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MECHANISM OF NATURAL ETCHING OF HEMATITE CRYSTALS

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ABSTRACT

Surface structures on the basal plane of hematite crystals from many localities have been observed with a phase contrast microscope. Patterns formed by natural etching are distinguished from the growth patterns, and their characteristics are described. The mechanism of etching is explained on the basis of these observations.

Etching principally takes place two-dimensionally. It preferentially starts at the step of growth layers or at the edges of screw dislocations which terminate on the surface. Etch pits are formed evenly all over the surface and the depth of etching is in the order of two or three unit cell heights. These features are explained on the basis of surface imperfections and an unsaturated zone on the finished surface of a crystal. It is also suggested that the depth of an unsaturated zone is that of two or three unit cells. From the difference in degree of etching, growth conditions of different localities are discussed.

INTRODUCTION

Most studies on natural etching of minerals published so far are mainly concerned with the morphology of etch pits or the relation between etch figures and the symmetry of the face concerned (Honess, 1927). In the field of metallurgy, attention has been paid to the relation between etch pits and dislocation points. It is well established that etching preferentially starts at a dislocation point in the case of metals. It is also widely believed that the process of dissolution is entirely the same as that of growth, but in the opposite direction. If this is so, etching process should also be two-dimensional, since the growth of crystals takes place mainly by two-dimensional spreading of layers. However, except in one case (Patel, 1957), most observations on etching patterns have reported that they are three-dimensional (Honess, 1927). Since most previous observations have been made with microscopes without phase contrast, it is possible that very thin etch features have been missed.

The writer has made detailed observations on the surface structures of the basal plane of natural hematite crystals from different localities with a very sensitive phase contrast microscope. The microscope used in this study is so sensitive that it can reveal growth layers having step height down to 2.3 Å (Sunagawa, 1958, 1961). Some of these observations on the growth patterns have been reported in this journal (Sunagawa, 1962). It was noticed that some of the surface patterns can be explained only in terms of etching, although they look like growth patterns. Careful observations have been carried out on these special patterns, and it is found that etching principally takes place two-dimensionally, as in the case of growth, and that only when screw dislocation points terminate on the surface, can etching start from these dislocation points and be effectively three-dimensional. However no preferential etching has been observed at the dislocation points of spirals. These observations give a view of the etching process entirely different from the results of previous studies.

Observations Under Low Magnification

As already reported in this journal (Sunagawa, 1962), the surface of the basal plane consists of many layers parallel to the plane. One or several centers, which are always elevations and thus growth centers, are usually observed on the surface. These surface patterns are clearly formed by growth originating from these centers.

The surface of the basal plane of some crystals from the Azores Islands also consists of layers, which appear at first sight to be growth patterns. However, there are two distinct differences from the usual growth patterns. These differences are shown by photomicrographs as follows.

Figure 1 shows one of the most typical examples. Both circular and deformed triangular centers are observed on the surface. Two characteristics are evident; one is that circular centers are all depressions whereas the triangular centers are all elevations; the other is that the fronts of

