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“TODOROKITE,” A NEW MANGANESE MINERAL  
FROM THE TODOROKI MINE,  
HOKKAIDO, JAPAN

By

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*With 2 Plates.*

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The Todoroki (禰) Mine is situated about 25 kilometers to the south-east of Ginzan (銀山) railway station in Siribesi (後志) Province, Hokkaido. It consists of workings on the auriferous quartz veins which have been deposited in the tertiary volcanic complex in this region. One of the veins, named Syûetu, is noted for its richness in various manganese minerals. Last autumn, Mr. T. TAKAKUWA, professor in the Faculty of Engineering in this University, kindly showed to the author an interesting specimen of black manganese-ore which had been found a little time ago in the Syûetu vein. The author afterwards had the opportunity of visiting this mine, and was able to see the mode of occurrence of the mineral.

Occurrence: This mineral occurs as an aggregate of very fine fibrous flakes, about 0.05 mm in length at the largest. These fibrous flakes are arranged in lamellar layers, in which the lamellae are vertical to the surface of the layer. See Pl. XL (I), fig. 1.

The fractured surface of the aggregate consequently looks like that of a broken piece of wood, but has, of course, no genetical relation to wood. It covers the wall of a druse in the oxidized zone of the deposit, and the layers, about 0.1–3 cm each in thickness, show a reniform surface because of their zonal development, which starts from a few points on the wall of the druse. One of the

largest druses is three to two meters wide at its opening, and is more than ten meters deep, being almost filled up with the new manganese mineral.

The flakes of this mineral aggregate so loosely that the mass looks like a sponge. The apparent specific gravity of the mass, dried in a dessicator with sulphuric acid, is therefore about 0.22, though the true density of this mineral is 3.67. The true density was measured in petroleum at 15° C with a pycnometer. One hundred grams of the wet sample, just arrived from the mine, were sacked by hand, and forty grams of water were removed. This water contained 15 milligrams of Cl' and 0.6 gramme of SO<sub>4</sub>' per liter.

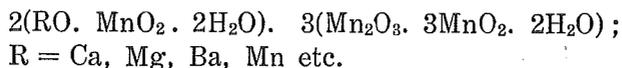
Chemical composition: The dried sample lost 1.56% in weight by heating at 120° for two hours, and 15.77% more at red heating. Of the latter loss, 6.05% constitutes the loss of oxygen, so that the amount of combined water is 9.72%. The amount of oxygen lost by ignition was known from the difference of free oxygen amounts determined before and after the ignition. The total amount of the free oxygen and that of manganese were determined by the iodometric method (Bunsen's method) and the sodium-bismuthate method respectively. The chemical composition of this mineral analysed by the author is as follows:

	wt. %
K <sub>2</sub> O . . . . .	0.54
Na <sub>2</sub> O . . . . .	0.21
MgO . . . . .	1.01
CaO . . . . .	3.28
BaO . . . . .	2.05
Al <sub>2</sub> O <sub>3</sub> . . . . .	0.28
Fe <sub>2</sub> O <sub>3</sub> . . . . .	0.20
MnO . . . . .	65.89
O . . . . .	12.07
H <sub>2</sub> O + . . . . .	9.72
H <sub>2</sub> O - . . . . .	1.56
SiO <sub>2</sub> . . . . .	0.45
TiO <sub>2</sub> . . . . .	tr.
CO <sub>2</sub> . . . . .	tr.
P <sub>2</sub> O <sub>5</sub> . . . . .	0.42
SO <sub>3</sub> . . . . .	0.28
Insoluble . . . . .	1.28
<hr/>	
Total . . . . .	99.24

The following molecular ratios were obtained from the results of the chemical analysis.

