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Author(s)	Tomisaka, Takesi
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ON THE RELATION BETWEEN INNER STRUCTURE AND CRYSTAL SURFACE OF DANBURITE FROM TOROKU, MIYAZAKI PREF., JAPAN

(Studies on the Irregularity of Crystal surface. Report 1)

By

Takesi TOMISAKA

Contribution from the Department of Geology and Mineralogy,
Faculty of Science, Hokkaido University, No. 401.

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1. Introduction

The morphology of the danburite crystals, which were found at the Toroku mine, Miyazaki Prefecture, Japan, has already been studied by Prof. Dr. Z. HARADA.¹⁾

According to him, the danburite crystals of that locality, having l (110), w (201), d (011), a (010) and b (100) faces, are colorless, transparent and prismatic. Of them, faces a (010) and b (100) are rather seldom to occur and c (001) is extremely rare. The prismatic face l (110) is very elongated. Faces a (010) and b (100) are rarely corroded, but very often almost smooth, though they occur usually as very small faces.

Of these faces of crystals above mentioned, peculiar features, being observed on the surface of faces l (110), d (011) and w (201) have already been noticed by some mineralogist. Namely dense striations are recognized on the l (110), being parallel to the c -axis, and also the lentil growth-projections. These lentil growth-projections show also the directions of their main axis to be parallel to the c -axis. On the face d (011), irregular growth-projections are also found, which features resemble somewhat to "ripples". Meanwhile, the peculiar features of the dome

w (201) attract the writer's attention. The faces now in consideration are always naturally etched and more clouded than other faces. Those peculiar features may be seen on Figs. 1 and 2. Fig. 1 shows the clouded face with numerous irregularly scattered cavities. Fig. 2 exhibits slightly less clouded than that of the preceding figure, but possessing quite definite longitudinal etch grooves. Although there are many intermediate types between these two types, the surface of the type Fig. 1 is always ashen-gray in color, and the thickness of the clouded layer is about 1 mm.

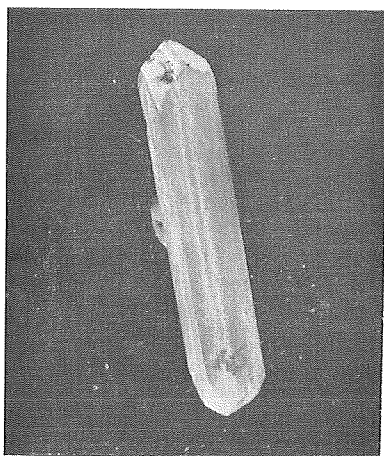


Fig. 1. Danburite crystal from Toroku. Natural size.

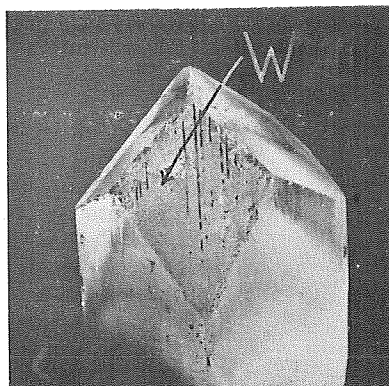


Fig. 2. Natural etch-grooves on dome w (201). $\times 2$.

Danburite crystals were found from Obira in Japan. On the crystals of danburite of that mine (Obira), natural accessory surface sculptures have been also discovered.

However, the mentioned surface-sculptures on crystals of Obira are quite different from those of Toroku mine.

Especially the difference being observed on the surface sculptures of w (201) between those two mines may be quite worthy of note.

According to late Prof. K. JIMBO,²⁾ the facial features on w (201) were described as follows:

"On w, there are sometimes small shallow depressions, which are usually less than 0.5mm in length, and resemble in outline the paper of Japanese fans. The longest side is very curved, the two lateral slopes down nearly parallel to the edges of combination of the faces w and l. The base is usually longer, but sometimes shorter than those two, and

is generally curved. It is sometimes reduced to nil, and the figures become triangular."

