the base etchant (etching time 10 sec). All  $\times 300$ .

TABLE 1

Etch pit morphologies on (001) face of apophyllite crystal, resulting from different concentrations of  $\text{NH}_4\text{F}$  in the base etchant or  $\text{NH}_4\text{HF}_2$  solution.

S.No.	Conc. of the $\text{NH}_4\text{F}$ in the base etchant (Moles)	Conc. of $\text{NH}_4\text{HF}_2$ * solution (N)	Shape of pits
1	0.6	0.6	
2	2.0	2.0	
3	3.0	3.0	
4	4.0	4.0	
5	6.0	6.0	

\* - Joshi and Ittyachen 1967c

on basal faces of apophyllite crystal, the shape of a pit being dependent on the concentration of poisoning salt in the solvent. For 0.6 moles of  $\text{NH}_4\text{F}$  in the base etchant, square pyramidal pits with their sides parallel to the  $\langle 100 \rangle$  direction were produced; however at higher concentration of poisoning salt in the solvent, i.e. for 6.0 moles, the square pits with sides parallel to the  $\langle 110 \rangle$  direction were formed. For intermediate concentrations, pits with blunt corners and octahedral pyramidal shapes were formed. Fig. 1 (a-e) shows

photomicrographs illustrating these changes. When a crystal is cleaved a pair of matched faces is obtained. The etch pit patterns on these faces show mirror symmetry (as the pits are formed at the sites where dislocations meet the surface). Fig. 2a shows one of the matched faces etched in the base etchant containing 0.6 moles of  $\text{NH}_4\text{F}$  and Fig. 2b shows its counterpart etched in the base etchant containing 6.0 moles of  $\text{NH}_4\text{F}$ . The sides of the etch pits in Fig. 2b appear to be making angle of  $45^\circ$  with the sides of etch pits in Fig. 2a, i.e. the pits have different orientations.

Similar results were also observed by Joshi and Ittyachen (1967c) for apophyllite dissolved in  $\text{NH}_4\text{HF}_2$  solution. These are tabulated in Table 1. In that study etchant concentration ranged from 0.6N to 6.0N. Further, we observed that when the basal face, which is pre-treated with solvent containing a low concentration of poisoning salt, is treated with the base etchant (dil HF), the outlines of shallow pits appear along the  $\langle 110 \rangle$  direction. These outlines are restored to the original  $\langle 100 \rangle$  direction when the crystal is treated again with the base etchant containing 0.6 moles of  $\text{NH}_4\text{F}$ . These results are shown in Fig. 3a, b and c.

It was found that the lateral growth of a pit along  $\langle 100 \rangle$  decreases as the concentration of poisoning salt in the solvent increases. Fig. 4a shows the variation in lateral growth rate of pit with concentration and temperature. The logarithmic value of  $V_{s\langle 100 \rangle}$  is given as a function of inverse temperature in Fig. 4b, from which the activation energy for dissolution was calculated (Patel and Arora, 1974). Values of activation energies for different concentration of  $\text{NH}_4\text{F}$  in the base etchant are tabulated in Table 2.

pH values of the etching solvents were measured and were found to increase with the increase in concentration of poisoning salt in the base etchant as shown in Fig 5.

