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Etching of Calcite

EXPERIMENTS on etching of calcite have been carried out earlier by a number of workers[1] and etch pits on calcite have been reported recently by H. Watts[2] and R. C. Stanley[3]. We have been carrying out experiments on etching of mineral crystals with different etching reagents for some time and have investigated calcite very thoroughly. Some typical results are reported here.

On etching cleavage faces of calcite with a strong

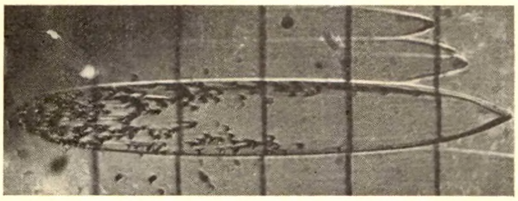
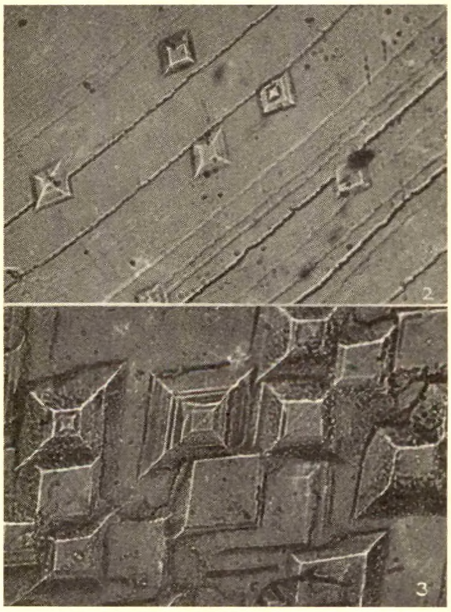


Fig. 1 (×500).



Figs. 2 and 3 (×55).

solution of sodium hydroxide for one hour, perfectly boat-shaped figures are obtained. A light profile photomicrograph is shown in Fig. 1. The depth of this particular etch pit is 1 μ at the centre and 0·8 μ at the ends.

The etch figures produced by ammonium chloride solution on a freshly cleaved surface of calcite are parallelograms, and these are oriented with their sides parallel to the edges; their depths vary from a few hundred angstroms to 2 microns, according to the etching time. Figs. 2 and 3 show photomicrographs for the two stages of etching for fifteen minutes and one hour respectively. In Fig. 2 the pits are more scattered and cleavage lines are found to be moving as reported earlier by Patel and Tolansky[4] in the case of the etching of mica. Multiple-beam interference pictures have also been taken over these etch pits for measuring their depths.

Detailed results will be published elsewhere.

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Aug. 20.

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ETCHING OF MICA BY FUSED ALKALIES

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ABSTRACT

Etching of mica cleavages by fused alkalies at higher temperatures produces triangular etch pits. The shape and orientations of these pits due to the etching action of fused sodium hydroxide and potassium hydroxide at different temperatures show faster attack by sodium hydroxide than by potassium hydroxide. The two faces obtained on cleaving are matched and the correspondence in different cases is discussed.

INTRODUCTION

Good accounts of the study of etch figures were given by Honess (1927) and Desch (1934). In recent years etching of crystal faces is taken up to investigate the dislocations and their movements or other imperfections. (For literature *see*, Vogal *et al* (1953), Omar, Pandya and Tolansky (1954), Amelinckx (1954), Hendrickson and Machlin (1955) Gilman and Johnston (1956)). The etch figures are observed by highly developed new techniques and it was felt that etching of mica, if studied, might give valuable information. R. De la Vault (1942, 1943, 1946) has studied etch figures on mica with different etchants and for different times. Recently Patel and Tolansky (1957) have also published their results on etching of mica with hydrofluoric acid and the present authors Pandya and Pandya (1958) had obtained similar results, only difference was in the method of etching, viz. Patel and Tolanksky kept the specimen over vapours of the hydrofluoric acid whereas the present authors had immersed the specimen in 40 per cent hydrofluoric acid. The work has been extended with other etchants and only these results are given in this report.

