AN ELECTRON MICROSCOPIC EXAMINATION OF SYNTHETIC TOURMALINE CRYSTALS

WILLIAM H. BARNES

National Research Council, Ottawa, Ontario.

ABSTRACT

Representative electron micrographs illustrating the forms of tourmaline crystals synthesized by Frondel, Hurlbut & Collette are reproduced. A few measurements on the sizes of the crystals are given and the behavior of the crystals during fusion in the electron beam is illustrated.

Tourmaline crystals have been synthesized by Frondel, Hurlbut & Collette (1947) using a hydrothermal method involving the recrystallization of powdered tourmaline glass heated with water solutions of magnesium and alkali borates. Since the crystals are very small (of the order of 0.5 μ) it was considered of interest to examine them in the electron microscope. Two samples (numbers 278 and 348) were kindly supplied by Dr. Clifford Frondel and were studied in an R.C.A. electron microscope, model EMU, equipped with a biased electron gun. Each sample was in the form of a fine powder having a light buff tint.

PREPARATION OF SPECIMENS

Suspensions of the crystals in distilled water were prepared by hand shaking, with the aid of a spatula and under the influence of a Tesla coil. No marked difference in dispersal was observed as a result of the different methods so that simple shaking of a small amount of the powder in distilled water contained in a closed vial was adopted as a general procedure. In some cases the larger particles were allowed to settle before removing a drop of the suspension to the specimen screen; in others, the suspension was shaken immediately before removal of the drop. Larger aggregates were observed in the latter case but individual crystals appeared to be of the same average size and to show the same forms as those in drops taken from the supernatant suspension after allowing the larger aggregates to settle. In all cases a drop of the aqueous suspension was placed on a thin film of formvar covering the stainless steel specimen screen and was allowed to dry in air (protected from dust contamination) before placing in the specimen holder of the microscope. In some cases two or three drops of the suspension were placed on the formvar, the water being allowed to evaporate completely after the addition of each drop.

OBSERVATIONS AND RESULTS

A general survey of preparations made up from the two samples showed (a) that the tourmaline is very well crystallized in both and (b) that there is no noticeable difference either in the habits or size range of the crystals in the two samples. Typical electron micrographs are shown in Fig. 1 where the scale line in each photograph represents a length of one micron.

Isolated single crystals are relatively rare and some of those observed probably were detached from the more common spherulitic clusters such as that shown in Fig. 1 A. Fan-shaped groups, as illustrated in Fig. 1 B, C, D, are very prevalent and may also be fragments of larger spherical aggregates. The majority of the crystals have an elongated prismatic habit. Dimensions, as measured on optical enlargements of the photographs, which actually are plane projections of the crystals, are as follows: length, 0.2μ to 2.5μ (24 crystals measured); breadth, 0.03μ to 0.4μ (79 crystals measured); ratio, length to breadth, 2.6 to 14 (22 crystals measured).

Virtually all the prisms in the photographs appear to be terminated by pyramidal faces on the ends away from the centers of the aggregates, *i.e.*, in the direction of growth. Although the opposite ends are visible only in a very few cases they appear to be terminated by the basal pinacoid, or by less steep oblique faces. These observations suggest that the outer ends of the prisms, in the direction of growth, are the antilogous poles (Frondel, 1948, p. 9). It should be noted, however, that the electron micrographs are plane projections and that the depth of focus of the electron microscope is relatively large. Thus a prism terminated by a pinacoid but inclined to the observer in a direction normal to the field of view may project as a rectangle terminated by a triangle. Stereoscopic photographs indicate that the depths of the crystal groups are from one-quarter to as much as the width of the field or more. The pyramidal terminations of some of the prisms in the plane photographs appear in a stereoscopic view to be due to the inclination of the crystals to the plane of projection. This is often difficult to decide because the crystals are so opaque in the photographs that only the silhouette edges are visible. Not all the crystals, however, have simple prismatic forms; more complex ones are shown in Fig. 1 E, F, G, H. The largest dimension of these more compact forms was found to vary from about 0.8μ to about 2.5μ. Several examples of parallel growth were observed. One of these is illustrated in Fig. 1 I; in others the central hole was enclosed completely.

