MINERALOGICAL MAGAZINE, DECEMBER 1973, VOL. 39, PP. 482–7

Stratigraphical etch patterns on the rhombohedral cleavages of natural quartz crystals

M. S. JOSHI AND BABY K. PAUL
Department of Physics, Sardar Patel University, Vallabh Vidyanagar, Gujarat State, India

SUMMARY. Rhombohedral cleavage faces of quartz have been etched hydrothermally and with fused KOH. Stratigraphical etch patterns were observed on isolated cleavages, matched cleavage faces, and opposite sides of a thin flake. The angle between the (10$\bar{1}$1) cleavage plane and the planes responsible for the stratigraphical patterns was almost equal to the interfacial angle, 46° 16′, between adjacent rhombohedral faces. It is concluded that the stratigraphical patterns formed by preferential etching reveal the edges of weak planes deposited during growth. The implications are discussed.

ETCHING is becoming an increasingly sensitive technique for revealing the sites of imperfections in crystals and studying their nature and density. Etch patterns on some crystals give information about their history and the mechanism of their growth. Such studies have been carried out by Patel *et al.* (1957, 1962, 1966) and Pandya *et al.* (1968), through the stratigraphical etching of cleavage surfaces of natural crystals. The present investigation reports the results of stratigraphical etching of quartz (10$\bar{1}$1) surfaces, including single cleavages and opposite faces of a thin cleavage flake.

Experimental. The present investigation was carried out on transparent single crystals of quartz, which were cleaved on (10$\bar{1}$1) surfaces with a sharp honed chisel along a previously inscribed line parallel to the trace of a cleavage plane. Freshly cleaved surfaces, examined under the microscope before etching, revealed only the presence of cleavage lines. These cleavage surfaces were then etched hydrothermally by the method exploited by Joshi *et al.* (1969, 1970) for the prism and rhombohedral faces of quartz crystals. In the present work the crystals were etched in a steel bomb of internal volume 20 ml, filled with 10 ml of distilled water and heated to 280 °C in a muffle furnace with temperature controlled to within ±5 °C. The crystals were etched for 10 hr, removed and thoroughly cleaned with conc. HNO_3, water, and H_2O_2.

Fused KOH (6 g. KOH and 3 ml water) at 250 °C was also used occasionally for etching experiments.

The crystals were silvered, to enhance contrast, and the etch patterns examined under an optical microscope.

Results. Fig. 1 illustrates a (10$\bar{1}$1) cleavage surface after hydrothermal etching. It is interesting to note that closely spaced ridges and grooves are formed parallel to [$\bar{1}\bar{1}$21]. In addition to these patterns a large number of oriented triangular etch pits are observed in three different plane strips (which are devoid of these rectilinear patterns), with the typical triangular shape of pits on the rhombohedral face, indicating the plane to be almost parallel to a $(10\bar{1}1)$ cleavage. The pits in other striated regions have been found to be rhomb shaped. It may further be noted that these rectilinear patterns are crossed by two parallel lines lying in the $\langle 1\bar{2}11\rangle$ direction making an angle of 86° with the original patterns lying in the $[\bar{1}\bar{1}21]$ directions.

An attempt was made to study the etch patterns on matched $(10\bar{1}1)$ cleavage planes. One surface was etched hydrothermally (fig. 2*a*), the other by fused KOH (fig. 2*b*). The perfect correspondence of the rectilinear patterns on the two matched surfaces indicates that the patterns are not merely a surface phenomenon, but are due to a structure that penetrates the crystal to some extent.

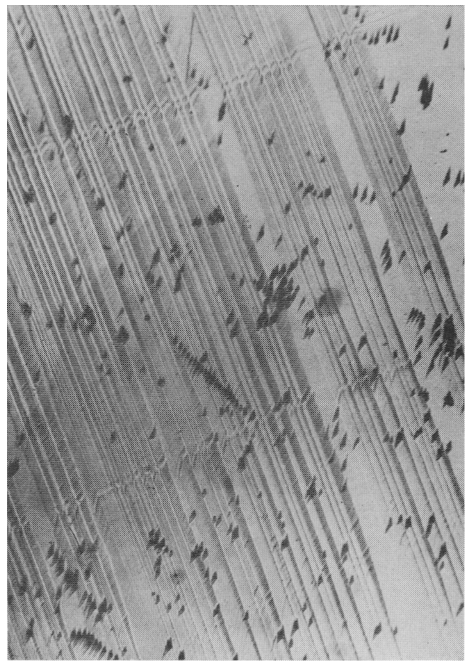

FIG. 1. A hydrothermally etched $(10\bar{1}1)$ cleavage surface, ×90.

