Bulletin of Glaciological Research 19 (2002) *13 – 17*

Article

The morphology and the growth rate of ice crystals growing in aqueous sucrose solution

Takehiko GONDA, Tadanori SEI and Yoshiyasu ARIMA
Division of General Education, Aichi Gakuin University, 12 Araike, Iwasaki, Nisshin 470-0195 Japan

(Received August 30, 2001 ; Revised manuscript received November 12, 2001)

Abstract

The mechanism to suppress the growth of ice crystals due to the sugar stored in plant cells at low temperature was experimentally investigated. By precisely observing the morphological change of ice crystals, it was found that there existed three mechanisms to suppress the growth rate of ice crystals growing in sucrose solution, depending on supercooling and sucrose concentration.

1. Introduction

It is well known that the plant cells are protected from freezing by the sugar stored in the cells when the plant tissue cells were encountered at low temperature (Levitt, 1971). There are some experimental studies on the mechanism to suppress the growth rate of ice crystals due to the sugar stored in plant cells at low temperature (Muhr and Blanshard, 1986). However, there are only a few studies on the morphological change of ice crystals with increasing supercooling and sucrose concentration. Mackenzie and Rapatz (1968) found that faceted ice crystals grew in an aqueous sucrose solution, which was also formed in an antifreeze protein (AFGP) solution (Knight and Devries, 1994).

On the other hand, there are many studies on the growth of ice crystal from pure water, which are concerned with the pattern formation of ice crystal and the growth mechanism (Tirmizi and Gill, 1987; 1989; Shimada and Furukawa, 1997).

The purpose of this study is to clarify the change in the growth rate of ice crystals with increasing supercooling and sucrose concentration from the standpoint of crystal growth.

2. Experimental apparatus and procedures

Figure 1 shows the schematic diagram of the growth chamber of ice crystals used in this study. Before cooling the growth chamber, a drop of aqueous sucrose solution (E) was put into a teflon ring of 5 mm in inner diameter and 0.5 mm in depth attached at a glass plate (D). After circulated the coolant of −20 °C into the upper and lower hollow cooling plates (A), an electric current of 4 A was flowed in forward direction to upper and lower thermoelectric modules (B). In

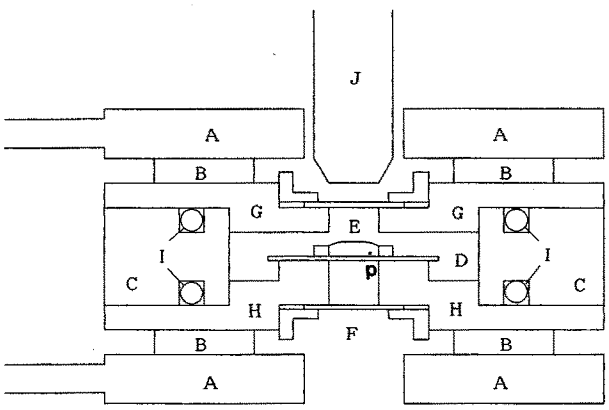

Fig. 1. Schematic diagram of the growth chamber of ice crystals. (A) : hollow cooling plate, (B) : thermoelectric module, (C) : insulator, (D) : glass plate, (E) : aqueous sucrose solution, (F) : glass window, (G, H) : copper plate, (I) : O-ring, (J) : microscope (P) : cu-co thermocouple.

this time, aqueous sucrose solution was cooled down to about −15 °C and thereafter frozen. Next, in order to melt the frozen specimen, an electric current of 0.5 A was flowed in opposite direction to upper and lower thermoelectric modules (B) after circulated the coolant of −10 °C into the upper and lower hollow cooling plates (A). The frozen specimen was melted until only one single ice crystal is formed within a microscope field of view. After that, the temperature of upper copper plate (G) was kept at 1 °C higher than melting point with respect to sucrose solution and that of lower copper plate(H) was kept at 1 °C lower than melting point with respect to sucrose solution. Moreover, the ice crystal was melted very slowly until a small circular disc is formed, carefully regulating an electric current which flows to the upper and lower thermoelectric modules (B). After that, a small circular disc was grown at various constant supercoolings and was observed in situ using a microscope (J). Here, the temperature of sucrose solution was determined by measuring the temperature of a position (P)on the glass plate (G). Moreover, the melting points of each sucrose concentration were determined by detecting the temperature which a small circular ice disc floating in sucrose solution neither grew nor melted. Thereafter, the supercooling was also determined by the depression from the temperature which a small circular ice disc began to melt in each sucrose concentration. The supercooling during the growth of ice crystals was held constant by regulating precisely the temperature of the copper plate (G) and the glass plate (D).

