ART. XXIV.—*Examination of some Triclinic Minerals by means of Etching Figures*; by T. L. WALKER, Geological Survey of India.

(Published by permission of the Director.)

WHEN crystals are acted upon by corroding reagents the crystal surfaces are seldom dissolved at a uniform rate. Frequently they become pitted with small corrosion or etching figures which are bounded by plane surfaces and which indicate the symmetry of the crystal surface upon which they occur. If a holohedral hexagonal crystal bounded by the prism (1010) and the basal pinacoid (0001) be etched, then there should be two kinds of etching figures. As the basal plane has six lines of symmetry, the corrosion figures on it must exhibit six lines of symmetry which must coincide with those of the basal plane. Hexagonal figures whose sides are parallel to the edges (0001) $\wedge$ (1010) would satisfy the requirements of symmetry (fig. 1, p. 184). The figures on the prismatic faces must be different from those on the basal plane. Since each prismatic face is symmetrical in two directions, the corrosion pits must also conform to these requirements and must have two lines of symmetry which must be identical in direction with the symmetry lines of the prismatic face on which they occur (fig. 2). If these conditions are not fulfilled, then we are compelled to conclude that the crystal in question is not physically and geometrically holohedral hexagonal but only apparently such.

As an illustration of this use of etching figures in crystallographic studies we may refer to the case of muscovite, which was supposed to be rhombic until Baumhauer* discovered that the figures produced on (001) by treating with fused caustic potash, did not show rhombic symmetry. As there appeared to be only one plane of symmetry in the figures while a rhombic basal pinacoid should possess two lines of symmetry, it was concluded that muscovite is only pseudo-rhombic but really monoclinic (fig. 3).

By employing this method the conclusions arrived at by purely geometrical studies have frequently been corrected.

Since etching figures reveal the crystal symmetry, faces which are crystallographically equivalent, such as the eight faces of a holohedral octahedron, the four prismatic faces of tetragonal, rhombic and monoclinic holohedral forms or the two basal planes of holohedral hexagonal crystals, must give similar figures. Parallel faces are generally equivalent but not always. In the case of parallel faces at opposite ends of

* Sitzber. Akad. München, 1874, p. 245, and 1879, p. 99.

a hemimorphic axis there can be no equivalence—the basal planes 0001 and 000 $\bar{1}$ in the hemimorphic tourmaline being crystallographically different ought to give different etching figures. This mineral is a representative of a large class of substances whose crystals have no crystallographic center and whose parallel planes are equivalent only when this is required by other elements of symmetry—lines or planes. Thus in the case of calamine, or hemimorphite, which is devoid of a center of symmetry, we should expect the basal planes 001 and 00 $\bar{1}$ to give different corrosion pits, but pairs of parallel prismatic faces should give similar etching figures. This is required by the presence of two planes of symmetry (100) and (010) and may be proved as follows: the prismatic faces $\bar{1}\bar{1}0$ and 110 are symmetrical about the symmetry plane (010), therefore these faces are equivalent and the etching figures on them must also be similar; but the faces 110 and $\bar{1}\bar{1}0$ are symmetrical with regard to the symmetry plane (100), therefore the faces are equivalent and the etching figures must be similar. But since the faces $\bar{1}\bar{1}0$ and $1\bar{1}0$ are both equivalent to the face 110, therefore they are equivalent to one another and will give similar etching figures, though the crystal possesses no centre of symmetry. In the same way it may be shown that all four prismatic faces are equivalent.

Very few experiments have been made with etching figures to determine the equivalence of pairs of parallel faces. I first made a few experiments to prove that parallel faces give similar figures when they belong to the same crystal form and different figures when they belong to different crystal forms, and then proceeded to examine some of the triclinic minerals with a view to determine which of them have equivalent parallel faces and which different. There are two recognized divisions in the triclinic system: first, crystals having surfaces in pairs which are crystallographically equivalent and give similar etching figures, and second, crystals whose surfaces are not always present in parallel pairs, and when they are, do not give similar corrosion figures and are not crystallographically equivalent. The first group are holohedral triclinic, and since they possess a centre of symmetry, Zirkel and others refer to them as *centro-symmetric*. The second group is often referred to as hemihedral triclinic or tetartohedral monoclinic, but as the crystals possess no element of symmetry, whether of line, plane or point, they are appropriately spoken of as *asymmetric*. Up to the present time no mineral representative of this latter group is known. A small number of complete artificial chemical salts crystallize in asymmetric forms.

