CLEAVAGE AND ETCHING OF BARITE

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ABSTRACT

Natural single crystals of barite ($BaSO_4$) obtained from Silver Band mines, Westmorland have been cleaved parallel to {001} and {110}. Interferometric examination has revealed that {110} cleavages are better than {001} cleavages. This may be due to the difference in the binding energy between the atoms in the same plane and the atoms in the neighbouring plane. The cleavages have been etched in H_2SO_4, and HCl. The pit densities differ when etched in different acids. Matched pairs have been etched one in H_2SO_4 and its counterpart in HCl. One to one correspondence is not observed on them. This is contrary to what has been reported so far in other mineral crystals. Cleavages once etched in one etchant are re-etched in the other etchant and correlation in the etch pattern is obtained. The implications are discussed.

INTRODUCTION

It has long been recognized that information regarding the history of growth of crystals and their dislocation content can be obtained by studying the nature of their cleavages and the etch patterns produced on them by some suitable etchants. We have studied in this laboratory the cleavages and etching of a number of mineral single crystals. Chief among these studies are those on calcite by Patel & Goswami (1962), on mica by Patel & Ramanathan (1962), on topaz by Patel & Goswami (1964), on calcium fluoride by Patel & Desai (1965), on diamond by Patel & Goswami (1963), on graphite by Patel & Bahl (1965) and on apatite by Patel *et al.* (1966). Studies on cleavage and etching on barite have not been reported. We were particularly interested in the study of barite because it has two perfect cleavages, one parallel to {001} and the other parallel to {110}. The mineral crystals so far investigated in this laboratory had only one cleavage and hence it was considered that studies on the two cleavages of barite might give some information which ordinarily may not be obtained from the studies on crystals having only one cleavage. This paper deals with the studies made on {001} and {110} cleavages of barite and the etch patterns produced on them.

EXPERIMENTAL

Natural single crystals of barite ($BaSO_4$) were obtained from Silver Band mine, Westmorland. Freshly cleaved {001} and {110} surfaces and the etch patterns produced on them were coated with thin silver films and examined optically by multiple beam interferometry. Sulphuric acid and hydrochloric acid were used as the etchants.

Observations and results

While cleaving the crystals it was observed that {001} cleavages can be produced much more easily by inserting a sharp razor blade parallel to this plane and pressing it against the crystal. To cleave the crystal parallel to {110} after keeping a sharp edge parallel to this plane, a blow to the blade was necessary. It was therefore decided to make a comparative study on both cleavages interferometrically. Thus Figs. 1 and 2 represent the multiple beam interferograms taken on typical {001} and {110} cleavage planes respectively. The interferograms clearly reveal that the cleavage {110} is smoother and better than the {001} cleavage.

Etch patterns on {001} cleavage

Figures 3(a) and 3(b) represent the etch patterns of freshly cleaved {001} matched planes etched simultaneously in HCl for 40 minutes and Figs. 4(a) and 4(b) represent the etch patterns produced on another matched pair when etched in H_2SO_4 for 20 minutes. Examination of these etch patterns reveals that:

1. The etch pattern consists of larger individual isolated pits and a number of small crowded pits.
2. There is one to one correspondence in number and positioning of pits on the matched pair.
3. The shapes of the pits are different when etched in different etchants.
4. The average density of pits observed on faces etched in HCl is 2.5×10^4 pits/cm^2 while on those etched in H_2SO_4 it is 4.2×10^4 pits/cm^2.

In order to investigate the difference in densities of pits on {001} when etched in two different etchants a matched pair of these faces was selected and one face was etched in HCl and the other in H_2SO_4. Thus Figs. 5(a) and 5(b) represent respectively the etch patterns produced in HCl and H_2SO_4. It is indeed interesting to observe that there is not a one to one correspondence in number and positions of the individual isolated pits on the matched pair. This is quite contrary to what has been observed and reported on other mineral crystals. For further investigations the surface shown in Fig. 5(a) which was etched in HCl was re-etched in H_2SO_4. Thus Fig. 5(c) shows the modified etch patterns after re-etching. Comparison of the etch patterns in Fig. 5(c) with the etch patterns in Fig. 5(a) reveals that new pits have been developed at those sites at which there were no corresponding pits in the etch pattern produced