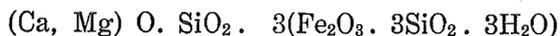
	From analysis	Calc. from the formula
MnO <sub>2</sub> . . . . .	5.79	5.99
Other acids . . . . .	0.14	
Mn <sub>2</sub> O <sub>3</sub> . . . . .	1.76	1.64
Other bases . . . . .	1.10	1.09
H <sub>2</sub> O . . . . .	5.40	5.47

The physical properties of this mineral which will be reported in the succeeding pages bear a close resemblance to those of nontronite, and the chemical formula of nontronite, which is the only comparable mineral, is Fe<sub>2</sub>O<sub>3</sub> . 3SiO<sub>2</sub> . 2H<sub>2</sub>O. So the author would give to the new manganese mineral the following formula :



Thus the dioxide of manganese is divided into two parts, the one forming acid radical, and the other constituting sesquioxide.

The formula written above shows an interesting resemblance to that of nontronite, given by E. S. LARSEN and G. STEIGER<sup>(1)</sup>, which was :—



The nontronite, analysed by LARSEN and STEIGER, was formed, as they reported, by hydrothermal alteration of hedenbergitic pyroxene. In the Syûetu vein where the new mineral here mentioned has been found, is found also a large quantity of fresh inesite, a mineral of the zeolite group with the composition of hydrous metasilicate of calcium and manganese. It is certain that the new mineral has been produced by the hydrothermal alteration of inesite. Some specimens are so perfectly metamorphosed that the texture of the original mineral is preserved (Pl. XL (I), figs. 1 and 2). Thus the genetical relations of this mineral and nontronite are analogous. The fact that this mineral is the alteration product of inesite, one of the metasilicate minerals, suggests giving the metamanganate form to the fore half of its chemical formula as written above.

When ignited at red heat, this mineral loses half of its free oxygen. By Bunsen's method, 65.98, 65.73 and 64.80% of MnO<sub>2</sub> were found before ignition, and 32.50 and 33.07% of MnO<sub>2</sub> after ignition. When we assume that the mineral with the composition of 2(RO . MnO<sub>2</sub> . 2H<sub>2</sub>O) . 3(Mn<sub>2</sub>O<sub>3</sub> . 3MnO<sub>2</sub> . 2H<sub>2</sub>O) changes to (2RMnO<sub>3</sub> + 5Mn<sub>3</sub>O<sub>4</sub>)

by ignition, the number of free oxygen atoms decreases from fourteen to seven.

**Morphology:** Single flakes of this mineral macerated in water show a rather sharp crystal boundary, as in figures 3-4 in Pl. XL (I). Though no definite data can be given, it may not be unreasonable to assume the monoclinic symmetry of these crystals. Then, taking the elongation direction of the flake as the crystallographic *c*-axis, the orientations of the faces (100), (001) and (010) will be taken as shown in figure 3. The obtuse angle  $\beta$  is then  $110^\circ$ . Cleavages, parallel to 010 and 100, are highly perfect. Twinning on a domatic face are quite frequent, as shown in figures 5-6 in Pl. XL (I). The angle between the *c*-axes of each individuals of the twinning is constantly  $60^\circ$ .

**Properties:** Very soft, and spoils fingers. Flattens and grows lumpy under the pestle and can be pressed to a felt-like plate. When wet, this mineral is rather plastic like clays, but if put in water and agitated, it easily breaks down and is dispersed in the water. It adheres on the surface of the vessel and glass rods, forming a thin film composed of fine foliated crystalline flakes. Colour black, with metallic lustre. Streaks on paper, on fingers and others are also black or lead grey with shining metallic lustre. Colour, lustre and feel to the fingers are quite like those of graphite.

X-ray photographs of this mineral were taken by the powder method at the Institute of Physics under the kind guidance of Prof. S. KAYA. K line from a Cu-anticathode was used, so that the patterns were not fully satisfactory owing to the strong absorption of the Cu-K line by this mineral. But it was possible to measure five lines on the photograph corresponding to the following atomic spacings.

$$d = 16.6 \text{ \AA}^\circ (\text{m}), \quad 22.0 (\text{s}), \quad 29.5 (\text{w}), \quad 43 (\text{m}), \quad 94 (\text{m})$$

By projecting X-ray beams perpendicularly to the elongation of fibres, patterns were obtained which showed the parallel arrangement of fibres by radiating bands. These facts show that this manganese mineral has a crystalline structure, while the large atomic spacings and weakness of lines well explain some colloidal properties exhibited by this mineral.