EXPERIMENTAL

Muscovite mica (Madras, now Andhra Pradesh) was studied in the present work. Silver films were deposited on the freshly cleaved surfaces by thermal evaporation in high vacuum. The surfaces were examined under microscope to see if irregularities existed before etching. They were then cleaned by hydrogen peroxide and kept for etching. This practice of examination before etching was not essential and was later discontinued. The specimens were etched by immersing them in fused alkalies, viz., sodium hydroxide and potassium hydroxide, in a nickel crucible, the range of temperatures being 330°C to 500°C for sodium hydroxide and 370°C to 500°C for potassium hydroxide and etching times varying from a second to about two minutes. They were examined under high power microscope at different stages after cleaning and depositing silver films over them. All the recent techniques of phase contrast microscopy, multiple beam interferometry and profile microscopy were used to examine the surfaces. Both the surfaces obtained on cleaving were compared each time. Separate experiments were also carried out by etching one face with one etchant and other one with a different etchant and the results were compared.

Observations and Results

Etch pits can be classified into two groups:

(*i*) micropits developed at random over the whole surface. The concentration of these pits is of the order of $6 \times 10^6/cm^2$.

(*ii*) large localized isolated pits of which some are pyramidal and some are truncated or flat bottomed.

Fig. (1) ×90 shows the results obtained by etching with sodium hydroxide at 340°C, whereas Figs. (2) ×90 represents the same with potassium hydroxide at 370°C. In the Fig. 3×750 is shown the initial stage of etching by fused potassium hydroxide. All these figures clearly show the different types of pits, these being elongated isosceles triangles in case of sodium hydroxide etching and short isosceles triangles resulting from the action of potassium hydroxide.

These elongated isosceles triangular pits are strictly oriented with their medians to the base parallel to the pinacoidal direction. Fig. 4×90 shows this orientation with reference to the percussion marks obtained in the usual way. The stronger ray of the percussion star which is parallel to b pinacoidal direction and the triangles are situated as seen in the Figure 4×90. Figure 5×90 is given for comparison with etchpits due to hydrofluoric acid as obtained by Patel and Tolansky (1957) also. All the etch pits are oriented in the same direction and their shorter diagonals are parallel to the b pinacoidal direction.

The etchpits in case of alkalies are triangles as opposed to parallelograms for hydrofluoric acid and the shapes of the triangles due to sodium hydroxide and potassium hydroxide are apparently different. For the pits due to sodium hydroxide, and potassium hydroxide etc. respectively, the vertices are on an isosceles triangle with equal angles of 65°, and 50° respectively as shown in Figs. (6)×360 and (7)×360 respectively. The sides are rounded as seen in these figures. Figures (8)×496 and (9)×496 show different types viz., flat bottomed and pyramidal etchpits with profile microscope; their depths are 4·3 μ and 2·3 μ respectively. It should be noted that prolonged etching increases only the size of the isolated etchpits and not their number, *i.e.*, concentration.

Figures (10)×360 and (11) ×360 show the matched faces etched by sodium hydroxide at 360°C for five seconds. Fig. (12) ×360 is obtained by superposing the negatives of the two faces one over the other. This clearly shows that there is a perfect matching of the pits but the cleavage lines are displaced. The orientation of these pits on the two faces are also opposite and not exactly like mirror images, and this is expected since the cleavage faces oppose each other. This point was not noticeable in the case of matching by hydrofluoric acid as the pits were symmetrical.

Fig. (13) ×360 shows one face etched by Sodium Hydroxide at 360°C and Fig. (14) ×360 the counterpart etched by potassium hydroxide at 400°C. Fig. (15) ×360 shows the print obtained by superposing the two negatives for comparison. There is a one-to-one resemblance with regards to the pits but the cleavage lines have moved.