Etching Figures on Tourmaline.—I selected a transparent greenish yellow crystal of tourmaline about a quarter of an inch in diameter. The prismatic zone was composed of the trigonal prism $\frac{\infty R}{2}$ ($10\bar{1}0$) and the prism of the second order ($11\bar{2}0$). One end was terminated by a single plane, the basis 0001, while the other end was not crystallographically terminated, a part of the crystal being broken off. The crystal was sent to R. Fuess of Berlin with the request to prepare two thin polished plates parallel to the base. After several fruitless attempts, I finally succeeded in obtaining good etching figures, by bringing the already slightly warmed tourmaline plate into a red-hot mixture of potassium bisulphate and coarsely powdered fluor spar. Below red heat no corrosion took place. After ten minutes the crystal was withdrawn from the red-hot fusion and allowed to cool slowly so as to prevent cracking. By treating with hot dilute hydrochloric acid it was easily cleansed from the coating of the corroding mixture. On examination with the microscope the face corresponding to the natural basis, 0001, was seen to be well covered with small figures which may be described as sharply angular equilateral triangles, with their sides parallel to the edges of the trigonal prism and basal plane and the angles pointing toward the above mentioned edge (fig. 4). The figures on the parallel face—the artificial basis $000\bar{1}$ —are also equilateral triangles, but the sides are curved and the angles blunt. A closer examination showed that the little figures are probably nine-sided and closely resemble sections through many tourmaline crystals whose prismatic zone is composed of the forms ($10\bar{1}0$) and ($11\bar{2}0$), the former predominating so as to give a trigonal habit to the crystal, with the latter forming narrow faces bevelling the edges of the trigonal prism. The chief sides of the corrosion figures are parallel to the edges of the trigonal prism and the base, but the angles of the triangle are turned away from the edge of the trigonal prism. This is shown in a more or less idealized form in fig. 5. Thinking this difference between sharp and blunt triangles might be due to the position or temperature of the crystal during the reaction, I etched the second polished plate, taking the precaution to hold it in such a position, by means of platinum pointed forceps, that both should be subject to exactly the same conditions. The resulting figures were quite like those on the first plate. The high temperature caused the greenish yellow crystal plates to become water-clear.

These figures are different, but as the basal planes of tourmaline contain three lines of symmetry the figures on *both* planes must also contain three lines of symmetry and these

must coincide with the lines of symmetry of the basal planes. A glance at figures 4 and 5 will show that this is the case. Although the trigonal axis of symmetry of tourmaline compels the figures to be built on the plan of the equilateral triangle, yet while conforming to this requirement the difference in the faces 0001 and 000 $\bar{1}$ is very clearly indicated by the difference of the etching figures.

Acid Dextro-Tartrate of Strontium.—This is one of the best known and most easily prepared of all the substances crystallizing in the asymmetric or hemihedral division of the triclinic system. Dr. Steeg & Co. of Homburg v. d. Höhe supplied me with a few very fine crystals for examination. These crystals possess one very perfect cleavage direction, which, according to the orientation proposed by A. Scacchi* and adopted by Liebisoh,† is taken to be the basal pinacoid (001) and (00 $\bar{1}$). Very thin cleavage plates are easily prepared which serve very well for etching. As the substance is readily soluble in water, good figures were prepared by placing the cleavage fragment between folds of a piece of *very* slightly moistened calico and pressing between the finger and thumb for twenty seconds. A microscopic examination showed that the figures on 001 were four-sided with their sides parallel to the edges of the cleavage plate. The four sides of the corrosion pits are nearly equal (fig. 6). On the parallel face 00 $\bar{1}$ the figures are also four-sided but very slender, almost reduced to mere lines at times (fig. 7). After etching and examining a large number of cleavage plates, I satisfied myself that these figures are unmistakably different and eminently characteristic for the two faces upon which they occur. It would be impossible to confuse them. So much is this so, that if a crystal were split into half a dozen cleavage plates and these etched, then by means of the difference of the figures the upper and lower surfaces could be distinguished and the crystal reconstructed with all the fragments properly oriented.