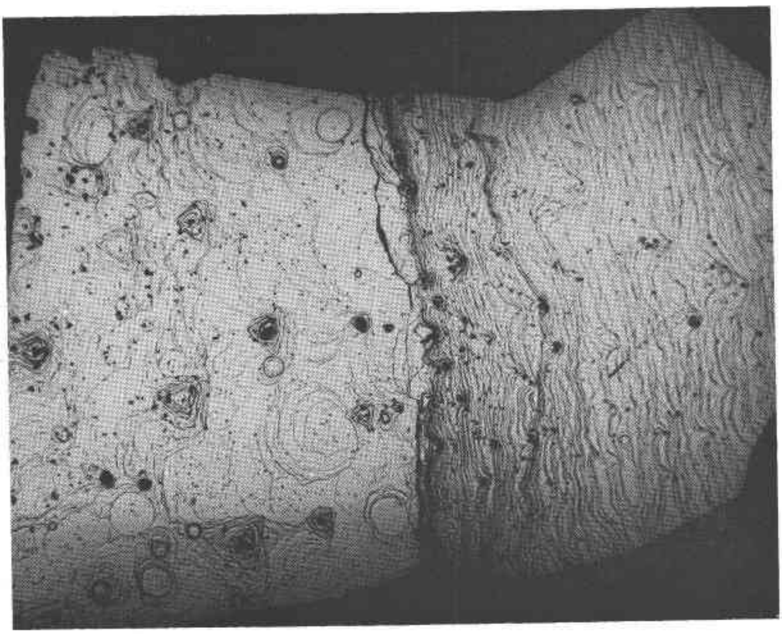

Fig. 1. Photomicrograph showing natural etching on the basal face of hematite from the Azores Islands. ×10.

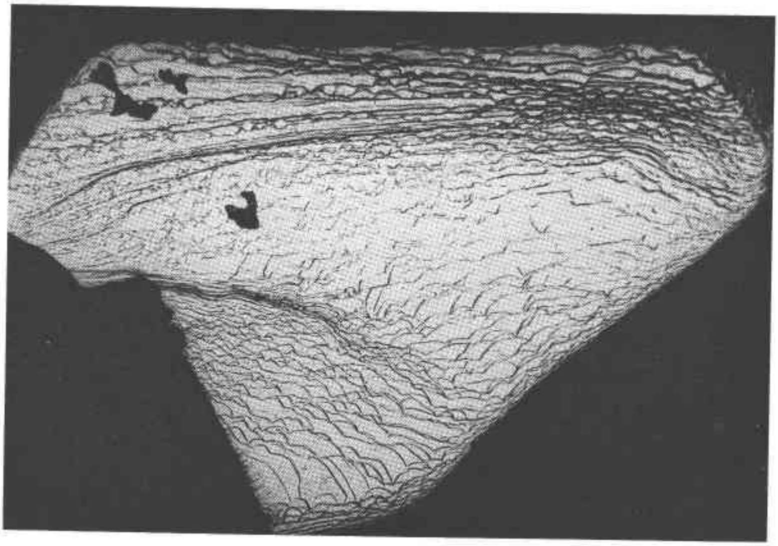

FIG. 2. Photomicrograph showing pronounced natural etching of hematite. There is no center, and the edges of layers are remarkably concave. ×8.

layers consisting of triangular centers have a concave form if they are seen from the higher side. Figure 2 shows an extreme case in which there is no center at all, and the fronts of layers are remarkably concave. Two characteristics observed here can not be explained on the basis of growth mechanism, for the following reasons:

1. It is impossible to explain the existence of a large number of depression centers on one surface by growth. In some cases, a few depression circles can be formed at the places which are not filled up by growth fronts spreading from several directions, but this is certainly not the case here, since no elevation centers but only depression centers are observed in some cases.
2. Looking from the higher side, growth fronts should take convex form, concave fronts being theoretically impossible in the case of growth. If etching takes place two dimensionally, etch fronts should have concave form, as schematically shown in Fig. 3.

Therefore, it is safe to conclude that the surface patterns observed on these crystals are in fact formed by etching, although they look like growth patterns.

These observations clearly show that the etching process is two-dimensional, as growth is, and that the direction of etching is opposite to that of growth.

Observations With a Phase Contrast Microscope

Unetched crystals usually have a molecularly flat surface of growth layers. Even when the surface is examined with a powerful phase contrast microscope, it is molecularly flat and no roughness of the surface is observed. But the surface of crystals from the Azores Islands usually is fairly rough. This roughness is clearly formed by natural etching, since it has several characteristic features. These features are described in the following.

Etch pits

Very minute etch pits are observed all over the surface of the many crystals examined. When they are small, they look circular, but developed etch pits have a triangular form oppositely orientated to the growth triangles (Fig. 4). It is noticed that the depth of a pit is not great and the bottoms of the pits have a smoother surface than the original surface. This was confirmed by the following observation. On some crystals, a special surface pattern is observed as shown in Fig. 5. As clearly seen in this positive phase contrast photomicrograph, the surface consists of many flat-bottomed triangular depressions which are randomly orientated. Some of these triangular patterns have saw-teeth edges which are parallel of the triangular etch pits. Therefore, these flat-bottom triangular depressions are formed by pronounced etching. A remarkably flat and smooth surface is observed at the bottom of these depressions. From a multiple-beam interferogram (Tolansky, 1948) of one of these surfaces, the depth of the depressions can be measured, and is found to be about 50 Å, which is nearly the height of three unit cells.