Under the microscope, the mineral is transparent, with various shades of brown colour, and shows neat extinction of light between

crossed nicols, the vibration direction of slower waves being parallel to the elongation of the fibre. The optic axial plane seems to be parallel to 010, so that the angle  $c \wedge Z$  is nearly zero. Indices of refraction are higher than that of methylen-iodide ( $n=1.74$ ), and double refraction  $\gamma-\alpha$  reaches nearly 0.02, Pleochroism distinct with  $Z > X$ , Z dark brown and X yellowish brown. The sharpness of pleochroism varies considerably with each crystal.

Under the blow-pipe, this mineral turns brown and loses its metallic lustre, but is not fusible. With fluxes it gives reactions of manganese. Treated with hot hydrochloric acid, it dissolves without residue, evolving free chlorine. The insoluble part, reported in the chemical composition, is composed of grains of quartz, rosy quartz and vein-quartz, spherulites of chalcedonic quartz, and small cubes of limonite pseudomorph after pyrite. In nitric acid it partly dissolves, and leaves a black residue composed of  $MnO_2$ . Boiled in concentrated sulphuric acid, it colours the solution distinctly purple red. Dissolves in acidified hydrogen peroxide with the greatest ease.

Genesis: In the Syûetu vein, the sequence of mineralization was as follows. Repeated depositions of quartz and inesite in a fissure were followed by the deposition of rhodochrosite, chalcedonic quartz and inesite-like zeolite. The larger part of inesite had been replaced by rhodochrosite in this stage, and the country rocks of the vein were kaolinized (Pl. XLI (II), fig. 1). In the mean time ore minerals such as pyrite, zincblende and galena were precipitated, often forming ring-ores. Afterwards when the circulating solutions acquired oxidizing power, inesite and inesite-like zeolite were decomposed, and a dark brown mineral of manganese was formed (Pl. XLI (II), fig. 2). The pyrite altered to limonite, keeping its cubic form, while the other ore minerals altered to sooty undeterminable materials. The last mineralizing solution is thought to have had great deal of alkali-carbonate or bicarbonate in solution, and deposited many veinlets of calcite after or with the oxidation of hydrous silicate of manganese.

Opal-like silica, one of the decomposition products formed by the oxidation of silicate, is shown in Pl. XLI (II), fig. 3. In the case of the similar decomposition of minerals composed of silicate of iron (nontronitisation), most of the opal remains in situ and forms chloropal, being mixed with nontronite, while opaline substances formed by the alteration of silicate of manganese is leached out from

the mass by the alkaline solution and deposits in other places as small spherulites or veinlets of opal or chalcedony. The black oxide of manganese, deprived of the admixed opaline substance by the alkaline solution, remains in its place and forms a loose aggregate of soft graphite-like mineral flakes as described in this paper. Therefore, the parallel and zonal arrangement of the mineral flakes has been inherited from inesite and inesite-like zeolite (See Pl. XL (I), fig. 2),

Inesite is found frequently in young gold-quartz veins deposited in the tertiary complexes of Japan. Refractive indices of the inesite which associates with the manganese mineral described above were measured by Mr. T. WATANABE by immersion in liquid as :

$$\alpha = 1.624, \quad \beta = 1.643, \quad \gamma = 1.651.$$

Optical orientation is similar to that of the data already published.