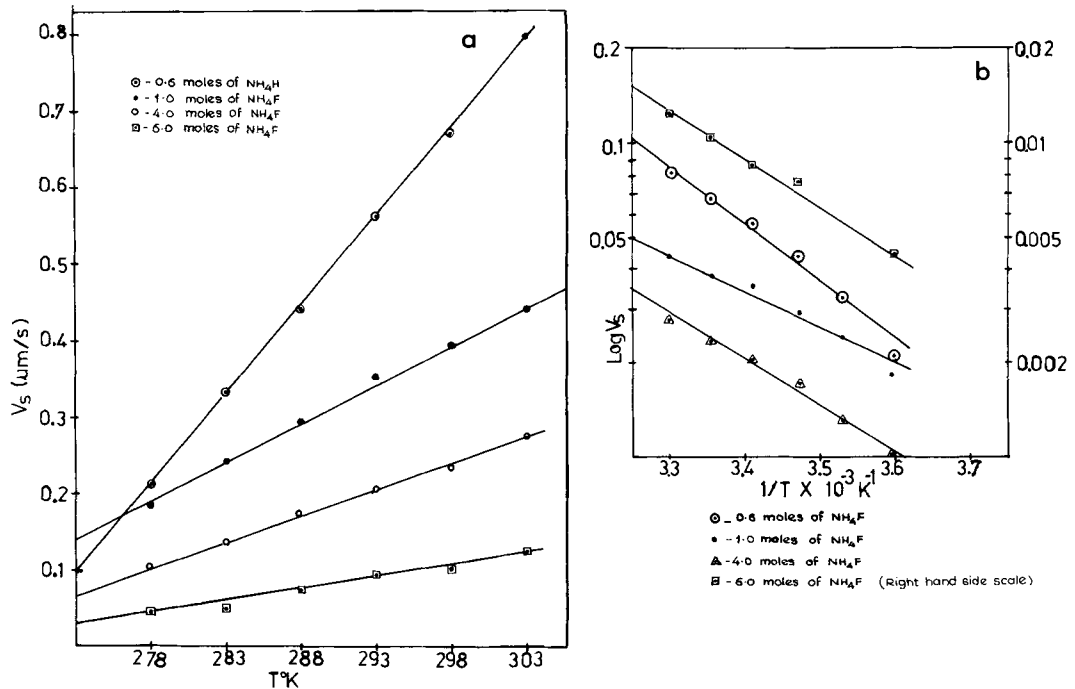


Fig. 4. (a) Variation in lateral dissolution velocity along  $\langle 100 \rangle$  direction with change in temperature and concentration of  $\text{NH}_4\text{F}$  in the base etchant. (b) Logarithmic variation of  $V_{s<100>}$  with inverse temperature.

TABLE 2

Activation energies for etching of (001) surface of apophyllite crystals in base etchant with different concentrations of  $\text{NH}_4\text{F}$ .

S.N.	conc. of $\text{NH}_4\text{F}$ in the base etchant (Moles)	Activation energy $E_d$ (eV)
1	0.6	0.0464
2	1.0	0.01769
3	4.0	0.01186
4	6.0	0.009438

The apophyllite has a tetragonal structure with  $a = 9.00 \text{ \AA}$  and  $c = 15.84 \text{ \AA}$ . The crystals show good external forms with  $a$  (100),  $p$  (111), and  $c$  (001) which is also a basal cleavage face. Fig. 10 shows a well developed crystal of apophyllite with  $a$ ,  $p$  and  $c$  faces.

Joshi and Ittyachen (1976a, 1968) have suggested that in the latter stage of growth of an apophyllite crystal, most of the growth occurs on the

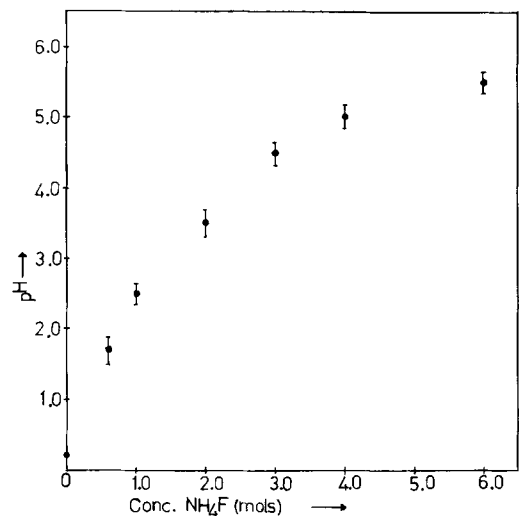


Fig. 5. Variation in pH with change in  $\text{NH}_4\text{F}$  concentration in the base etchant.

$a$  faces. The edges of the growth layers of the  $a$  faces which also extend on the basal plane with their traces parallel to the  $\langle 100 \rangle$  direction, are

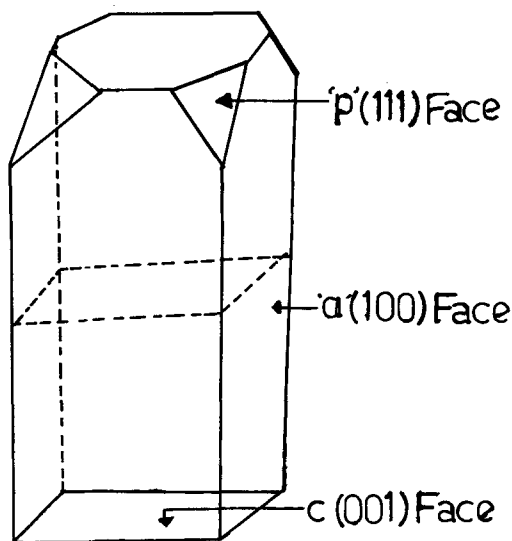


Fig. 6. Apophyllite crystal showing well developed  $a$ ,  $p$  and  $c$  faces.

less resistant to etch than the edges of growth layers on  $p$  faces (which also extend on the basal plane with their traces in the  $\langle 110 \rangle$  direction). Consequently square etch pits with their sides parallel to  $\langle 100 \rangle$  may be expected on the basal cleavage at lower concentration of the etchant. At higher concentrations the edges of the growth layers of  $p$  faces extending on the basal cleavage become etched, and hence square pits with their sides parallel to  $\langle 110 \rangle$  are formed.

However, the formation of a square etch pit with its sides parallel to  $\langle 100 \rangle$  suggest that the dissolution rate along  $\langle 110 \rangle$  is  $\sqrt{2}$  times greater than that along  $\langle 100 \rangle$  (Fig. 7). The rates of dissolution are reversed for further increase in  $\text{NH}_4\text{F}$  concentration, causing the change in orientation of etch pit.

