HYDROTHERMAL CRYSTALLIZATION AND DISSOLUTION OF QUARTZ

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ABSTRACT

The process of hydrothermal crystallization and dissolution of quartz crystals have been investigated by means of designed experiments. The possible structures of the dissolved molecules and the forms of their condensation and process of conversion before and during crystallization have been proposed. The normal and effective growth of crystals was realized by the temperature difference method.

Some of the observations made on the resulting crystals are noted or tentatively explained.

1. In some cases, if small crystals that fell down during their growth and reached the prism faces m $\{10\bar{1}0\}$ of large growing crystals, parallel attachment between them was very frequently resulted, and the crystal growth was promoted at the location of contact and thus forming a stepped growth pyramid.

2. Very large and widely spaced growth spirals centred on projected peaks were observed on r $\{1\bar{1}01\}$ faces. Between the steps of very large heights there appeared some much lower but clearly visible steps, indicating the possibility of bunching of more elementary microscopic steps.

3. On the faces having the highest velocities of growth such as the X $\{51\bar{6}1\}$ faces and the $\{0001\}$ basal faces the growth profiles more or less resemble liquid drops. There are parallel and sometimes interlaced markings on the "drops" that formed on the basal faces which look not only like growth layers but also like gliding lines. The oxile direction of the inclined "drops" are mostly parallel to the neighbouring R $\{10\bar{1}1\}$ faces. The "drops" on opposite $\{0001\}$ faces of the crystal are directed oppositely.

4. When quartz crystal was partly dissolved in hydrothermal solution stepped profile with rounded margins appeared on r-face$\{1\bar{1}01\}$, and layered pattern on the prism faces. They are mostly convex and some of them are concave.

The results of experimental investigations are:

1) The colloidal chemical behaviour of the cooled solution once used for crystal growth under hydrothermal conditions has been investigated by means of ultramicroscopy and cataphoresis and in some cases by their combination, and the flocculated aggregates have been analysed successively before and after each thermal reaction and stages of recrystallization or phase changes up to 1050°C.

The phase changes are:

$$\left[\begin{array}{l}\text{Molecules or ions in hydrothermal}\\ \text{solution + a portion of colloidal}\\ \text{particles}\end{array}\right] \xrightarrow{\text{Cooling}} \left[\begin{array}{l}\text{Colloidal particles + a}\\ \text{portion of molecules}\\ \text{or ions}\end{array}\right] \xrightarrow{\text{Cataphoresis}}$$

[Sponge like flocculated mass having a quasi-lattice approaching α-cristobalite, water content near to $SiO \cdot H_2O$] $\xrightarrow{\text{at 150°C dehydration, at 600—900°C gradually changes to}}$

[a quasi-lattice approaching to β-tridymite (high temperature)] $\xrightarrow{\text{at 900—1050°C recrystallized to}}$ [α-cristobalite (low temperature)]

2) When the once cooled solution was brought to a new hydrothermal condition of lower temperature and pressure, and subjected to cataphoresis, the total amount of flocculated aggregates collected at the anode was very much reduced, but the X-ray pattern of the sponge-like mass was nearly the same as in the previous case.

The following assumptions were proposed:

1) The most reasonable and representative subdivision of molecules in quartz crystals is perhaps the six-linked ring molecule occupying a volume of 2 unit cells, and owing to their body-centred close packing in a derived orthorhombic cell, a layer of such ring molecules corresponds to a step height of 1 unit cell. Eight O atoms are shared with 10 neighbouring "true molecules". The formula of the ring molecule in crystal should be $Si_6O_{10}O_{8/2}$. The corresponding molecules in solution are hydrated six-linked ring molecules $Si_6O_6(OH)_{12}$.

2) A group of five ring molecules in crystals, four surrounding one and all sharing one O atom with the central one, become a big derived tetrahedra molecule that occupies the height of three unit cells. Ordered or disordered ring, ribbon or sheat molecules in solution are convenient material for the crystallization of both the six-linked ring molecule or big tetrahedra molecules in crystals involving more or less "breaking" of Si-O bonds.