Fig. (17) ×360 illustrates one face etched by 40 per cent hydrofluoric acid whereas in the Fig. (16) ×360 is shown the counterpart etched by sodium hydroxide. Fig. (18) is a print obtained by superposition of the two Figures (16) and (17). Again there is a point-to-point correspondence with regards to the number and positioning of etchpits but a shift of the cleavage lines is seen.

Some typical measured depths on an interferogram are $1{\cdot}35\,\mu$ to $2{\cdot}16\,\mu$ obtained by counting the number of fringes in the pits and multiplying them by $\lambda/_2$ where λ for the green mercury light is 5461 A.

Discussion

Re.De la Vault (1944, 1946) has carried out very extensive work on etching of all types of mica from the chemical aspect of noting the quickness of attack of the different etching reagents and their mixtures. He has given a number of diagrams for the etch figures.

The triangular pits are expected with fused alkali as etchants, as pointed out by De la Vault (1946). Fused sodium hydroxide is having a faster reaction than potassium hydroxide and could be explained on the chemical reaction on different atoms in the crystal. The temperature of an etchant is an important factor for the quickness of reaction and a separate experiment to study this effect was carried out. In one case etching was carried out at a lower temperature for longer time and the other counterpart was etched at a higher temperature but for a shorter time. The one etched at a higher temperature showed faster reaction by way of larger etch pits.

The presence of flat-bottomed pits indicates that the imperfection existed only up to the base and hence the reaction is not penetrating further preferentially but the attack is more on the sides. The etching on both faces of the same piece of mica show that there is no relation between the two and the number of pits and their locations are different in the two faces. This suggests that the imperfections are not much extended in depth. In the present work the etch pits obtained by two different etchants on the two counterparts of cleavage faces show point-to-point correspondence except for the movement of the cleavage lines, as explained by Patel and Tolansky. This suggests that the isolated pits could be due to lattice distortions in these areas produced by some chemical impurity centres. If they were just chemical impurities or inclusions, the two different etchants viz., hydrofluoric acid and sodium hydroxide would not necessarily have reacted at the same places and affected the counterparts equally.

The dislocation movement as observed by Gilman and Johnston (1956) with lithium fluoride crystals could not be observed by a similar experiment with mica. The possibility of dislocations as being responsible for etch pits is therefore ruled out.