Classification: Among the minerals chiefly composed of dioxide of manganese, there are more than twenty species which are reported to be colloidal in character, and they are grouped under the name "manganomelane<sup>(2)</sup>." Their chemical compositions vary to some extent with each specimen, because the strong adsorption of cations by dioxide of manganese does not allow the keeping of constant chemical composition by these minerals. The classification based on chemical composition alone has therefore only a subordinate meaning. The author attempts to classify them by the difference of crystallinity and hardness, in the following four divisions :

- I. Crystalline manganomelane
- II. Wad
- III. Abnormal psilomelane
- IV. Psilomelane

"Crystalline manganomelane" or crystalline psilomelane is very soft, and is colloidal in some properties, though its form, optical properties, temperature of dehydration and patterns on X-ray photographs show that they apparently keep a crystalline structure. They are usually found as fibrous flakes often arranged parallel or concentrically radial. The so-called "Glaskopf" structure is quite common.

"Wad" is in its typical form a perfect gel. It is very soft, and has no definite form and structure. Optically isotropic, it gives only one or two weak bands on an X-ray powder photograph, which is characteristic of colloidal minerals.

"Psilomelane" and "abnormal psilomelane" are the hardened products of the alteration of wad and crystalline manganomelane. The crystalline structure of the latter is still kept, but does not appear on the form. The chief cause of this alteration may be compression and dehydration. Abnormal psilomelane includes those on the way of this alteration, and is softer than psilomelane, the hardness being between 1.5 and 3 on Mohs' scale.

Each division is subdivided into five groups by chemical composition.  $MnO_2$ ,  $MnO$  and  $H_2O$  are common to all species, so the classification is based on the kind of predominating bases other than  $MnO$ . Minerals of group (a) are the purest, containing no bases other than  $MnO$  or  $Mn_2O_3$ ; those of group (b) contain plenty of alkalis, those of group (c) alkaline-earths and magnesia, those of group (d) iron ( $Fe^{III}$ ) and alumina, while minerals of group (e) contain oxides of heavy metals. In the following table minerals grouped under the name of manganomelane are arranged according to the author's scheme. The characteristic bases of each mineral are written in parentheses.

Table of Minerals of Manganomelane Group.

I. Crystalline manganomelane

- (a) Todorokite: The new mineral now described
- (b) Unknown
- (c) {Romanechite (Ba)  
Rancieite (Ca, Mg)}
- (d) Calvonigrite ( $Fe^{III}$ )
- (e) Coronadite (Pb)

II. Wad

- (a) Wad
- (b) Unknown
- (c) Unknown
- (d) {Reissacherite ( $Fe^{III}$ )  
Bog manganese, Pelagite ( $Fe^{III}$ , Al)}
- (e) {Rabdionite (Co, Cu,  $Fe^{III}$ )  
Lubeckite (Cu, Co)  
Lepidophaeite (Cu)  
Zinkdibraunite, Tunnerite (Zn)}

## III. Abnormal psilomelane

- (a) Abnormal psilomelane
- (b) Unknown
- (c) Unknown
- (d) Lithiophorite (Al, Li)
- (e) {
  - Brostenite (Fe<sup>II</sup>)
  - Kakochlor (Co, Li)
  - Pelocnite (Cu, Fe)
  - Asbolite (Co, Ni)
  - Wackenrodite (Pb)

## IV. Psilomelane

- (a) Psilomelane
- (b) {
  - Li-psilomelane
  - K-psilomelane
- (c) {
  - Ba-Li-psilomelane
  - Ba-psilomelane
- (d) Skemmatite, Groroilite, Beldongrite (Fe<sup>III</sup>)
- (e) {
  - Lampadite (Cu)
  - Cesarolith (Pb)

The new mineral from the Todoroki Mine is very soft and macroscopically shows some resemblance to wad. Properties relating to the force of cohesion and some reactions against reagents also show its colloidal nature as already described, but, from the observations under the microscope and on the X-ray patterns, it is obvious that this mineral has a crystalline structure. It is not strange that minerals built up with a feeble crystalline structure show colloidal properties in some respects. This new mineral is, therefore, a member of the crystalline manganomelane group, and, as it contains no other prominent bases than MnO, is the purest species of this group. It belongs to division I, group (a) in the table above given. No mineral which must occupy that position has yet been reported, so the author now proposes the name "todorokite" (輝石) for such mineral species, with the new mineral from the Todoroki Mine as one of its representatives.