Characteristic of these tourmaline samples is the presence of a thin micaceous by-product of which small sheets are attached to the edges of the crystals in Fig. 1 C, D. Better examples will be found in Fig. 1 J,
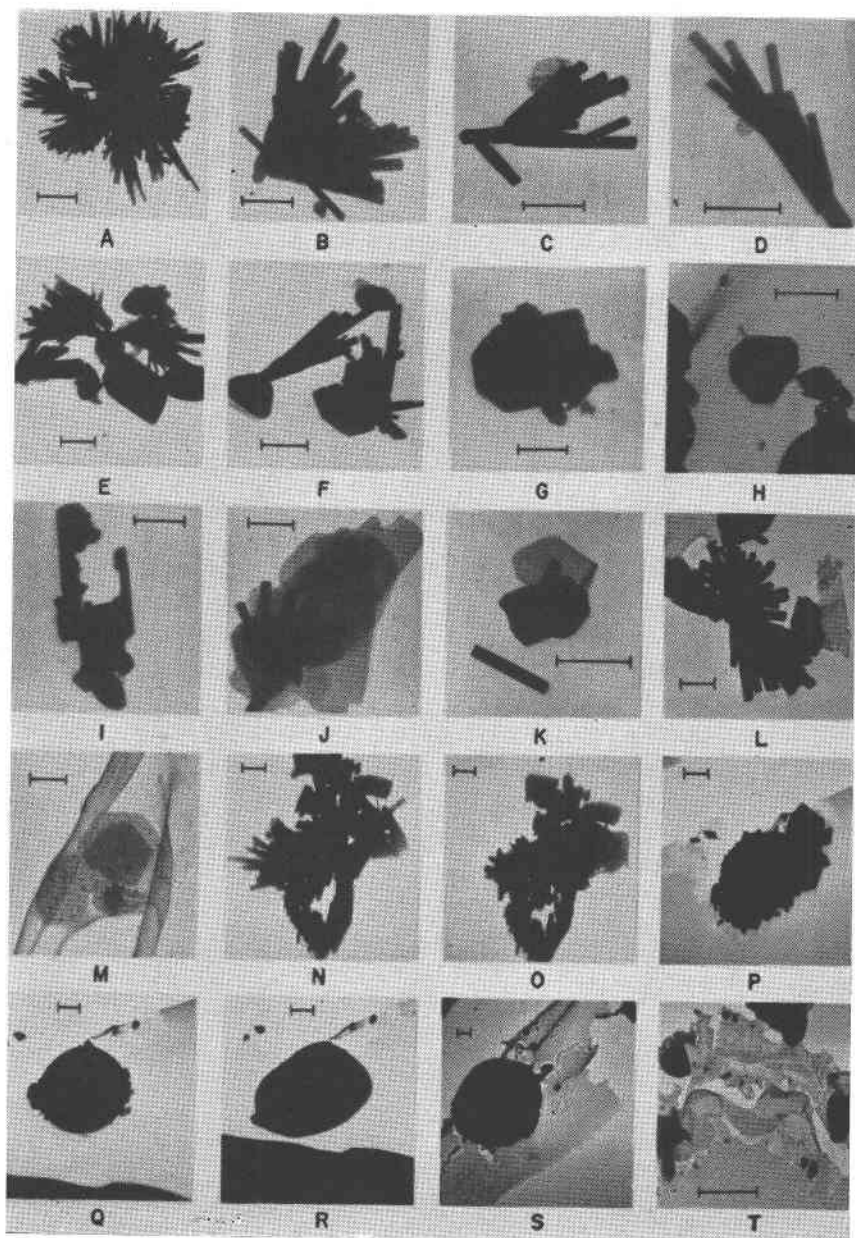
FIG. 1. Electron micrographs of synthetic tourmaline crystals.
(For explanation, see text.)

K, L, M. In addition to the isolated prismatic crystal in Fig. 1 K, the irregular dark and light patches represent thick and thin sheets of the micaceous material, the former partially wrapped around a prism whose end is outlined against the lighter sheet. (It should be mentioned that the disc that appears as a possible hole in the darker sheet of mica is due to the visible light from the electron gun filament; it will also be observed in the center of Fig. 1 J.)