The accessory surface sculptures, which are formed on the surface of the crystals of many minerals, have already been studied relating to crystallomorphology or crystallogeny. The properties of the delicate phenomena of the surfaces are extremely important for the symmetry-judgement and for the induction of the form-system. It is also useful for the controversy on the paragenetic relation of these minerals.

The writer has treated the abnormal phenomena, in which only the face *w* is clouded and distinctly etched, on the aspect that crystals grow and decompose gradually, adapting to their environments.

This report is a datum to explain how the form of a crystal may be influenced by some inner structural features.

2. Chemical and X-ray investigations

A) Chemical Composition

The transparent portion, the clouded portion and the ashen-gray portion on *w* (201) of the crystal were chemically analysed respectively.

On these analyses special attention was paid for the quantitative determination of Boron. Table 1 shows the results.

From these analyses it is clear that Boron contents decrease gradually in accordance with the approach to the surface from the inner part. On the contrary, the clouded portion as well as the ashen-gray one contains large amounts of Fe_2O_3 and Al_2O_3 as impurities.

These impurities are almost negligible in the transparent portion.

TABLE 1. Chemical Compositions

	Transparent portion	Clouded portion	Ashen-gray portion
SiO_2	48.41%	48.67%	48.51%
B_2O_3	28.62	25.23	23.14
CaO	22.84	21.47	21.01
Fe_2O_3	0.32	1.13	2.15
Al_2O_3	0.14	2.01	4.12
MgO	0.10	0.30	0.25
H_2O	0.42	1.57	1.55
Total	100.85	100.38	100.73

B) X-ray Laue- and Powder-Photographs

1. To investigate whether the crystallographic orientations of the clouded portion and the ashen-gray portion correspond to those of the transparent portion or not.

2. Whether the clouded portion and the ashen-gray portion is composed of aggregation of minute crystalline grains or a part of the single crystal.

3. Whether the clouded portion and the ashen-gray portion show the same X-ray Laue pattern as that of the transparent portion, or diffuse spots.

To solve the above three problems, two thin sections, which were about 0.3 mm in thickness and parallel to the face w, of the clouded portion and the transparent portion were prepared.

After X-ray Laue photographs were taken, they were compared with each other, but the photographs from both thin sections of the transparent and clouded portions are in accordance with each other.

The lattice irregularities were not seen also in X-ray diffraction patterns. Moreover, X-ray powder photographs of each portion, transparent, clouded and ashen-gray, were proved to be almost identical.

C) Solubility for Hydrochloric Acid

It has been already described that the clouded portion of the danburite crystal has a scanty content of Boron, considerably in comparison with the ideal chemical composition of danburite. However, the X-ray diffraction of the clouded portion shows that even this portion keeps regular lattice.

The increase of atoms Fe, Mg, Al can not be explained by replacement of those atoms for Boron, but rather it must be considered that those atoms, taking a form of oxide, permeated secondarily along the lineage boundaries of the crystal, because large amounts of Al and Fe were retained in the solution, when the extreme fine powder of the clouded portion was washed with hydrochloric acid.

The result of etching experiment by fluoric hydrogen shows that the clouded portion is apt to be etched more easily than the transparent portion (namely the resistance of the clouded portion for fluoric hydrogen is weaker than that of the transparent portion).

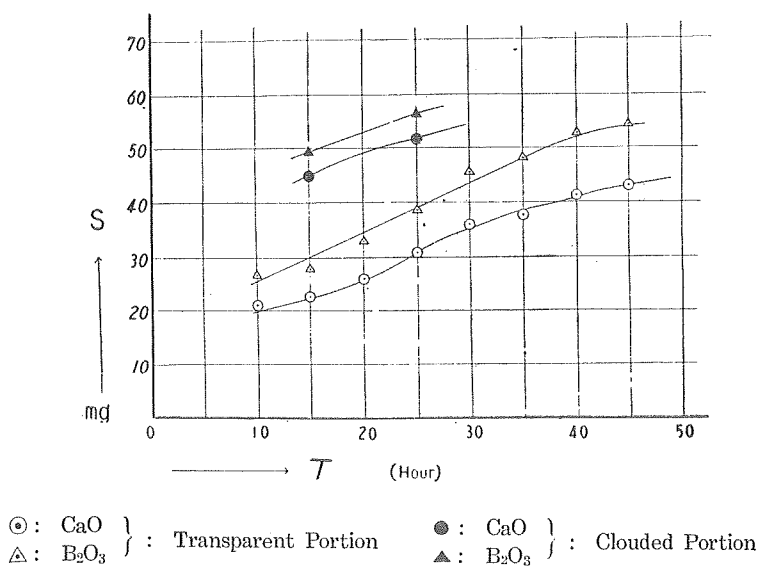
Following this experiment, further investigations were carried out to clarify the quantitative relations of the solubility for hydrochloric acid between the clouded and transparent portions.