Summary: A new manganese mineral found recently in the Todoroki Mine, Hokkaido, Japan, was studied in its form, physical properties and chemical composition.

The results of the investigations are as follows :

Chemical composition:  $3(\text{Mn}_2\text{O}_3 \cdot 3\text{MnO}_2 \cdot 2\text{H}_2\text{O}) \cdot 2(\text{RO} \cdot \text{MnO}_2 \cdot 2\text{H}_2\text{O})$ ; R=Ca, Mg, Ba,  $\text{Mn}^{\text{II}}$ , etc. Probably monoclinic, with perfect cleavages parallel to (100) and (010). Macroscopically it resembles graphite. Occurs as minute fibrous flakes. Under the microscope, is brown with marked pleochroism  $Z > X$ . Optical plane parallel to 010,  $Z \wedge c$  nearly zero. Indices of refraction  $> 1.74$ . Density, 3.67 at 15°C. Perfectly soluble in hydrochloric acid. Gives lilac colour to the solution when boiled in concentrated sulphuric acid.

The genesis of the mineral was discussed. Inesite and inesite-like zeolite  $\longrightarrow$  brown oxide of manganese and opal  $\longrightarrow$  leaching out of opal and formation of this mineral.

A classification of the minerals of the manganomelane group was attempted under the author's scheme, and it was shown that the new mineral belonged to the purest species of crystalline manganomelane. As such a mineral had not yet been reported, this mineral was named "todorokite" after the name of the mine where it had first been noticed.

The author paid attention to the close resemblance of todorokite and nontronite. The morphological and physical, especially the optical properties of both minerals are analogous in many respects, and their genetical relations also possess several common features. Similar chemical formulae can be written for both of them,  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$  of todorokite corresponding to  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  of nontronite respectively.

Acknowledgments: The author wishes to express his sincere thanks to Prof. T. TAKAKUWA, Prof. S. KAYA and Mr. T. WATANABE for their kind advices, and to Prof. Z. HARADA for reading through this paper.

#### Literature

- (1) E. S. LARSEN and G. STEIGER: *Am. J. Sci.*, 15, 1 (1928),
  - (2) C. DOELTER: *Handbuch d. Mineralchemie*, III 2, 862 (1926),
-

Plate XL (I)

PLATE XL (I)

- Fig. 1. "Todorokite," showing zonal arrangement of layers.  $\times 2/3$ .
- Fig. 2. Zonal arrangement of fibrous inosite.  $\times 3/5$ .
- Fig. 3. Single crystal flake.  $\times$  ca. 2000.
- Fig. 4. Photomicrograph of crystalline flakes of "todorokite."  $\times 216$ .
- Fig. 5. Twinned crystals of todorokite  $\times$  ca. 2000.
- Fig. 6. Photomicrograph of twinned crystals.  $\times 216$ .

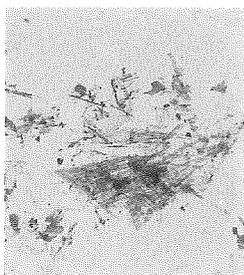


Fig. 6.