So far as I know, the only previous experiments made with etching figures with a view to determining the crystallographic equivalence of pairs of parallel faces, are those made by Miers on spangolite. This hemimorphic hexagonal mineral had been described by Penfield from a single specimen from Arizona, when Miers found it on some specimens of Cornish copper minerals. In his description in the *Mineralogical Magazine* he says: "In order to obtain independent evidence of the hemimorphic character of this mineral, experiments were next made upon etched figures, it being thought that possibly some

* A. Scacchi, *Atti. Accad. delle Sc. Fis. e Mat.*, Napoli, 1, 1863.

† *Grundriss der Krystallographie*, p. 176, Leipzig, 1896.

difference might be found between the etching upon the upper and under surface of a cleavage plate. This was found to be the case; cleavage plates exposed to the action of dilute hydrochloric acid showed upon both sides the characteristic etched triangles figured by Penfield. These were identical in form, but very different in dimensions; the plates were invariably attacked with much greater rapidity upon the lower or attached end than upon the surface directed toward the unattached end of the crystal.*

I was not aware of Miers' experiments till after those on tourmaline and acid dextro-tartrate of strontium were completed and this paper written in almost its present form.

From the experiments above described I think the desired confirmation has been given to the statement:—*Crystal faces belonging to the same crystal form give identical or similar etching figures, while faces belonging to different crystal forms give different etching figures even if the faces be parallel to each other; or conversely, if parallel faces give different etching figures, the faces do not belong to the same crystal form.*

Taking the above statement as a basis, I proceeded to examine some of the common triclinic minerals with a view to determining which of them are centrosymmetric and which asymmetric.

Axinite.—I was fortunate enough to obtain a few of the beautiful crystals from Bourg d'Oisans in Dauphiné. This mineral has been crystallographically described by many authors, so that several different ways of orienting the crystals are in common use. The references in this note are to Naumann's orientation, which is probably the one most generally used by English and American mineralogists.

By acting upon the crystals for five minutes with a hot mixture of equal volumes of concentrated sulphuric and hydrofluoric acids, very sharp figures were obtained. The most easily examined and at the same time most striking are those on $\bar{1}\bar{1}1$, which is the face designated by the letter *r* by Naumann and Schrauf. The figures contain no line of symmetry. Those on $\bar{1}\bar{1}1$ and $\bar{1}\bar{1}\bar{1}$ are illustrated in figures 8 and 9 and are related to one another in the same way as the right hand is to the left. This, however, is in accord with crystallographic characteristics of the system, the faces being related to each other in the same way, so far as outline is concerned. This dissimilarity is well seen in the case of the pyramidal faces in the rhombic system. The eight faces of a simple rhombic unit pyramid are all scalene triangles; the triangular faces 111 ,

* Min. Magazine, vol. x, p. 276, 1894.

$\bar{1}\bar{1}1$, $1\bar{1}\bar{1}$ and $\bar{1}\bar{1}\bar{1}$ are equal to one another and are identical in form—these triangles can be placed upon one another so as to coincide *without being turned over*. The faces $1\bar{1}1$, $11\bar{1}$, $\bar{1}\bar{1}\bar{1}$ and $\bar{1}11$ bear to each the same relationship and may be made to coincide by superposition *without being turned over*. The triangles of the first group cannot be made to coincide except by turning over. The triangles of these two distinct groups are related to one another as right and left. Suppose that on such faces we have etching figures, triangular in outline and with their edges parallel to those of the triangular face upon which they occur. They too must be related to one another as right and left, but with this difference, that the corrosion pits have three dimensions, and by turning over the triangular outlines may coincide, but the pits will then project in opposite directions and will form a closed space which will be symmetrical about the plane of contact. This is quite like the relation that the valves of a clam shell bear to one another—they can never be so turned as to fit into one another. So also the cast of a corrosion pit on a pyramid face of one of the above groups cannot be fitted into a pit on a face of the other group. The one is the mirror image of the other turned about 180° . The figures accompanying this paper have generally been turned in this way so that the image relationship may be plainly seen.