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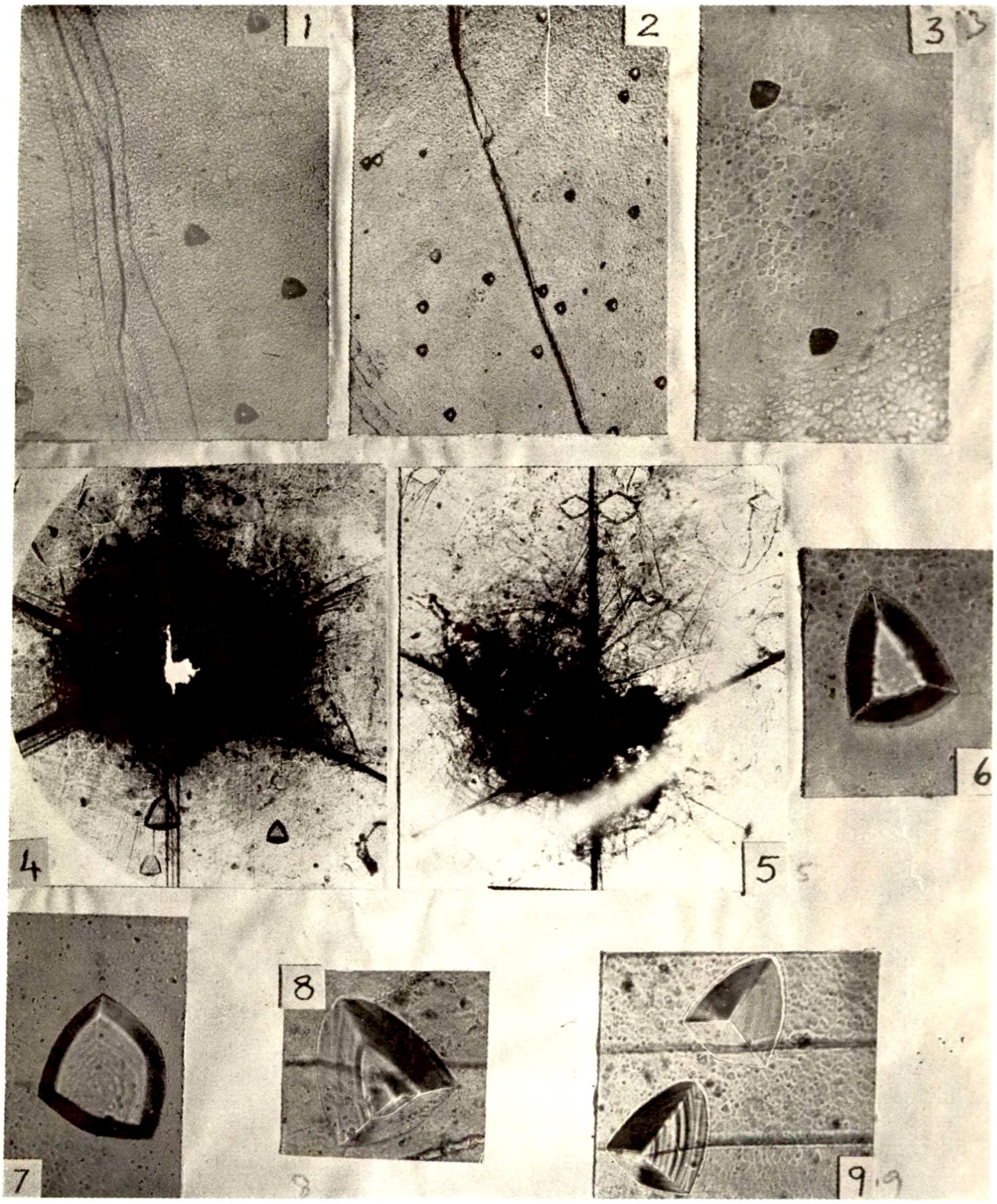

FIG. 1 × 90 FIG. 2. ×90. FIG. 3. ×750.
FIG. 4. ×90. FIG. 5. ×90. FIG. 6. ×360.
FIG. 7. ×360. FIG. 8. ×496. FIG. 9. ×496.