3. Experimental results

3.1. Morphology of ice crystals grown from pure water

According to the paper by Sei and Gonda (1992), when a small ice disc was grown from pure water at 0.1 °C supercooling, the shape of the ice crystal remained circular disc up to the size of about 200 μm in diameter. And, the prismatic facets were formed at the size above about 200 μm. After that, unstable growth occurred at the size above about 500 μm.

On the other hand, when a small ice disc was grown from pure water at 0.4 °C supercooling, the shape of the ice crystal remained circular disc up to the size of about 300 μm in diameter. However, when the ice crystal was grown above about 300 μm, faceted-like ice crystal was formed. After that, many perturbation with circular tip occurred at the periphery of the ice crystal at the size above about 650 μm.

3.2. Morphology of ice crystals grown in aqueous sucrose solution

Figure 2 shows an ice crystal grown in aqueous sucrose solution of 41.5 wt % at 0.1 °C supercooling with respect to sucrose solution. Here, the first photograph of the figure is defined as 0 sec. when a circular ice disc of about 15 μm in diameter grew (a), a hexagonal ice crystal of about 18 μm with prismatic facets grew (b). The crystal shape remained similar shape up to the size of about 50 μm (h). It was found that the faceted growth of ice crystal grown in sucrose solution occurred in considerably small size than that in pure water.

Figure 3 shows an ice crystal grown in aqueous sucrose solution of 41 wt % at 0.3 ℃ supercooling. When a circular ice disc of about 15 μm in diameter grew (a), a circular ice disc of about 26 μm with the instability at the periphery (b). After that, hexagonal flower- shape ice crystal grew with time elapsed (h).

Figure 4 shows an ice crystal grown in aqueous sucrose solution of 50 wt % at 0.4 °C supercooling.

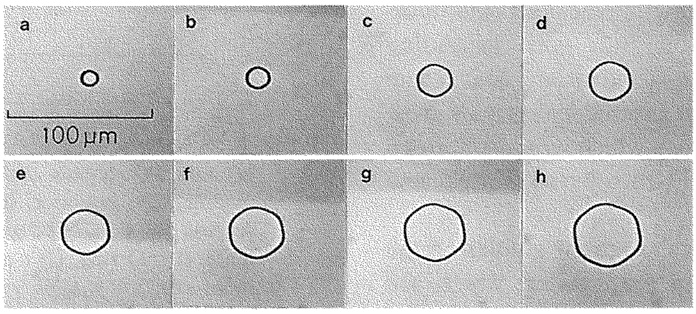

Fig. 2. Ice crystal grown in aqueous sucrose solution of 41.5 wt % at 0.1 °C supercooling. (a) 0, (b) 40, (c) 80, (d) 100, (e) 120, (f) 140, (g)160, (h) 180 sec.

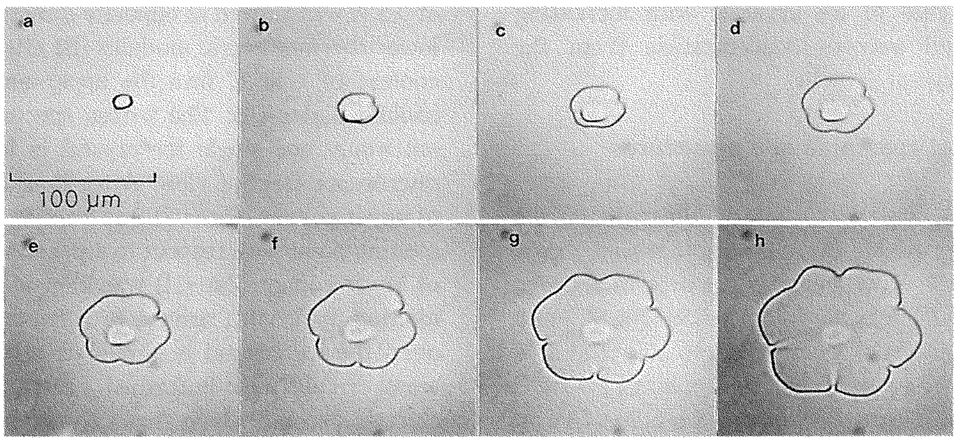

Fig. 3. Ice crystal grown in aqueous sucrose solution of 41.5 wt %at 0.3 °C supercooling. (a) 0, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60, (g) 80, (h) 100 sec.