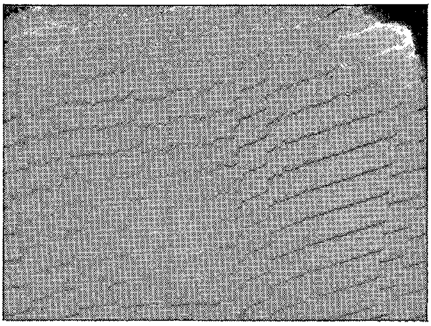
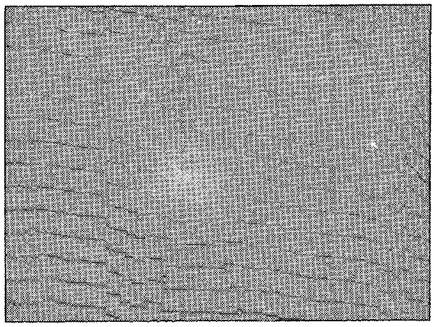
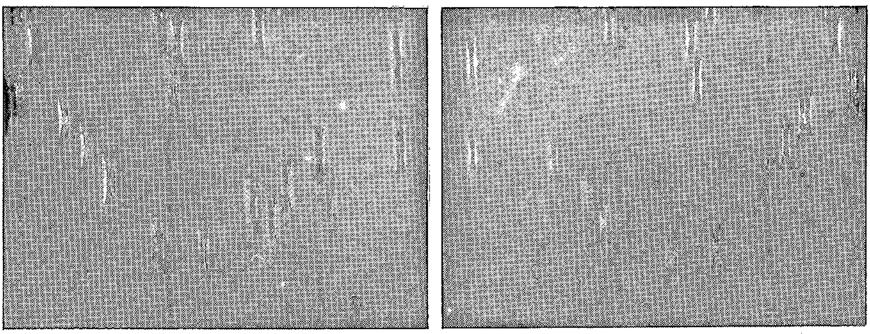
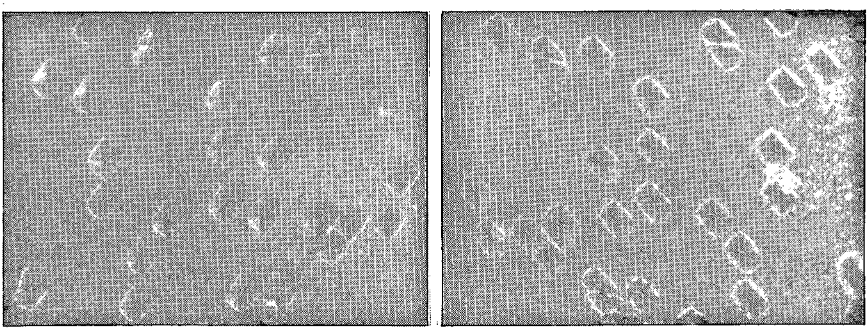





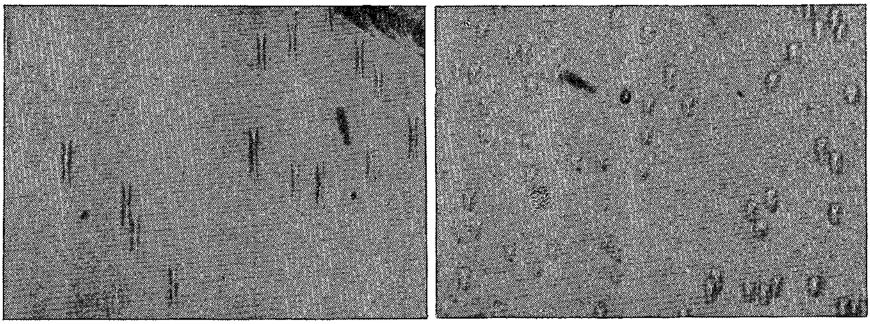
FIG. 1 (top left). Interferogram taken on a typical {001} cleavage. (×20).

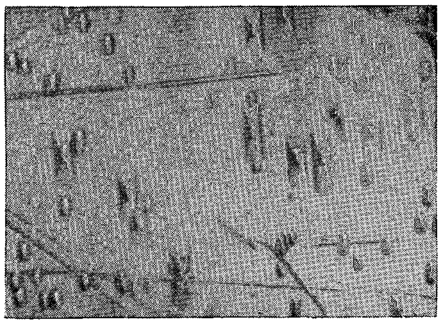
FIG. 2 (top right). Interferogram taken on a typical {110} cleavage. (×20).

FIGS. 3(a, b) (middle). Etch patterns on matched {001} cleavage planes etched simultaneously in HCl. (×200).