For clearness it would be well to refer to figures which agree in all respects as identical—those on all the faces of either of the above groups are *identical*; figures which have the right and left relationship may be referred to as *similar*, while all corrosion pits not belonging to either of these classes may be designated as *different*.

The dagger-shaped figures on the faces $1\bar{1}1$ and $\bar{1}1\bar{1}$ of axinite crystals being *similar*, we must conclude that the mineral is centro-symmetric.

Cyanite.—Pale blue crystals from St. Gothard were used. They are well developed in the zone of the vertical axis showing the forms (100) (010) and (110). The crystals are contained in paragonite schist and are elongated in the direction of the vertical axis. As the mineral is very cleavable along (100), good material is easily obtained for etching. Their cleavage fragments, which had been previously carefully warmed, to avoid decrepitation or unnecessary shattering from suddenly heating, were plunged into a red-hot mixture of potassium bisulphate and coarsely powdered fluorspar. After one or two minutes they were taken out, allowed to cool slowly and then cleansed by boiling with hydrochloric acid. Very satisfactory figures were obtained. Those on 100 are shown in fig. 10

and are similar to those on $\bar{1}00$ (fig. 11), thus indicating that the mineral is centro-symmetric triclinic.

Chalcanthite, or Copper Vitriol.—This triclinic mineral rarely occurs in well developed crystals, so that the crystals etched were artificial and grown from a saturated solution of copper sulphate. About twenty grams of ordinary "blue stone" was dissolved in hot water to concentration, acidified with a few drops of sulphuric acid, filtered and allowed to cool, when the larger portion crystallized out. The solution was poured into a second dish and after twenty-four hours half a dozen well-formed crystals had separated. These were used for examination. The corrosion figures were obtained by increasing the temperature of the saturated solution, from which the crystals had grown, about two degrees. When the warm (comparatively) mother liquor had reacted for sixty seconds the crystals were removed and quickly dried with filter paper. The figures resulting in fig. 12 are those formed on the front face of the left hemiprism $1\bar{1}0$. Those on the parallel face $\bar{1}10$ are seen in fig. 13. As the corrosion figures on the parallel faces are similar, we conclude that chalcanthite is centro-symmetric triclinic.

Rhodonite.—Fragments of rose-colored crystals from Långbangshytta, Wernmland, Sweden, were treated for one minute with a warm mixture of equal volumes of concentrated sulphuric and hydrofluoric acids. As this mineral is very rich in crystal forms and exhibits many different types, accordingly having only fragmentary crystals to work upon, it was difficult to determine with certainty the symbols for the faces. The corrosion figures from two parallel faces are represented in figs. 14 and 15. The faces in question were largely developed, striated and were cut obliquely by the two principal cleavages, presumably (110) and $(1\bar{1}0)$. Though not certain, I have assigned the figures to the basal pinacoids 001 and $00\bar{1}$ according to Dana's crystallographic orientation of the mineral. The striation referred to is parallel to the longer direction of the etching figures. The corrosion pits are such as to warrant the conclusion that the mineral is centro-symmetric triclinic.

Albite.—The material employed for this examination consisted in two or three small water-clear crystals from the Alps. Cleavage fragments parallel to (001) were easily prepared, on which the angle of optical extinction was measured under the microscope and found to be $+4^{\circ}54'$, thus proving the crystals to be a plagioclase free from lime, that is albite. By treating