In appearance, the micaceous material varies from heavily spotted, as in the sheets in the folds of the broken and curled edge of the formvar film in Fig. 1 M to clear and beautifully formed, as in the example on the right hand side of Fig. 1 L. Under magnification, and particularly stereoscopically, the latter looks like muscovite. Basal cleavage, elastic deformation of the sheets and what appears to be ribbon parting have been observed in other photographs. A few cases of relatively thick masses of small fragments of this material have been noticed.

During examination of the tourmaline crystals on the fluorescent screen in the microscope many of the groups of crystals showed a tendency to fuse in the electron beam. The same effect has been observed with other materials. It can be controlled to some extent by manipulation of the beam current and intensity dials; it is most frequently observed with the electron beam highly concentrated on the specimen at cross-over and with the beam current turned up. Not all groups of the tourmaline crystals could be fused in the electron beam but the phenomenon seemed to be more frequent with radiating clusters of long narrow prisms. Larger aggregates generally were more susceptible than smaller ones and very rarely were attempts to melt individual crystals successful. In most cases of fusion the formvar film ruptured either at the crystals or very close to them. Aggregates touching or near the wire of the specimen screen appeared to be the most vulnerable. In some cases plastic bending of the crystals occurred prior to melting.

Under favorable conditions it was possible to arrest the fusion process at successive stages. Thus in Fig. 1, N shows a group of crystals that has just started to shrink under the electron bombardment; its initial appearance can be deduced (at least in the original negative) from the marks on the formvar film. In O the group has become further consolidated and the rounded outlines of some fused crystals can be seen. Subsequent stages, including rupture of the supporting film, are illustrated in P, Q and R. The black region across the bottom of the last two plates is the image of the edge of the specimen screen wire towards which the broken formvar screen tends to draw.

The molten mass frequently behaves in a very dramatic way under continued bombardment; it seethes and bubbles, due presumably to the

escape of water vapor, oxygen and fluorine, from the release of OH⁻ and F⁻. Frequently, small particles of molten material are ejected from the mass and move around on the formvar film leaving tracks in their wake as shown in Fig. 1 S.

Since tourmaline melts between about 1050° and 1200° C. for iron-rich types to above 1725° C. for lithia-tourmaline (Frondel, Hurlbut & Collette, 1947, p. 680), the present observations are in qualitative agreement with Watson's conclusion (1948, p. 718) "that local temperatures of at least the order of 1600° C. can be achieved in electron microscopes, using a biased gun."*

Usually there is no change in the appearance of the thin formvar supporting film other than rupture and the marks left by the passage of these molten particles. An unusual film, however, appears in Fig. 1 T where the formvar has a grainy, brittle appearance due possibly to light shadow casting by evaporation from the molten tourmaline. Watson has noted a similar effect in his study of "pseudo-structures." Stereoscopically the two clear particles on the northwest edge of the globule in the upper left corner of the photograph appear to be transparent crystals with well-defined faces. This is observed in a less striking manner with the clear section that forms the upper part of the black mass on the right hand edge of the field. These are the only definite indications of possible recrystallization of the molten material observed during the investigation. Admittedly, however, it is more probable that the effect is caused by peculiar convolutions of the broken formvar film.

I am indebted to Miss Helen Jago and to Miss Ivy Michel for technical assistance in the preparation of specimens and the processing of the plates and prints.

REFERENCES

FRONDEL, C., HURLBUT, C. S. & COLLETTE, R. C. (1947): Synthesis of tourmaline—*Am. Mineral.*, **32**, 680–681.

FRONDEL, C. (1948): Tourmaline pressure gauges—*Am. Mineral.*, **33**, 1–17.

WATSON, J. H. L. (1948): Pseudostructures in electron microscope specimens—*J. App. Phys.*, **19**, 713–720.

* In Watson's paper (1948, p. 718), SiO_2 should read TiO_2. At the melting point, (1640° C.), titanium dioxide, in the form of rutile, decomposes and part of the activity of the molten material observed by Watson probably was due to the evolution of oxygen.