FIGS. 4(a, b) (lower). Etch patterns on matched {001} cleavage planes etched simultaneously in H_2SO_4. (×200).

by HCl. The re-etching in H_2SO_4 has produced complete correspondence in the etch patterns. The pits nucleated during re-etching in Fig. 5(c) can be easily distinguished from the old pits from the difference in their shapes and sizes.





FIGS. 5(a, b) (top). Matched pair of {001} cleavage planes etched in HCl (left) and H_2SO_4 respectively. (×100).

FIG. 5(c) (lower). The cleavage plane {001} etched in HCl was re-etched in H_2SO_4. (×100).

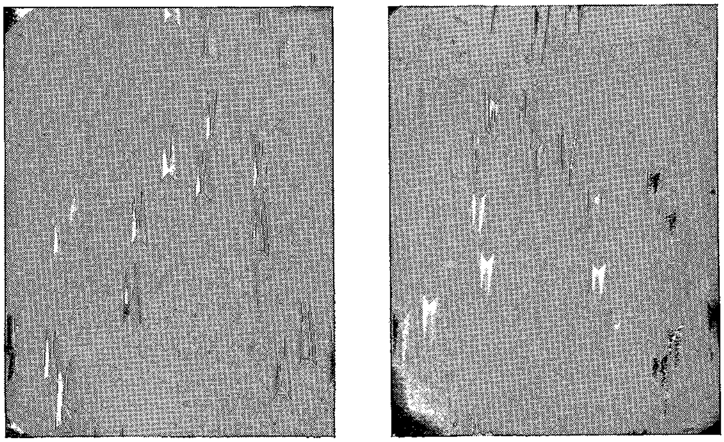
Etching of {110} *cleavages*

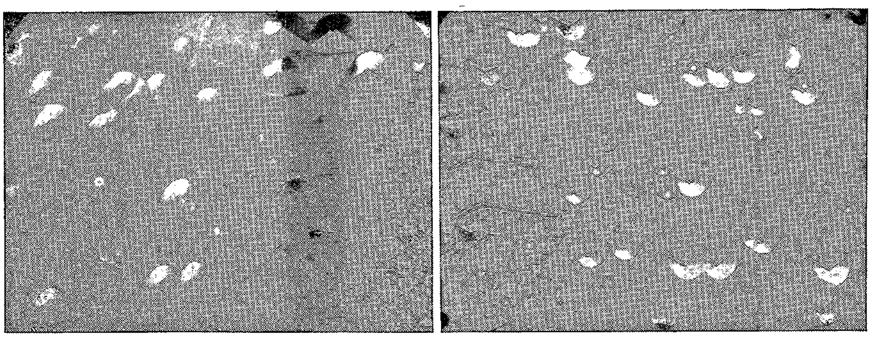
The experiments described above for {001} cleavage faces were also tried on {110} cleavage planes. Thus Figs. 6(a) and 6(b) and 7(a) and (7b) represent the etch patterns produced on {110} matched cleavage planes when etched in HCl and H_2SO_4 respectively. As with {001} planes the density of pits produced by etching in HCl is less than the density of pits produced by etching in H_2SO_4; the densities being 2×10^4 pits/cm^2 and 3.5×10^4 pits/cm^2.

Attention is drawn to the following features in Figs. 7(a) and 7(b):

1. All pits are not of the same size.
2. There is one to one correspondence in the etch patterns on matched pair.
3. Correspondence exists also in the sizes of the pits. A large pit on one face has a corresponding large pit on the matched face. The same holds true for smaller pits.

As in the case of {001} a {110} plane was first etched in HCl and then re-etched in H_2SO_4 and the etch pattern thus produced was compared





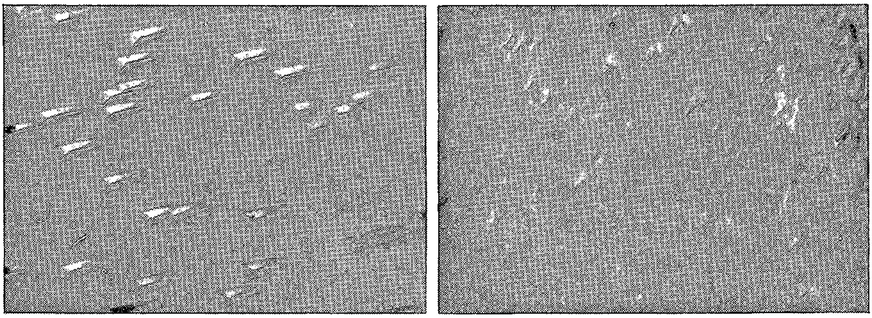
FIGS. 6(a, b) (top). Etch patterns on matched {110} cleavage planes etched simultaneously in HCl. (×100).