The dissolution rates at active sites depend on the concentration of hydrogen ions, hydronium ions, water dipoles or hydroxyl ions. These factors are pH dependent. Murphy and Helgeson (1987 *a* and *b*) have cited a number of silicates in which the dissolution and the detachment reactions at the active sites are pH dependent. The observed decrease in  $V_{s\langle 100 \rangle}$  with increase of pH in apophyllite crystals, is in agreement with the above argument. However the observed change in orientation of the pit cannot be attributed to change of pH alone, because at two different values of pH (lower and higher) (Fig. 5) the dissolution velocity along  $\langle 100 \rangle$  is observed to be faster than that along  $\langle 110 \rangle$ .

The shape of an etch pit and its orientation is determined by the relative rates of chemical attack along different crystallographic directions. These rates in turn depend on the interaction between aqueous complexes formed in the etchant (by poison) and on the geometrical arrangements of the ions on a crystal surface. The chemical constitution of these complexes depends on the concentration of the salt in the solution as well as on the concentration of another substance having an anion in common with the additive salt; each successive complex thus formed is more stable (Bjerum *et al.*, 1958).

Our results can be explained on the basis of the theory of adsorption of aqueous complexes at the active sites. The complexes formed in the etchant at lower concentration of poison become adsorbed along the  $\langle 100 \rangle$  direction on basal face of apophyllite crystal; this adsorption inhibits dissolution along  $\langle 100 \rangle$ , causing a  $\langle 100 \rangle$  oriented pit. Similarly the observed  $\langle 110 \rangle$  oriented pits can be explained on the basis of adsorption of aqueous complexes formed at higher concentration of  $\text{NH}_4\text{F}$  in the base etchant along the  $\langle 110 \rangle$  direction. It seems that the directional dissolution at the active sites can be attributed to aqueous complexes present in the etching solution.

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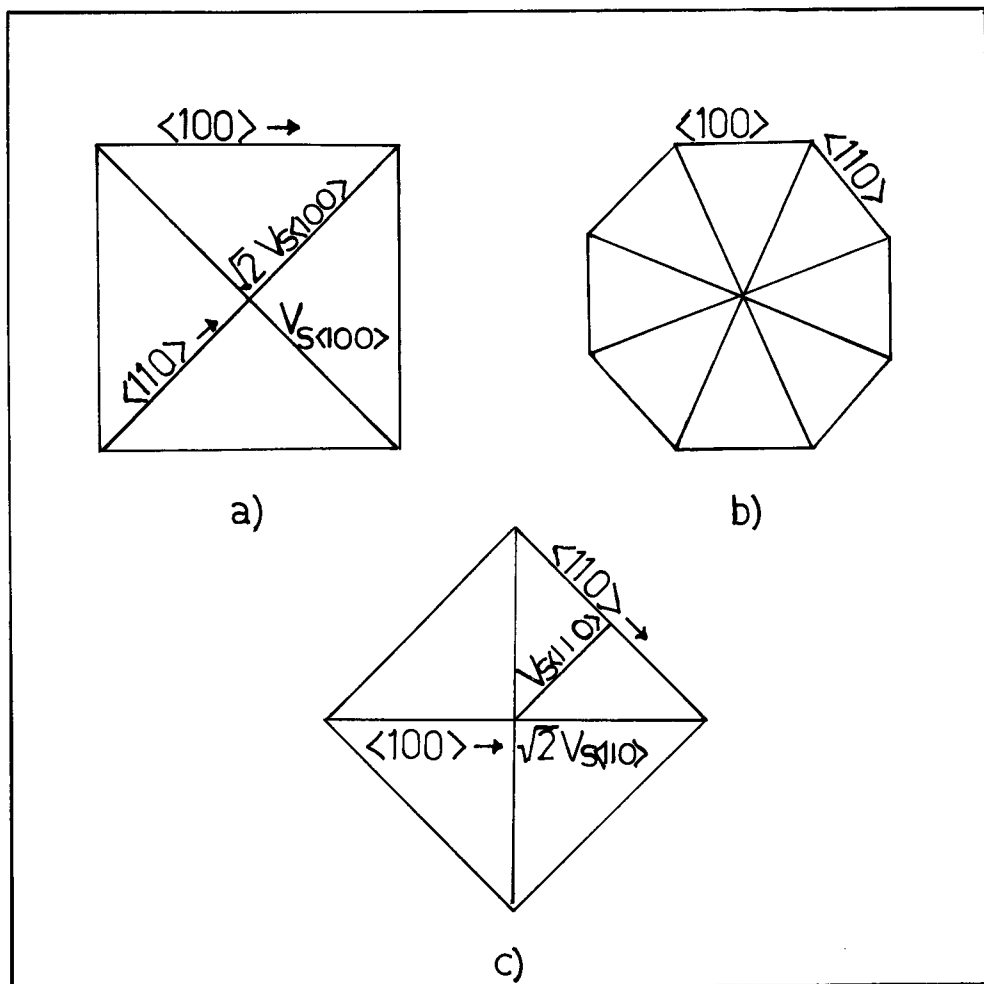


Fig. 7. Shape of etch pit showing the relation between dissolution velocities along  $\langle 100 \rangle$  and  $\langle 110 \rangle$  directions. The base etchant contains (a) 0.6 M  $\text{NH}_4\text{F}$ , (b) 4.0 M  $\text{NH}_4\text{F}$  and (c) 6.0 M  $\text{NH}_4\text{F}$ .

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