Although solubilities of the transparent portion were determined in several cases during 10 hours to 45 hours after the materials were kept within the solution, it could be observed only in two cases on the clouded portion, the material for those experiments being not so much in quantity. (See Table II and Fig. 3)

TABLE II. Soluble. Amount by Hydrochloric Acid

Time (Hour)	Soluble Amount (in 0.1 N-HCl 250 cc)			
	Transparent Portion		Clouded Portion	
	CaO	B ₂ O ₃	CaO	B ₂ O ₃
10	21.1 mm	27.7 mm	— mm	— mm
15	22.6	27.8	45.1	49.1
20	26.1	33.1	—	—
25	31.0	38.8	51.5	56.2
30	36.2	45.8	—	—
35	37.9	48.0	—	—
40	41.4	51.5	—	—
45	43.1	54.1	—	—

(The size of grains, being used in these experiments, is 0.043 mm—0.061 mm)



The experiment is as follows: A definite quantity of the powdered material, sized in 0.043–0.061 mm, is put into a 500 cc quartz flask, which contains 250 cc of hydrochloric acid. And then the flask is kept at 100°C. To avoid evaporation of the solution, a refrigerator is set on the flask.

The solution was filtered, and the amounts of B_2O_3 , SiO_2 and CaO in the filtrate were quantitatively determined. SiO_2 content was slightly higher than the amount calculated from the chemical formula. The surplus of SiO_2 content above mentioned might be due to dissolving of the flask and refrigerator.

The amount of soluble B_2O_3 was determined by the Mannit Method. To determine the amount of soluble CaO , the titration method of potassium permanganate was used. Table II and Fig. 3 show the results.

This figure shows how the clouded portion is more easily soluble in the acid than the transparent portion.

From this experiment, some differences may be presumed in the texture between the transparent and clouded portion, although it could be not clarified from the X-ray photographs.

The writer believes that the lattice imperfection in consequence of the deficiency of Boron atoms in the crystal lattice may bring on such unusual solubility in the acid, at the clouded portion of the crystal.

3. The Evidence for Lineage Structure*

As the result of immersing a danburite crystal in a mixed solution made of sulphuric acid and hydrogen fluoride (H_2SO_4 : $HF = 1:3$) at 50°C for 5 hours, originally brilliant surfaces of the faces $a(010)$, $b(100)$, $l(110)$ and $d(011)$ became etched and tarnished. On the other hand, a distinct etch-depression of irregular cavities and longitudinal etch-grooves was produced on the face $w(201)$, which is clearly shown in Fig. 4.

Thin sections were made being vertical to each face, and observations were made under the microscope, in what way the acid permeates and reacts from the crystal surface to its inner portion.

As Fig. 4 shows, a large number of small cracks are recognized at the clouded portion $w(201)$, which did not exist before the artificial etching.

The direction of elongation of these cracks is definite and coincides

* M. J. BUERGER: Z. Kristallog., 89 (1934), 195-220.

with the direction of the natural contamination, before the etching.

And it must be noted that such cracks observed on the face $w(201)$ were almost not recognized on other faces.

Meanwhile it is believed usually that crystals become dendritic or plume-like when they grow rapidly or under an extreme condition of various preventions. As an excellent example for this, dendrites were compiled by V. GOLDSCHMIDT³⁹⁾ for ice crystals. And it is usual that metal crystals which are grown from melts are formed as dendrites.