These observations clearly show the following two points;

1. Etch pits do not deepen themselves three-dimensionally, but develop two-dimensionally after their depth has reached two or three unit cell height.
2. Etching progresses two-dimensionally, exposing a new fresh surface behind.

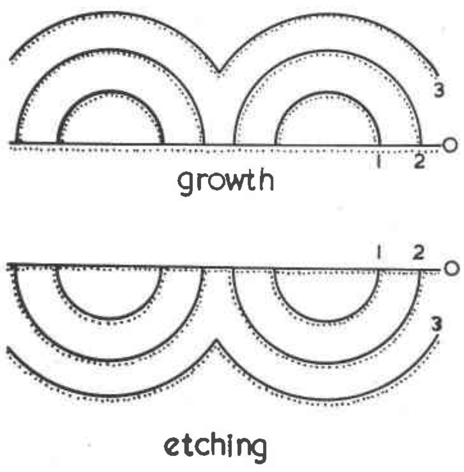

Fig. 3. Schematic diagram of growth and etch fronts. Dots indicate higher side.

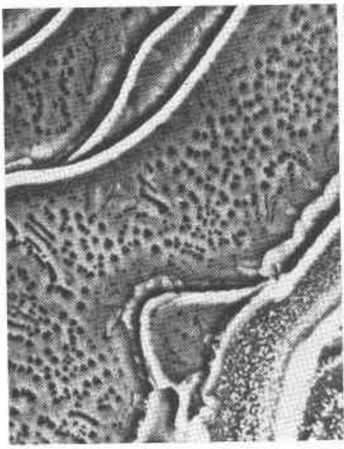
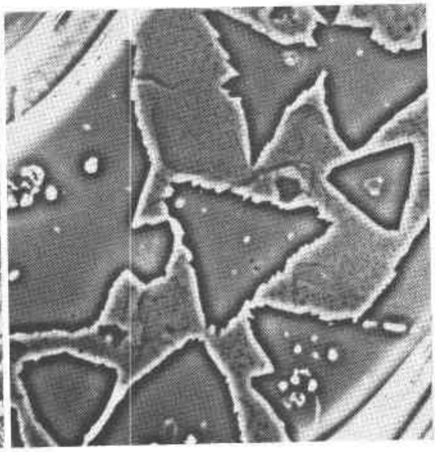

FIG. 4. (left) Positive phase contrast photomicrograph showing pronounced etch pits. ×190.

FIG. 5. (right) Flat bottom depressions formed by pronounced etching of the surface of thick layers. Positive phase contrast. ×190.

Etching along growth fronts

On some crystals from the Azores Islands, triangular or circular spirals are observed on the surface of thick growth layers. These spirals differ from the usual pure growth spirals in one important aspect. Figure 6 is an example of these spirals. Spiral fronts consist of two lines; the outer line is straight and the inner line is ragged. This clearly shows that the original growth fronts are straight lines, but recede to the inner ragged lines by two-dimensional etching. On the surface of spiral layers, minute etch pits are observed, but the degree of etching at spiral fronts is clearly stronger than that on the surface. This suggests that etching preferentially takes place at the growth fronts. In Fig. 6b the outer straight edges are regularly triangular, while inner ragged lines are more or less circular. This is because etching progresses more at the corners than at the edges. As seen in these photomicrographs, the surface newly exposed by etching has a smoother surface than the original one.

Figure 7a shows fringes of equal chromatic order (Tolansky, 1948) running across one of these spiral patterns. From these fringes, three points are clear:

1. The original step height of the spiral is very small,
2. The depth of the etched part is large compared with the original step height of the spiral, and found to be about 50 Å,
3. The surface of the etched part is very smooth.