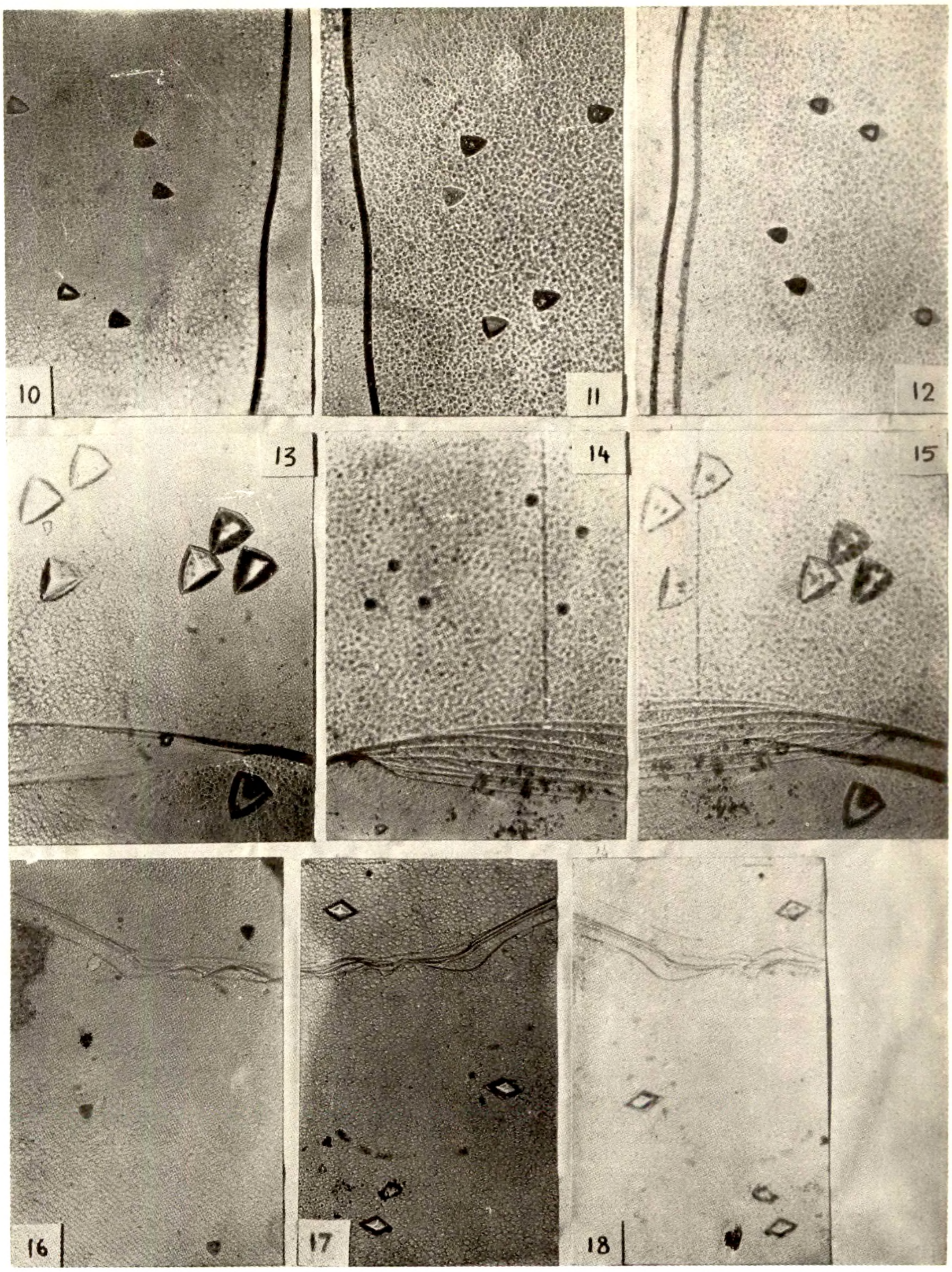

Fig. 10. ×360.
Fig. 11. ×360.
Fig. 12. ×360.
Fig. 13. ×360.
Fig. 14. ×360.
Fig. 15. ×360.
Fig. 16. ×360.
Fig. 17. ×360.
Fig. 18. ×360.

ETCHING OF FLUORITE

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ETCHING OF FLUORITE

EXPERIMENTS on etching of crystal surfaces have been reported in recent years.[1-4] We report here some interesting results obtained in the case of fluorspar in our Laboratory.

The two (111) faces obtained on cleaving a crystal of fluorite by means of a sharp blow with a pointed edge, were etched by sulphuric acid at room temperature for different times. The etched surfaces were then coated with highly reflecting silver films and examined under a microscope. It is observed that in the initial stages, there is general etching with scattered triangular etch pits. As the etching period is increased, etch pits resembling the familiar block pattern, as reported in the case of diamond, appeared at some places. The more scattered triangular etch pits were found to be randomly distributed but oriented in definite directions and to have point-to-point correspondence in the two faces. These pits may be due to inclusions or other types of imperfections such as dislocations. The detailed results will be published elsewhere.

Physics Dept., M. S. University of Baroda, Baroda, *June* 9, 1958.

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