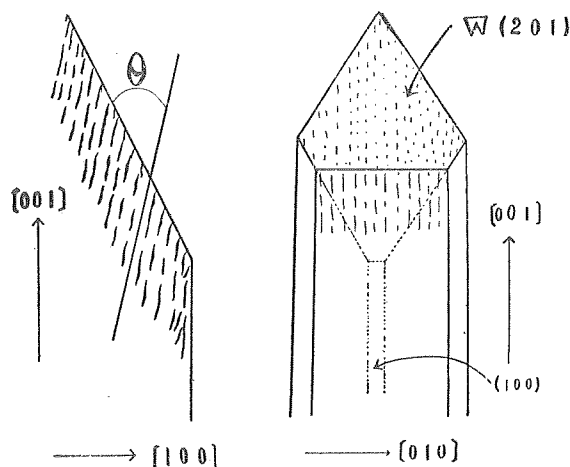


Fig. 4. Schematic diagrams of etch-figures and etch-cracks by artificial etching.

Crystals, grown under suitable condition, exhibit regular polyhedral form. The writer supposes that in such crystals the arrangement of a group of some structural units is apt to be irregular, such as dendritic. Both the cracks made by artificial etching shown in Fig. 4 and the contaminations by natural alteration of the clouded portion (face w) show the same direction and the same angle θ , which is between 38° and 43° (Fig. 4). This direction corresponds to none of the usual crystallographic orientation of danburite crystal. (See Fig. 5).

Judging from the above facts, it can be said that the inward coordinate system is discontinuous by the irregularity of lattice arrangement owing to crystal growth, and BUEGER's hypothesis on lineage structure due to crystal growth is correct in the case of danburite crystal.

Also, the directions of cracks by artificial etching and of [contami-

nation by natural alteration coincide with the direction of lineage boundaries as well.

4. Structural Consideration

The crystal structure of danburite has been explained by C. DUNBAR and F. MACHATSCHKI¹⁾ in 1930.

According to them, Si_2O_7 and B_2O_7 which adjoin each other but do not adjoin Si_2O_7 itself or B_2O_7 itself, build its framework, and Ca^{++} is arranged as satisfying plus-valency.

If such structure is real, its general framework might be managed by $\text{Si}_2\text{O}_7\text{-B}_2\text{O}_7$.

To avoid the derangement of the figure, the distribution of oxygen atoms was eliminated, and the relation of mutual coordination of atoms, Ca, B, Si is indicated in Figs. 5, 6 and 7.

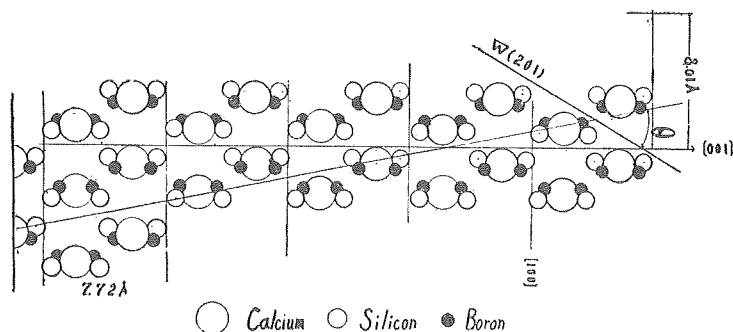


Fig. 5. Relation between the direction of etch-cracks and the arrangement of atoms.

In the figure, angle θ is $38^\circ\text{--}43^\circ$, and toward such direction the cracks caused by etching are produced. As shown in the figure, this direction is not represented by crystallographically simple indices, and crystal faces of such angle-relations do not appear in natural danburite crystal. But, as indicated in Fig. 4, there are longitudinal artificial etch-grooves on face $w(201)$, and they occur parallel to face (010) . In some crystals partings naturally occur in such directions. Also, at times, natural etch-grooves are observed (Fig. 2).

According to the arrangement of atoms in Figs. 6 and 7, the following explanations may be given.

Fig. 6 makes evident that layers of B_2O_7 and Si_2O_7 are arranged parallel to face (010) alternately.