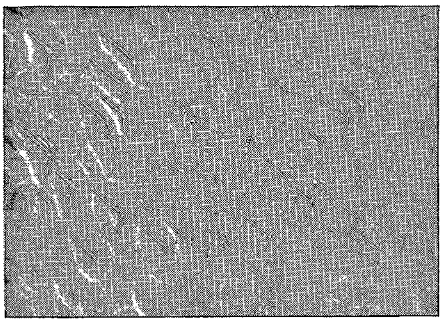
FIGS. 7(a, b) (lower). Etch patterns on matched {110} cleavage planes etched simultaneously in H_2SO_4. (×100).

with the etch pattern produced on its matched plane etched in full HCl. Thus Figs. 8(a) and 8(b) represent the etch patterns produced on a {110} matched pair when etched in HCl and H_2SO_4 respectively. Fig. 8(c) represents the modified etch pattern of Fig. 8(a) after re-etching in H_2SO_4. Attention is drawn to the following:

1. Pits produced by HCl are of the same size while those produced by H_2SO_4 are of unequal sizes.
2. One to one correspondence is not observed on the matched pair.
3. Pits which have no correspondence on a matched plane are smaller compared to pits having correspondence.
4. Re-etching has produced complete correspondence.

It may be mentioned that when matched pairs of cleavages are etched, one in KOH and the other in H_2SO_4, complete correspondence in number





FIGS. 8(a, b) (top). Matched pair of {110} cleavage planes etched in HCl and H_2SO_4 respectively. (×200).

FIG. 8(c) (lower). The cleavage plane {110} etched in HCl was re-etched in H_2SO_4. (×200).

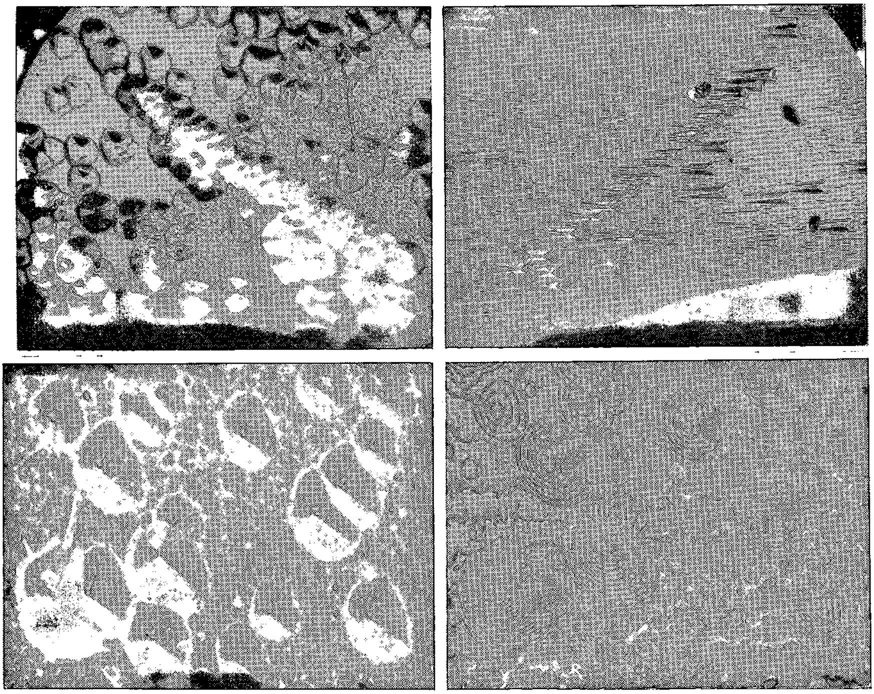
and position of the pits is obtained. Figures 9(a) and 9(b) are the etch patterns on a matched {110} plane etched in KOH and HCl respectively in which a row of pits having perfect matching is observed. This observation has an important bearing in considering why no correspondence is obtained on a matched pair when one is etched in HCl and the other in H_2SO_4.