Therefore, the profile of these etched spirals can be schematically drawn

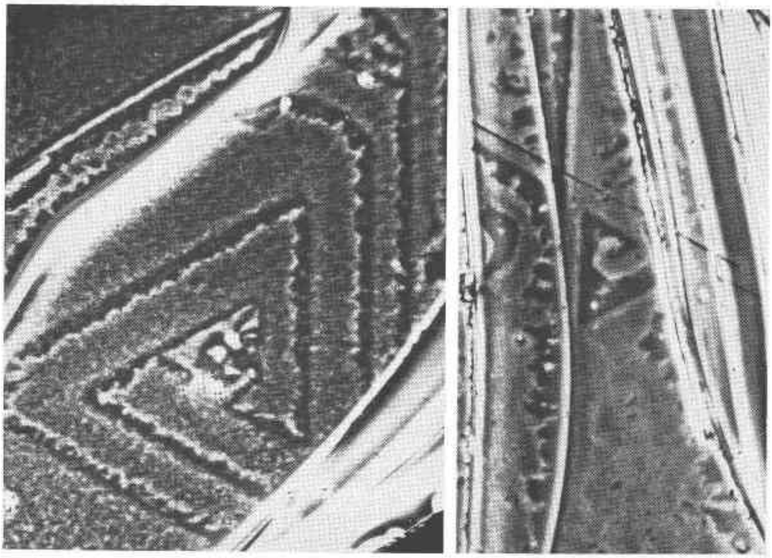

FIG. 6. (a) left), (b) right). Positive phase contrast photomicrographs showing typical spirals which have been naturally etched. ×230.

as in Fig. 7b. This shows that etching preferentially starts from growth fronts, but at first deepens to two or three unit cell depth and then develops two-dimensionally. This depth is the same order as that of etch pits.

Figure 8 shows three examples of triangular cones arranged according to the degree of etching; (1) unetched triangular cones; (2) slightly etched along the fronts; and (3) strongly etched triangular cones. The phenomenon of preferential etching is quite a universal feature.

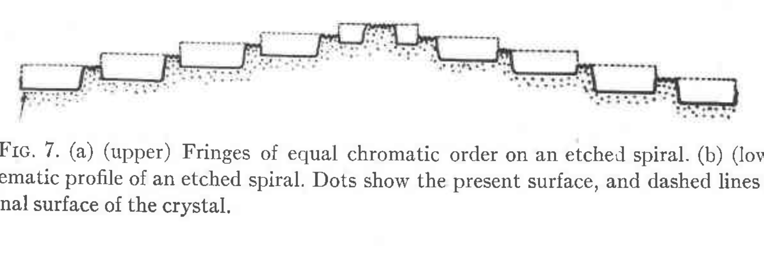

FIG. 7. (a) (upper) Fringes of equal chromatic order on an etched spiral. (b) (lower) Schematic profile of an etched spiral. Dots show the present surface, and dashed lines the orginal surface of the crystal.

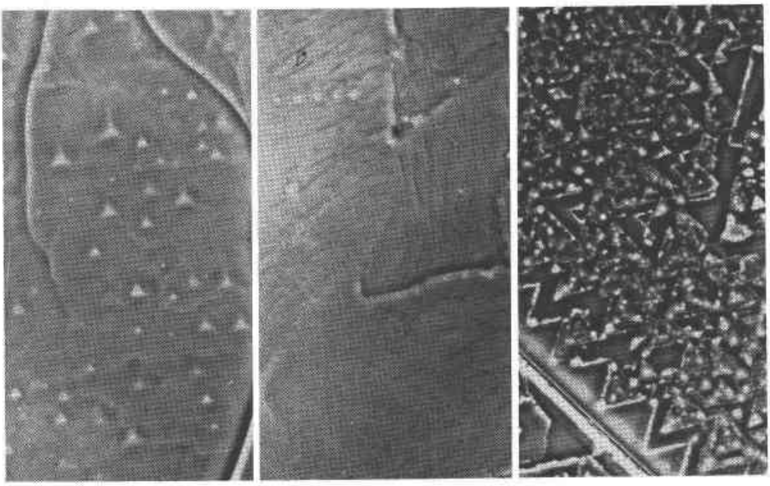

FIG. 8. Positive phase contrast photomicrographs of triangular cones arranged according to degree of etching. ×190.