3) During the course of cooling of the hydrothermal solution the amount of colloidal particles in total volume should certainly be increased at the expense of the molecules in state of true solution, for the smaller molecules' polymererization may continue several steps further. On the contrary, when the hydrothermal condition is building or rebuilding up, the statistical equilibrium size of the molecular aggregates is determined at the compromise of temperature and pressure.

4) When the crystal begins to dissolve, the material passing into solution is mostly segregated in domains, their further dispersion resulted in hydrated molecules of different sizes and forms. On the contrary, during crystallization the process of convertion of the molecules is mainly the loss of (OH) and sharing of O.

It is reasonable to assume the existance of transitional boundary layers surrounding the crystals that are growing as well as that are subjected to solvation.

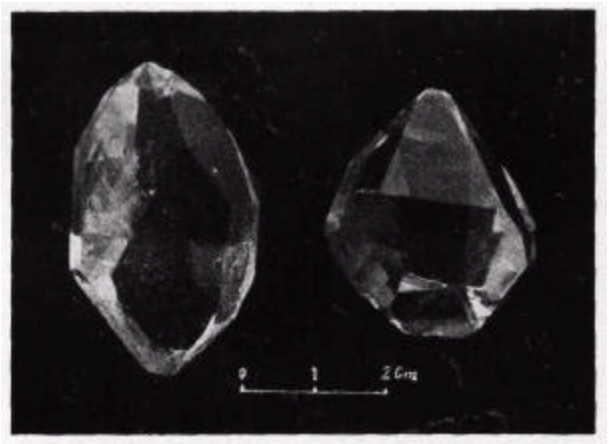

图 1　由溶解区营养料生长的石英晶体

图 2　在实验后由高压釜倾出的溶液中生长的石英晶体

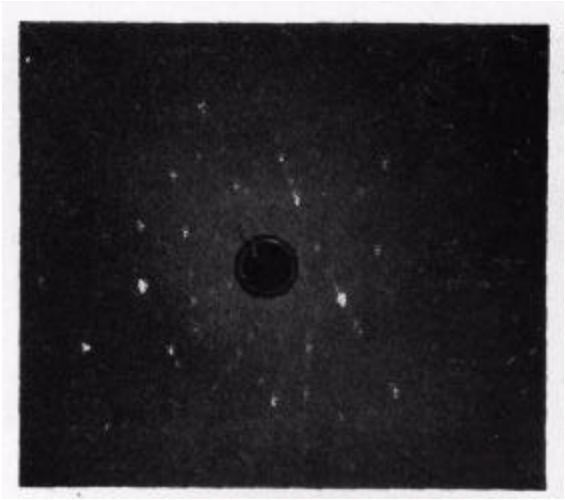

图 3　配向丛生小晶羣背射劳厄照相

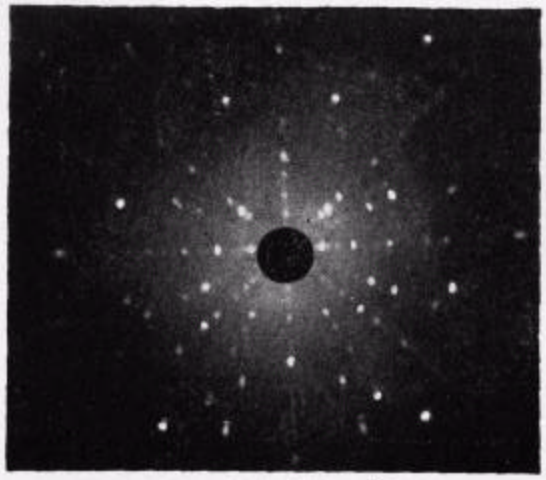

图 4 配向附生的小晶体背射劳厄照相

图 5 柱面 m{10$\bar{1}$0} 上平行附生的石英小晶芽及六角坦锥结构

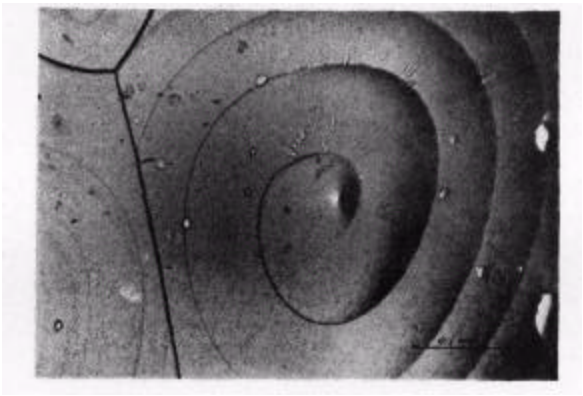

图 6 小菱面 r{1$\bar{1}$01} 上的生长螺旋

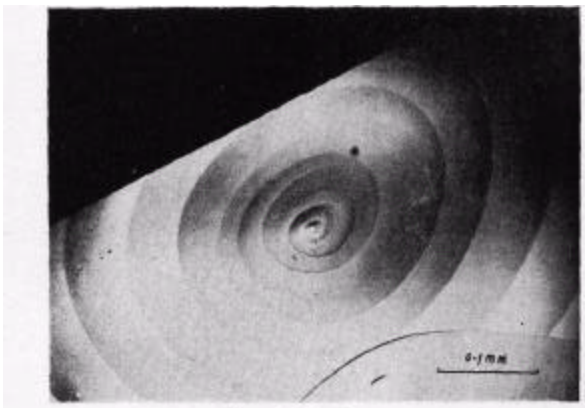

图 7 小菱面 r{1$\bar{1}$01} 上的生长螺旋

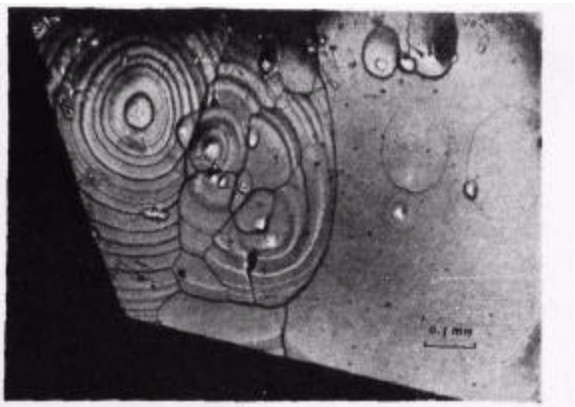

图 8 小菱面 r{1$\bar{1}$01} 上的同心圆状结构

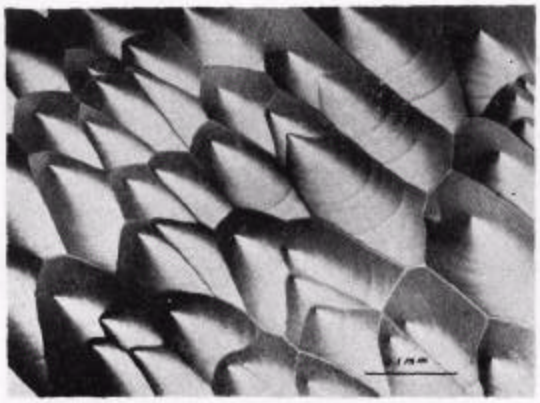

图 9　底面{0001}上的成羣的倾斜液滴状结构

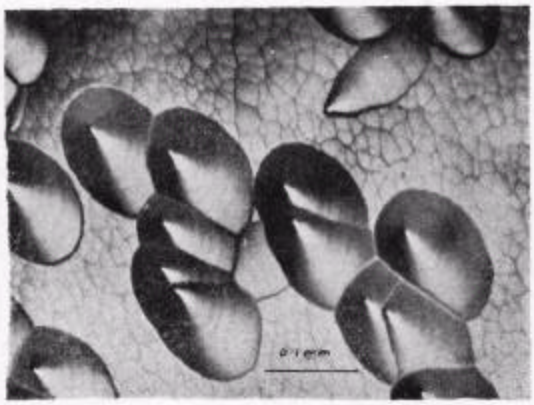

图 10　底面{0001}上的分立的倾斜液滴状结构

图 11　柱面 m{10$\bar{1}$0} 上层状的溶蚀象

图 12　小菱面 r{1$\bar{1}$01} 上的溶蚀象

图 13　电泳迭合物