In order to discover how far this structure penetrates into the crystal, a flake about 500 μm thick was obtained by cleavage and etched in steam at 280 °C for 10 hr in the autoclave, as described above. The etch pattern on one side of the flake is illustrated in fig. 3*a*. Faint rectilinear patterns were also observed on the opposite face of this flake, which was then etched for one hour in fused KOH at 250 °C, producing the surface illustrated in fig. 3*b*. Comparison of figs. 3*a* and 3*b* shows that the 'structure' extends through the thickness of the flake, and that the rectilinear features have almost certainly been produced by stratigraphical etching. If this deduction is correct, the 'structures' can be expected to extend into the crystal to an appreciable depth.

Additional evidence was sought about the penetration of the stratigraphical patterns within the crystal. A rhombohedral cleavage (the 'primary' cleavage) was obtained and hydrothermally etched, producing linear stratigraphical patterns. Part of this surface was cleaved again, forming another rhombohedral cleavage (the 'secondary' cleavage). The results of etching are shown in fig. 4; the stratigraphical etch pattern clearly continues from the primary (higher) to the secondary (lower) cleavage, strengthening the earlier tentative conclusion that the pattern penetrates fairly deeply into the crystal.

Using the method described by Patel *et al.* (1957) an attempt was made to work out the angle θ between the rhombohedral cleavage plane and the planes constituting the stratigraphical pattern. A considerable displacement of the rectilinear pattern is produced when the lines cross high cleavage steps; two examples are illustrated in figs. 5*a*

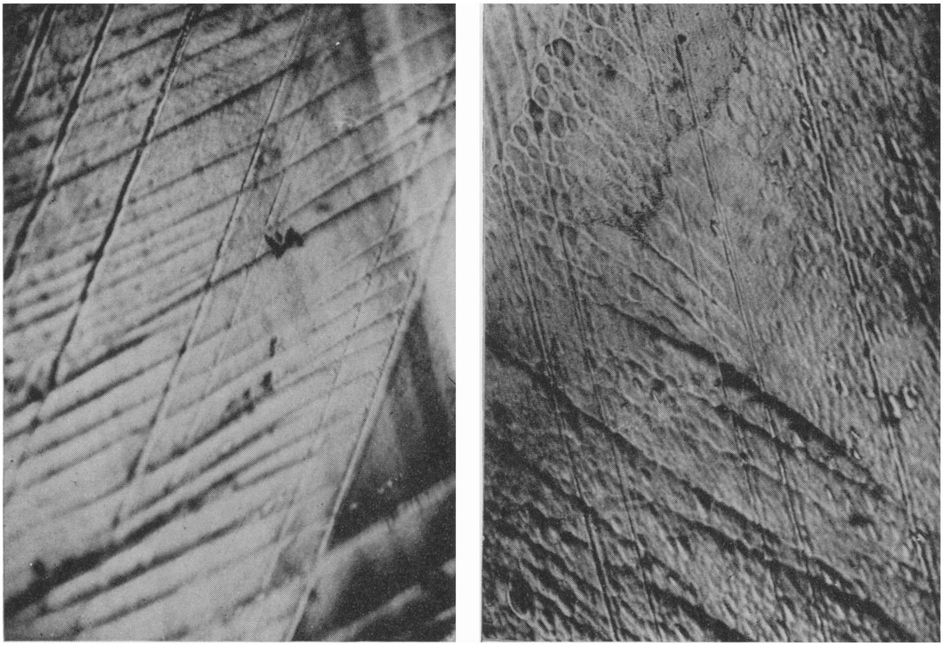

FIG. 2. A matched pair of cleavage planes, one (*a*, left) etched hydrothermally, the other (*b*, right) with fused KOH. $\times 170$.