According to the studies of etch pits of metals, it is generally believed that etch pits are preferentially formed at the dislocation points. However, as can be clearly seen in Figs. 7 and 8, evidence of preferential etch-

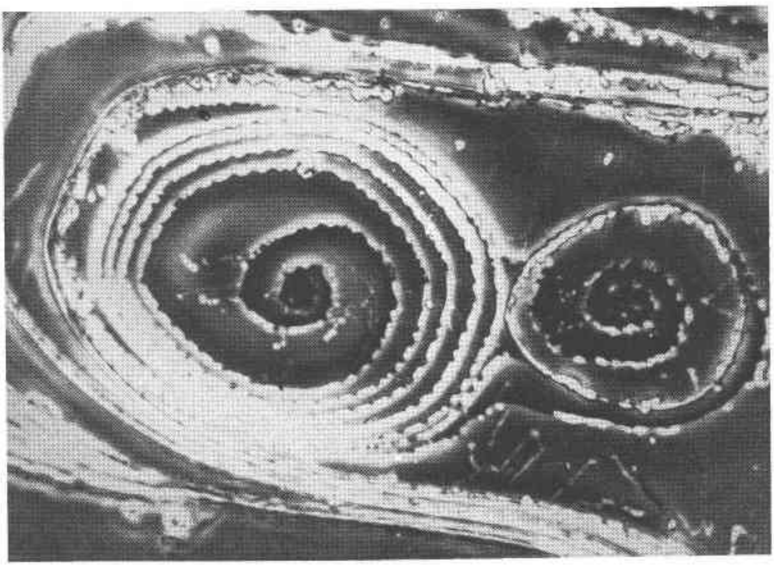

FIG. 9. Positive phase contrast photomicrograph of one of the simplest depression spirals observed on the basal face of hematite. ×880.

ing at the dislocation points is not observed at the center of a spiral pattern, which is a termination point of a screw dislocation on the surface. The degree of etching at this point is as strong as at the fronts of spirals. Therefore, it can be concluded that etching can preferentially start from the place where there is an imperfection or a step. It is also predicted from these observations that even if etching is pronounced, elevation spirals will remain as elevation, and depression spirals will not be formed as a result of pronounced etching of elevation spirals.

Depression spirals

On the surface of thick layers or at the bottom of circular depressions of the crystals from the Azores Islands, depression spirals are commonly ob-

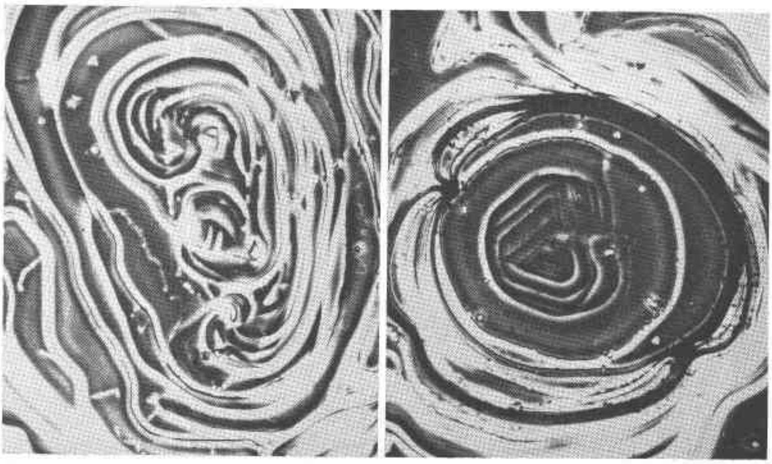

FIG. 10. Two examples of complicated depression spirals. Positive phase contrast. ×195.

served. Figure 9 is an example of the simplest depression spirals observed on the surface of a thick layer. Two right handed spirals are observed on this photomicrograph. At the center, the spacing between successive arms is wide, but after a few turns it decreases. One noteworthy point is that these spirals have saw-tooth fronts. Figure 10 shows two examples of fairly complex depression spirals. At the bottom of most of the circular centers, spiral depressions originating from a group or a row of dislocations are also observed. Generally speaking, these depression spirals have more complex patterns than usual elevation spirals, and the spacing between successive arms becomes narrower after a few turns.