for thirty seconds with a half-and-half mixture of sulphuric and hydrofluoric acids, very interesting figures were obtained. At first sight there seems to be no regularity about them, but it is soon seen that all the figures can be referred to a very simple primitive corrosion pit which resembles in outline a right-angled triangle whose sides are 3, 4 and 5, the shortest side being parallel to the brachypinacoidal edge and the smallest angle directed towards the left. The figure on 00 $\bar{1}$ is similar and has its smallest angle pointing in the opposite direction. Figure 16 represents a basal cleavage fragment from an albite crystal simply twinned according to the albite law. On the left are the figures on 001 and on the right those on 00 $\bar{1}$. The primitive figures are seen to give, on further development, such pits as those shown immediately below them. The arrow-headed corrosion figures are the commonest and appear to be the adult or final form. All intermediate stages in development between these are plainly seen under the microscope. The offshoot from the primitive form may take place from one of the angles and produce nail-shaped figures. This can take place from any of the three angles and can be traced through all the intermediate stages. It is commonest from the right angle of the triangle, as is the case in the instance figured.

Since the primitive form gives rise to four different final forms or types and a large number of intermediate stages, it is not surprising that at first sight one should not see any definite order. The first, third and fourth types are the commonest.

This development from simplicity and uniformity to variety and complexity appears to be almost as common in crystal life as biologists have shown it to be for organic life. Minute crystals and tiny etching figures give promise of a heterogeneity and variety which they do not actually possess in their earlier stages of development.

But there is another form of etching figure to be noted. Suppose a figure should begin exactly on the line of contact between twinning lamellæ, the figures would develop symmetrically on both sides of the line of contact. This is illustrated in figure 16. These figures possess a plane of symmetry and are such as we might expect on the basal plane of a monoclinic crystal. If the albite twinning lamellæ were very, very thin, then all the figures would be like these, because every figure would be large enough to extend across several lamellæ. This only proves by means of etching figures what has been long known from geometrical crystallographic studies—viz, that twinning increases the symmetry of a crystal.

Some of the pits above described are represented in the

See next page for Explanation of Plate.

drawings as if some of their surfaces were curved. This only means that there are a large number of faces present, so that the figures *appear* to have curved surfaces, just as prisms of tourmaline often appear to be rounded. There does not seem to be any reason to depart from the opinion of Baumhauer and Becke, who hold that the surfaces of etching figures are never curved but always plane.

The small number of minerals dealt with in this paper were selected generally because they were most easily obtained in suitable specimens, at other times because they gave definite results. I hope to describe more of the triclinic minerals at a future time.

My thanks are due to Babu Nrependra Nath Bose, who has redrawn the figures from sketches made by myself.

Indian Museum, Calcutta, Nov. 1st, 1897.

EXPLANATIONS OF PLATE.

FIGURE 1.—Corrosion figures such as might be formed on the basal plane of a holohedral hexagonal crystal.

FIGURE 2.—Corrosion figures showing the symmetry of the prismatic face of a holohedral hexagonal crystal.

FIGURE 3.—Figures on basal plane of muscovite showing monoclinic symmetry—produced by fused KOH.

FIGURES 4 and 5.—Figures on 0001 and 000 $\bar{1}$ of tourmaline showing the physical difference between the two parallel planes—produced by red hot fusion of KHSO₄ and CaF₂—time 2 minutes.

FIGURES 6 and 7.—Figures on 001 and 00 $\bar{1}$ of acid dextro-tartrate of strontium. Produced by pressing between very slightly moistened folds of calico for 20 seconds.

FIGURES 8 and 9.—Figures on 1 $\bar{1}$ 1 and 11 $\bar{1}$ of axinite—produced by a hot mixture of equal volumes of strong H₂SO₄ and HF acting for 5 minutes.

FIGURES 10 and 11.—Cyanite, 100 and 100 $\bar{1}$ —KHSO₄ and CaF₂ at red heat for 1 to 2 minutes.

FIGURES 12 and 13.—Copper vitriol, 1 $\bar{1}$ 0 and 110. Produced by raising the temperature of the mother liquor in which the crystals had grown 2°C. and allowing the slightly warmed solution to corrode for sixty seconds.

FIGURES 14 and 15.—Rhodonite, 001 and 00 $\bar{1}$, hot mixture of equal volumes of strong H₂SO₄ and HF—time 60 seconds.

FIGURE 16.—Albite simply twinned—shows figures on 001 and 00 $\bar{1}$ —same reagent as in 14 and 15—time 30 seconds.