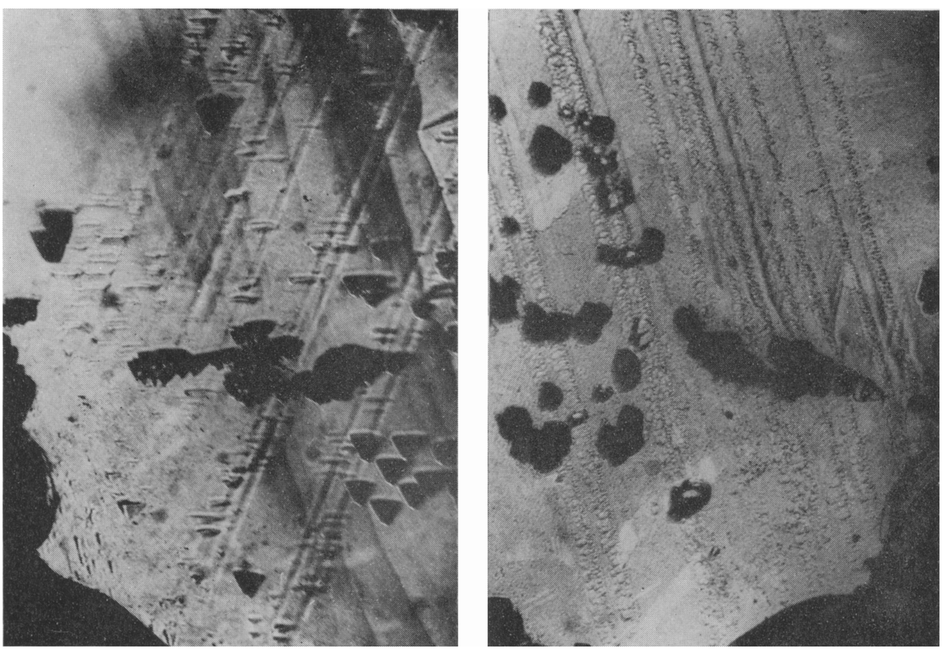

FIG. 3. Etch patterns on the two faces *a*, left; *b*, right of a $(10\bar{1}1)$ cleavage flake 500 μm thick. $\times 90$.

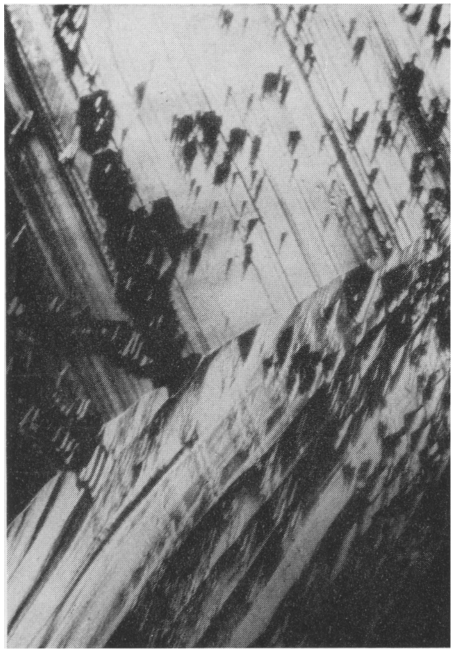

FIG. 4. A rhombohedral cleavage etched hydrothermally, then part of the area cleaved again and etched. ×90.

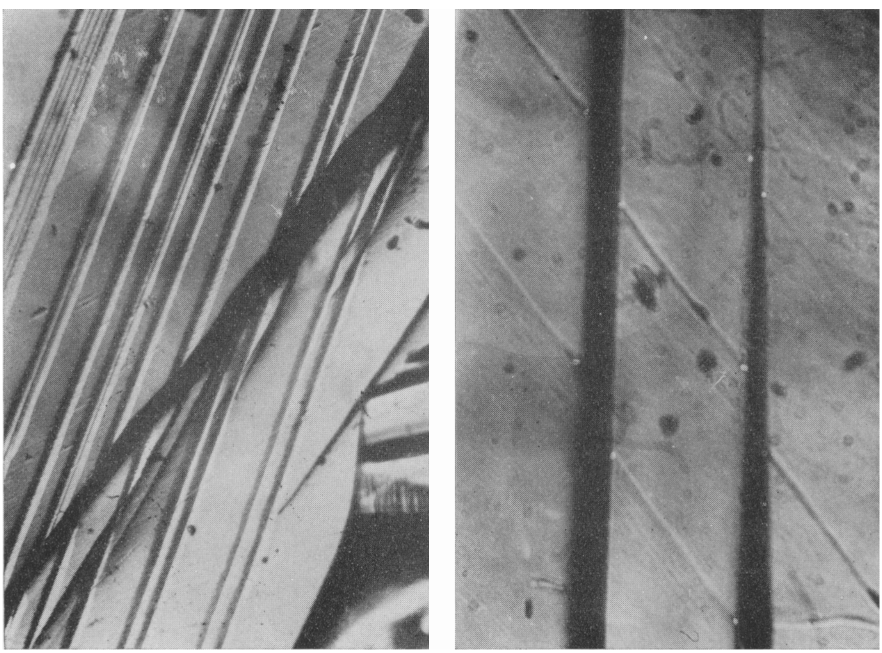

FIG. 5. Displacement of the rectilinear pattern at cleavage steps. *a* (left), of a pattern parallel to [$10\bar{1}\bar{1}$]; *b* (right) of a pattern parallel to [$\bar{1}\bar{1}21$]. ×90.