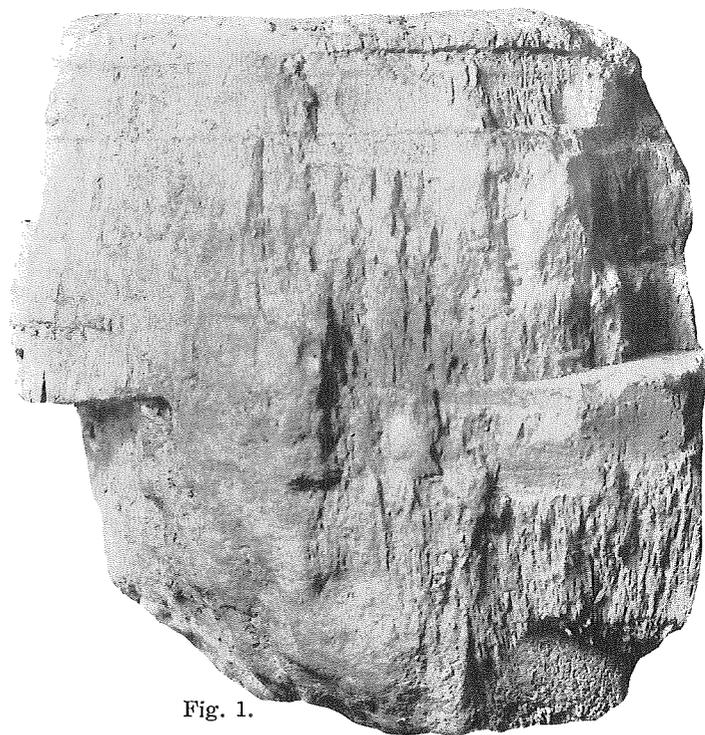


Fig. 1.

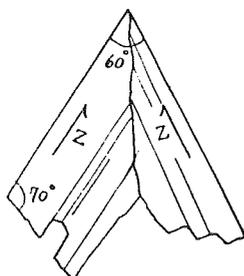


Fig. 5.

Fig. 4.

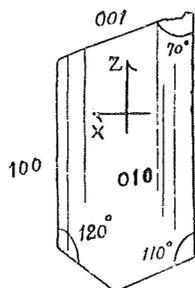
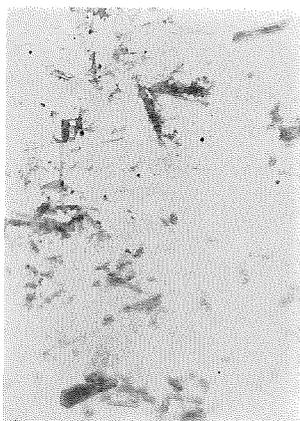


Fig. 3.

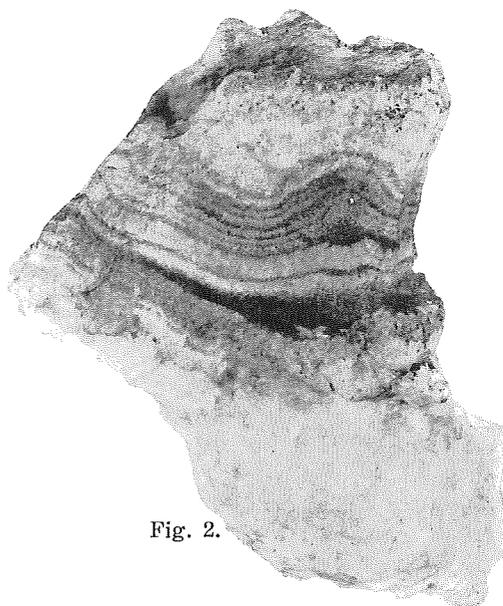


Fig. 2.

**Plate XLI (II)**

PLATE XLI (II)

- Fig. 1. Photomicrograph of vein-stuff. ×68  
*i* ..... inesite,            *r* ..... rhodochrosite
- Fig. 2. Photomicrograph of a veinlet of inesite-like zeolitic mineral. Brown oxide of manganese is seen as the oxidation product. This veinlet penetrates a mass of inesite, and its middle part is filled with calcite. ×68.
- Fig. 3. Photomicrograph of the alteration product in inesite. Opal-like silica and brown oxide of manganese are intimately mixed. ×216.