The structure and the depth of the pits were examined by multiple beam interference fringes. Fig. 10(a) represents the etch pattern on {110} cleavage when etched in H_2SO_4 while Fig. 10(b) is the interferogram on it. The interferogram reveals that:

1. In addition to the individual isolated pits the etchants bring about the general dissolution of the surface.

2. The bigger pits are deeper compared to the smaller pits, the sizes of the pits vary from 0.5μ to 4μ.

3. The inside structure of the pits is more or less spherical as revealed by the nature of the fringe pattern within the pit.



FIGS. 9(a, b) (top). Low angle grain boundary on matched {110} cleavage planes, one piece etched in KOH (left) and the other in HCl. (×100).

FIGS. 10(a, b). Typical etch pattern on {110} cleavage etched in H_2SO_4 (left) and interferogram taken on the region shown in figure 10(a). (×200).

DISCUSSION

In order to produce good cleavage the differences of binding energy between the atoms across the cleavage plane should be larger. The force necessary to produce a cleavage will be proportional to the binding energy between the atoms whose bonds are to be broken in the cleavage process. The greater ease of {001} cleavage in barite compared to {110} cleavage suggests that the binding energy between the atoms in the two neighbouring {001} planes may be less than the binding energy between the atoms in the two neighbouring {110} planes. The {110} cleavages are smoother than {001} cleavages which suggests that the difference in binding energy between the atoms across {110} planes and in these planes may be greater for {110} planes than for {001} planes. If this difference is larger, the cleavage initiated along a certain plane would ordinarily not deflect from its original direction and thus a better cleavage will result.

The density of pits observed on {001} cleavage is greater than the density of pits on {110} cleavage suggesting that the number of imperfections threading through {001} planes may be greater than those threading through {110} planes. This difference in the density of the imperfections may also be responsible for the smoother surfaces of {110} cleavages compared with {001} because the imperfections may help the cleavage fracture to deflect from its original path, thus producing inferior cleavage. Greater energy of binding between the atoms in the plane together with fewer imperfections passing through the cleavage plane may produce smoother surfaces and *vice versa*. The observed differences in the density of dislocations passing through {110} and {001} cleavage planes may be explained by assuming that the dislocation lines may have preferred orientation in the crystal. This also suggests that the preferred orientation may be more inclined to {001} than with {110} faces.

The lack of one to one correspondence in pits on a matched pair when one is etched in HCl and the other in H_2SO_4 may be due to the difference in physical nature of these dislocations. As in the case of NaCl type crystals here also both the core energy and elastic energy of the edge dislocations may exceed that of screw dislocations. Therefore edge dislocations should have etched at a faster rate than screw dislocations as Cabrera (1957) has shown. This was supported recently in sodium fluoride by Davison & Levinson (1966). In the case of barite, it is quite possible that HCl has revealed only edge dislocations whereas H_2SO_4 is capable of revealing both edge and screw type. As the energy of screw dislocations is smaller, the size of the pits revealed is comparatively smaller and shallow. The perfect correspondence of pits on a low angle grain boundary when etched in HCl and KOH supports our view that HCl reveal only edge dislocations. This explains why no correlation is observed on matched pair when they are etched in two acids.

References

CABRERA, N. (1957): *Semiconductor physics*. R. H. Kingston (Ed.). (University of Pennsylvania, Philadelphia, p. 337).

DANA, E. S. & Ford, W. E. (1963): A text book of mineralogy, Wiley, New York, 748.

DAVISON, J. W. & SOLOMON LEVINSON (1966): Selective etch for new edge dislocations in Sodium fluoride. *J. Appl. Phys.* **37**, 4888–91.

PATEL, A. R. & BAHL, O. P. (1965): Optical and interferometric studies on the cleavage of graphite and their etch patterns. *Acta Cryst.* **19**, 627–28.

——— & DESAI, C. C. (1965): Etching of calcium fluoride cleavages. *Acta Cryst.* **18**, 373–374.

———& DESAI, C. C. & AGARWAL, M. K. (1966): Cleavage and etching of the prism faces of apatite. *Acta Cryst.* **20**, 796–98.

——— & GOSWAMI, K. N. (1962): Etching of calcite cleavages. *Acta Cryst.* **15**, 47–49.

——— & GOSWAMI, K. N. (1964): Etching of topaz cleavages. *Acta Cryst.* **17**, 569–70.

——— & GOSWAMI, K. N. (1963): Optical and interferometric studies on cleavages of synthetic diamond and their etch pattern. *Brit. J. Appl. Phys.* **14**, 284–86.

——— & RAMANTHAN, S. (1962): Etching of mica cleavages. *Acta Cryst.* **15**, 860–61.

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