As described in the previous paper on the mechanism of growth of hematite (Sunagawa, 1962), some depression spirals can be formed on the surface of thick growth layers by growth. However, this mechanism can not be applied to the depression spirals observed here, for the following reasons.

1. Spiral fronts sometimes have saw-tooth structure.
2. Many depression spirals are situated at the bottom of depression circles, which are considered to be formed by etching.
3. Most of the spirals observed on one surface are depressions.
4. The morphology of these spirals differs from that of both elevation and depression spirals formed by growth.

Now, consider that a screw dislocation (not a spiral hillock) terminates on the surface when the crystal is etched. Since there is a dislocation edge exposed on the surface, etching will preferentially start from the edge,

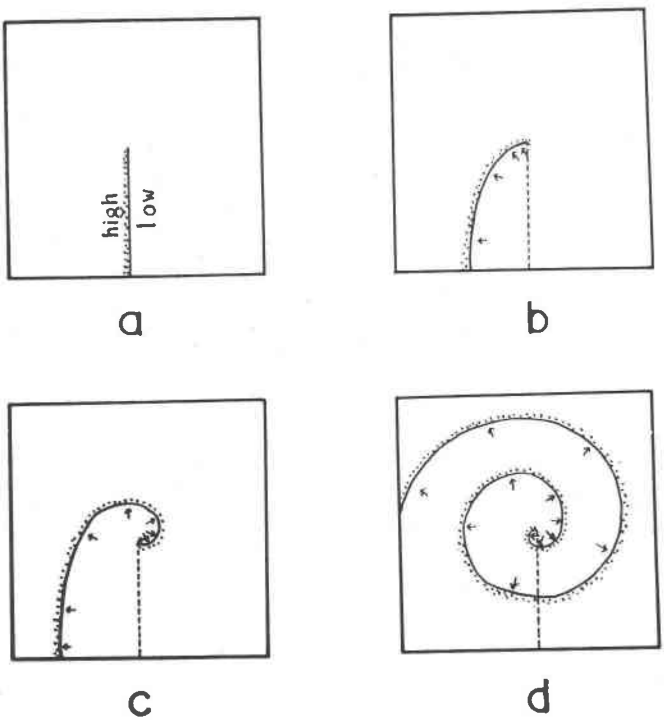

FIG. 11. Diagrams showing the process of formation of a depression spiral by etching.

and the etch front will rotate around the dislocation point, as schematically shown in Fig. 11. Thus, depression spirals are formed by etching.

In this case too, the process of etching is principally two-dimensional, but because etch fronts rotate around the dislocation point, it is effectively three-dimensional.

Depression circular centers

As described earlier, there are many depression circles on the surface of the crystals from the Azores Islands. In many cases, only depression circles can be observed on the surface, and no elevation centers.

When the surface of these depression circles is observed under a phase contrast microscope, it is noticed in many cases that there are depression spirals originating from a row or a group of dislocations. Therefore, it can be said that most of the depression circles are formed by etching along dislocation edges. However, no depression spiral is observed on some of the depression circles. Figure 12 is a phase contrast photomicrograph of the