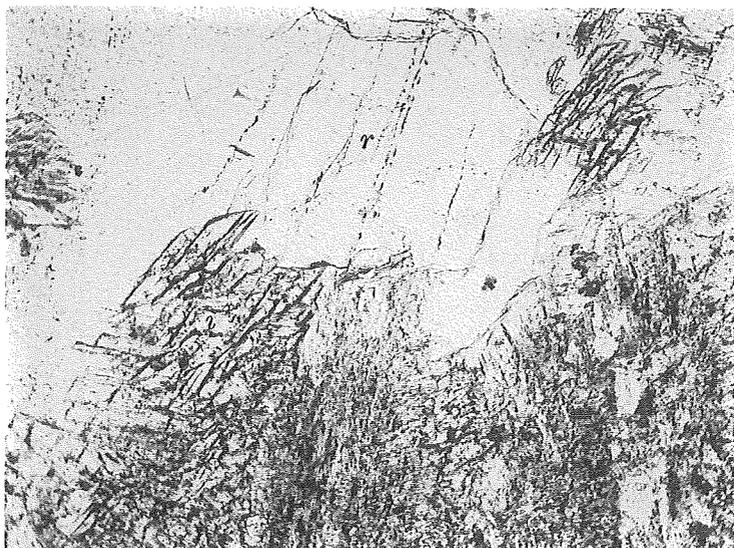


Fig. 1.

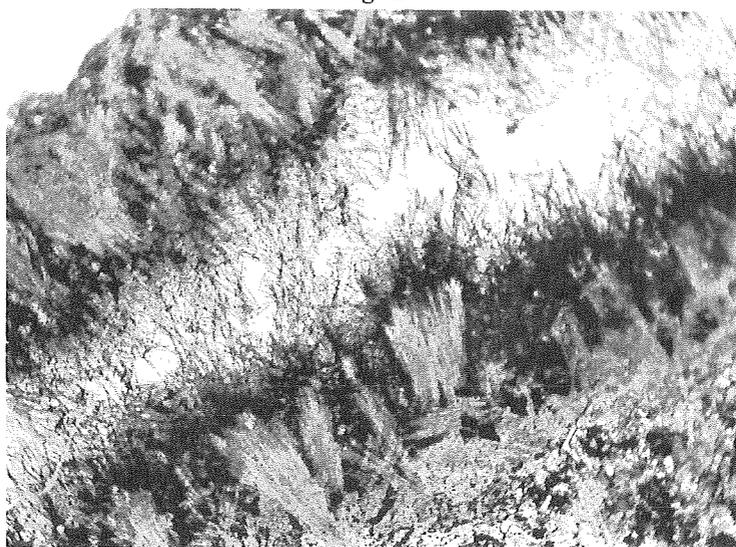


Fig. 2.

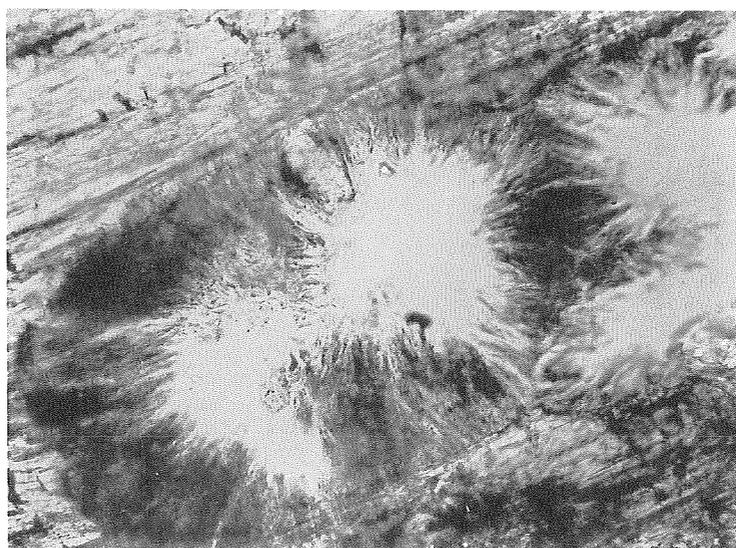


Fig. 3.