and 5*b*. The displacement of the rectilinear pattern was measured at five positions on a cleavage step, the height of which was also measured at these positions, using the method of Tolansky (1952). From the values of the displacement d and step height h, the angle θ was computed; the results are presented in Table I for two different directions, $[10\bar{1}\bar{1}]$ (fig. 5*a*) and $[\bar{1}\bar{1}21]$ (fig. 5*b*). The calculated values of θ agree satisfactorily with the interfacial angle (46° 16′) between a $(10\bar{1}1)$ face and the neighbouring rhombohedral faces $(01\bar{1}1)$ and $(1\bar{1}01)$.

TABLE I. *The angle* $\theta = \tan^{-1}$ (h.m/d), *where h is the step height, d the shift in the pattern at the step, and m the magnification, for two directions. m* = 90 *throughout*

Direction $[10\bar{1}1]$ (fig. 5*a*)			*Direction* $[\bar{1}\bar{1}21]$ (fig. 5*b*)		
h	d	θ	h	d	θ
21 μm	0·182 cm	46° 6′	50 μm	0·438 cm	45° 48′
24	0·203	46° 30′	41	0·359	45° 48′
18	0·157	45° 43′	48	0·405	46° 48′
30	0·261	45° 59′	43	0·372	46° 6′
26	0·223	46° 24′	45	0·385	46° 27′
	Mean θ	46° 8′		Mean θ	46° 11′

Discussion. The exact correspondence of the stratigraphical patterns on the matched faces and on opposite surfaces of a thin flake, and the continuation of these rectilinear traces on the 'primary' and 'secondary' rhombohedral cleavage surfaces suggest that the patterns revealed by etching extend far into the crystal, indicating successive positions of the rhombohedral faces during growth. The planes responsible for the stratigraphical patterns are inclined at angles of 46° 8′±9′ (fig. 5*a*) or 46° 11′±9′ (fig. 5*b*) to the cleavage plane $(10\bar{1}1)$ and correspond to rhombohedral faces $(01\bar{1}1)$ or $(1\bar{1}01)$, which must have been present during growth. Hence it is concluded that these crystals might have grown by deposition of layers (layer-by-layer growth) on the $\{10\bar{1}1\}$ and $\{01\bar{1}1\}$ faces. The layers on $\{01\bar{1}1\}$ are cut by the $\{10\bar{1}1\}$ cleavage planes, the intersection of which is responsible for the rectilinear traces on $\{10\bar{1}1\}$ produced by etching. Further, the traces lying in the $\langle 1\bar{2}11\rangle$ direction may be attributed to the intersection of the $(\bar{1}011)$ plane with the $(10\bar{1}1)$ cleavage plane. When these traces lying in the $\langle 1\bar{2}11\rangle$ direction and the traces formed by the intersection of the $(01\bar{1}1)$ plane and the $(10\bar{1}1)$ cleavage plane (i.e. the traces lying in the $\langle \bar{1}\bar{1}21\rangle$ directions) cut each other on the observation plane (i.e. the $(10\bar{1}1)$ cleavage plane), it was observed that they make an angle of 86° with each other. This is to be expected since the angle $(\bar{1}011):(01\bar{1}1)$ is 85° 46′. This fact gives additional evidence of layer-by-layer growth on other rhombohedral faces as well.

Acknowledgement. One of the authors (B. K. P.) gratefully acknowledges C. S. I. R., Government of India, for financial assistance.

REFERENCES

JOSHI (M. S.) and KOTRU (P. N.), 1969. *Soviet Phys. Cryst.* **14**, 427.
—— —— and ITTYACHEN (M. A.), 1970. Ibid. **15**, 83.
PANDYA (J. R.) and SARAF (C. L.), 1968. *Min. Mag.* **36**, 750.
PATEL (A. R.) and GOSWAMI (K. N.), 1962. *Acta Cryst.* **15**, 47.
—— and PATEL (R. P.), 1966. *Zeits. Krist.* **123**, 153.
—— and TOLANSKY (S.), 1957. *Proc. Roy. Soc.* **A**, **243**, 41.
TOLANSKY (S.), 1952. *Zeits. Elektrochem.* **56**, 263.

[*Manuscript received 12 December 1972*]