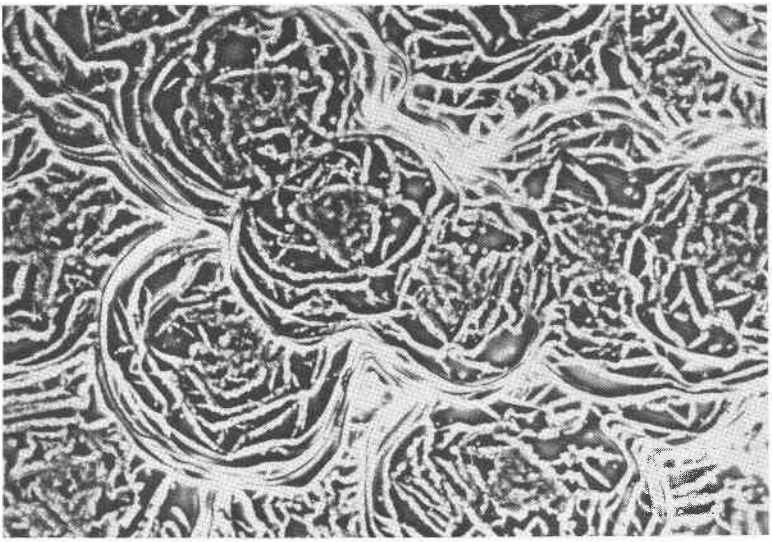

FIG. 12. A positive phase contrast photomicrograph showing the formation of depression circles by many pronounced concave etch fronts. Irregular lines are overgrown foreign material. ×185.

depression circles of this type. In this photomicrograph, it is noticed that the circles are not complete, and that they actually consist of pronounced concave etch fronts. Therefore, it is believed that some of the depression circles are formed by pronounced concave etch fronts.

OBSERVATIONS ON THE CRYSTALS FROM OTHER LOCALITIES

The above observations were made on the crystals from the Azores Islands, Portugal. Similar investigation has been carried out on the crystals from the following localities; Ayumikotan, Sasazawa, Saganoshima, Gihofuji (Japan); Vesuvius, Stromboli (Italy); Ascension Island; British West Indies.

None of these crystals exhibits pronounced etch pattern as observed on the crystals from the Azores Islands. Their surface structures are all typical growth patterns consisting of a few elevation growth centers and growth centers and growth layers parallel to the basal plane. No depression centers have been observed on these crystals.

However, on some crystals from Ayumikotan, Saganoshima, Stromboli and the British West Indies, some evidences of weak etching have been observed. On some crystals from Ayumikotan and Saganoshima, irregu-

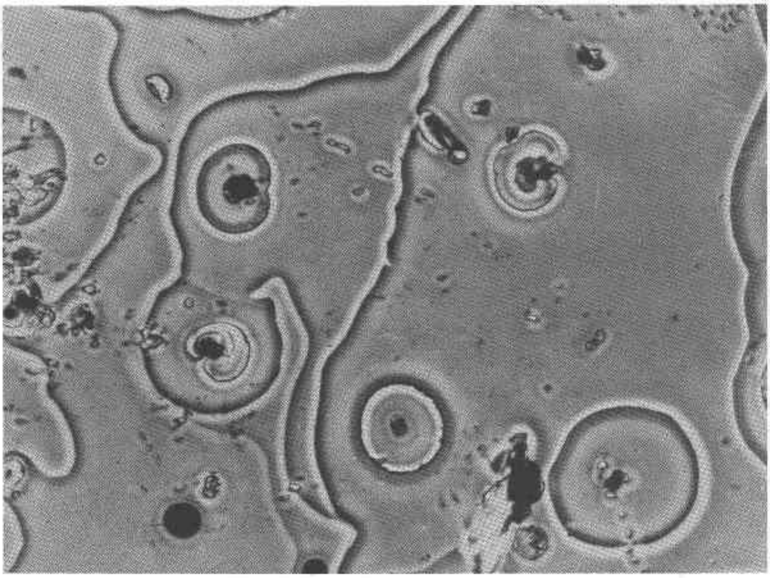

FIG. 13. A positive phase contrast photomicrograph of natural etch patterns on the basal face of hematite from Ayumikotan, Japan. ×185.

lar depression patterns of very small depth have been observed, a phase contrast photomicrograph of a typical example of which is shown in Fig. 13. Triangular etch pits are also observed on some crystals from Saganoshima. Minute etch pits along growth fronts of elevation spirals are observed on the crystals from Stromboli. Some of the crystals from the British West Indies show two-dimensional etching along the edges of very thin growth layers. In any case, etching features are fundamentally similar to those of the crystals from the Azores Islands, and the two-dimensional etching process can be clearly seen in every case, although the degree of etching is much less.