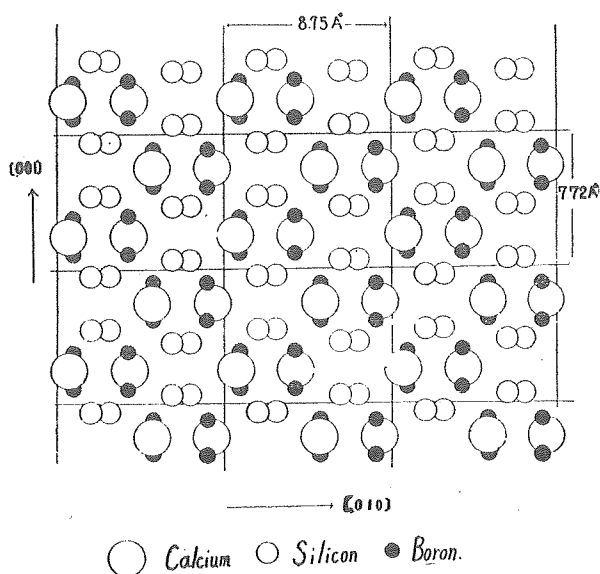


Fig. 6. Projection of the danburite structure on (100)

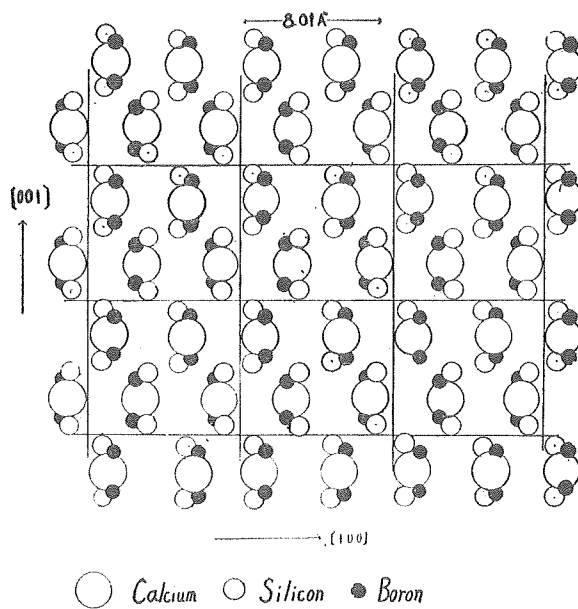


Fig. 7. Projection of the danburite structure on (010)

Compared to this, if a lattice-plane parallel to face (100) is thought of, it would be too difficult to think of distinguishing the layers of B_2O_7 and Si_2O_7 separately, as showed in Fig. 7.

However, to think of intermixing of B_2O_7 - and Si_2O_7 - groups is rather proper.

The above mentioned facts give us a radical reason to explain that the clouded phenomena of such a surface, relating to deficiency of Boron atoms, are of selective nature for the faces.

Crystal is a natural product, whose polyhedron is collaborated by regular periodic arrangement of atoms and disturbances against such regularities in their growth.

It has been recognized that danburite crystals have lineage-like structure. Then, in the interior of the crystal bodies imperfect portions would be formed, which are derived from irregularity of lattice arrangement. It is not yet thoroughly investigated, that the distinct lattice-imperfection occurs only on face w.

The data of ideal-structure above mentioned explain that the arrangement of atoms will make a condition to diffuse out Boron atoms from faces belonging to the zone [010] rather more easily than from those belonging to the zone [100].

However, if the ideal crystals would be placed in any sort of environment, the regular arrangement of atoms should not be allowed to diffuse out Boron atoms to the exterior from such regular structure.

In order to explain the diffusion of Boron atoms on face w, a secondary structure which is originated from growth of the crystal must be considered.

5. Summary

The clouded phenomena of face w of danburite crystals from Toroku can be summarised as follows:—

The lack of Boron contents in the clouded portion is not originated by crystal growth, but rather it is related to the secondary alterations after growth of crystals.

The diffusing out of Boron atoms only on the face w of the crystal cannot be explained not only by the irregularity of lattice arrangement due to lineage structure, but also by the arrangement of Boron atoms in the ideal structure of danburite crystal.

The writer wishes to express his indebtedness to Prof. Z. HARADA for careful criticism and valuable suggestions during the course of this study.

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