Now, all hematite crystals examined in this study come from volcanic lava, and not from hydrothermal or contact deposits. They clearly crystallized when iron chloride gas, which originates from a magma reservoir and migrates through lavas as a post-volcanic action, meets oxidation conditions such as underground water, etc. Therefore, after forming Fe_2O_3,Cl will combine with H in water forming HCl, which is a strong etching agent of hematite. Thus, if more water is supplied, more HCl will be formed, which will result in stronger etching.

Crystals from the Azores Islands come from Ponta de Serreta, Terceira Island, which is a very small volcanic island in the ocean. Therefore, it is possible that the crystals have grown under the sea, under which conditions more HCl is expected to be formed. As a result, crystals are strongly etched. Saganoshima and Stromboli are also volcanic islands, and crystals from Ayumikotan occur in andesitic agglomerate situated near the sea coast. Crystals from these localities show etching phenomenon, though it is weaker than the case of the Azores Islands. On the contrary, crystals from Sasazawa, Gihofuji, Vesuvius and British West Indies occur in volcanic lava flow of inland volcanoes, and they do not show clear evidence of natural etching. Therefore, it is concluded that the degree of etching is due to the water supply, and that the crystals grown in the lava of submarine volcanoes receive stronger etching than the crystals grown in the lavas of inland volcanoes.

Summary and Conclusions

Surface structures of the basal plane of many hematite crystals from different localities have been observed with a phase contrast microscope. Among these crystals, those from the Azores Islands show clear evidences of natural etching. Characteristics of natural etch patterns observed on these crystals are summarized as follows:

1. Coarse pattern.
   a) Coarse surface structures look like growth patterns commonly observed on the crystals from other localities.
   b) Many circular depression centers are observed on the surface, and sometimes there are only depression centers and no elevation centers.
   c) Fronts of layers show remarkable concave form.
2. Fine structures.
   a) Etch pits do not deepen three-dimensionally, but develop two-dimensionally after their depth has reached two or three unit cell height.
   b) Fresh surface is exposed by etching.
   c) Etching preferentially takes place along the edges of growth layers, and no predominate etching has been observed at the dislocation points of growth spirals.
   d) When the edges of screw dislocations are terminated on the surface, etching preferentially starts at these edges and rotates around the dislocation points, thus forming depression spirals.

From these observations, the following conclusions are clear:

1. Etching principally takes place two-dimensionally, and preferentially starts at the places where there are steps or imperfections on the surface,
2. At the same time, minute etch pits are formed evenly all over the surface,
3. Depth of etching is greater than the height of thinnest growth layers and of the order of two or three unit cell heights, both in the case of etching along steps and etch pits,
4. Fresh surface is exposed by etching.

As reported by the writer (Sunagawa, 1962), growth of hematite takes place by two-dimensional spreading and piling up of growth layers parallel to the basal plane. Therefore, the process of etching is fundamentally the same as that of growth, but different in the direction and in the unit of depth or height. This process of etching is quite reasonable and there is no need of further explanation, though such a process has never been found in previous studies.

However, further consideration is necessary about the reasons for points 2, 3 and 4. Since etch pits are formed evenly all over the surface and do not deepen three-dimensionally, it is possible that these points are neither screw nor edge dislocation points, but the normal surface itself. It is difficult to draw a conclusive explanation as to why etch pits are formed evenly, why the depth of etching is in the order of two or three unit cell heights, or why fresh surface is exposed by etching. However, as one of the most plausible explanations, the following can be proposed.

It is well known that the growing surface of a crystal is unsaturated or incomplete. Even when growth is finished, the uppermost surface remains unsaturated. The depth of the unsaturated zone is not yet clarified. Therefore, the finished surface will contain many vacancies, etc., from which etching can start. If etching starts from these points, etch pits thus formed will deepen until they reach a saturated zone. They can then not deepen further, and will develop sideways. Since the surface thus exposed by etching is the top surface of the saturated zone, it has a fresh and smoother surface than the original one, as is actually observed. Therefore, if we accept this explanation, all phenomena observed are satisfactorily accounted for. Furthermore, it can be said that the depth of unsaturated zone of a hematite crystal is in the order of two or three unit cell heights.

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