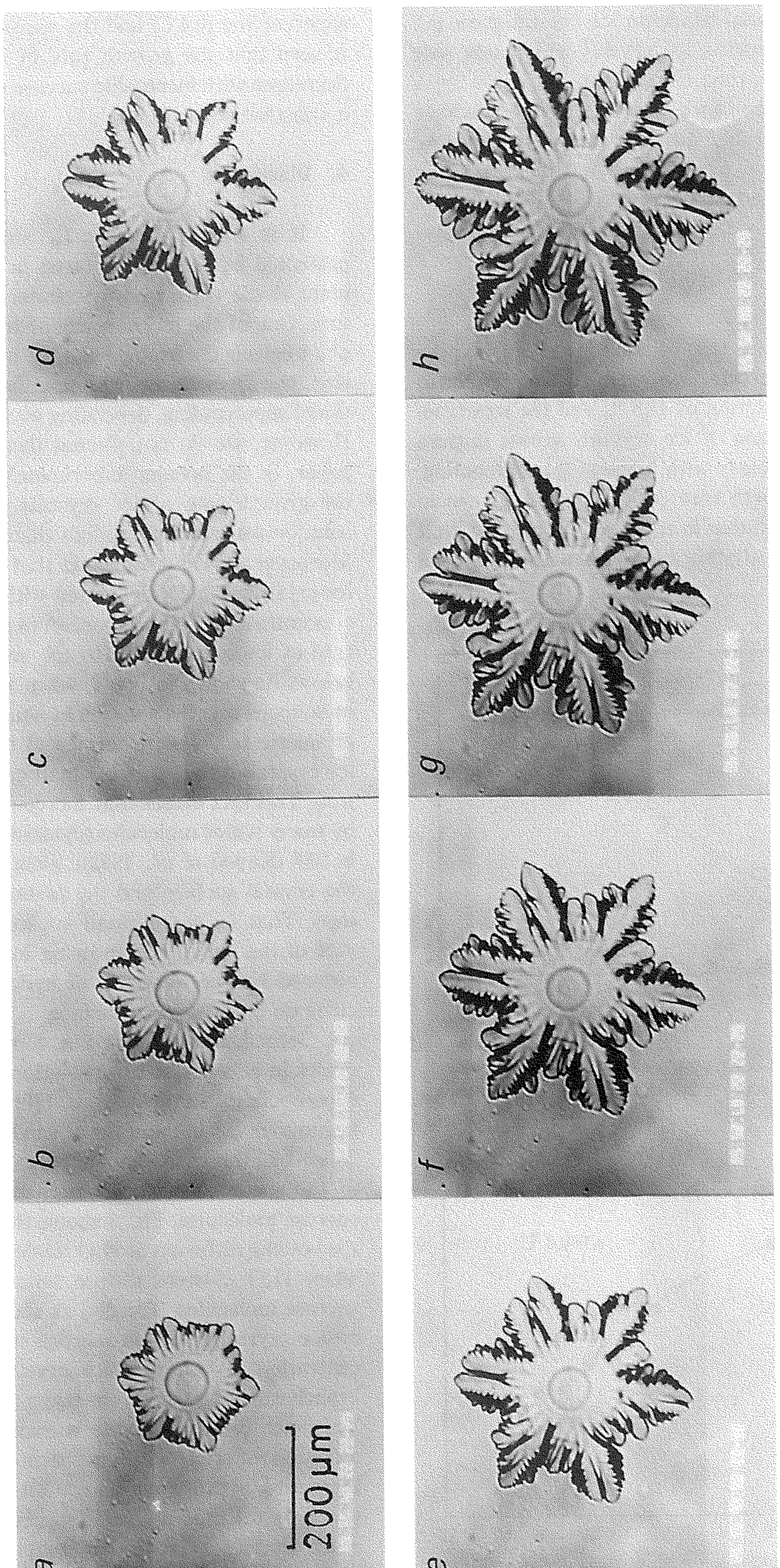

Fig. 4. Ice crystal grown in aqueous scrose solution of 50 wt % at 0.4 °C supercooling.
(a) 0, (b) 30, (c) 60, (d) 90, (e) 120, (f)150, (g) 180, (h) 210 sec.

After a circular ice disc with infinitesimal perturbation was formed at the size of about 700 μm in diameter, a hexagonal dendritic ice crystal grew (a). After that, the dendritic ice crystal with many side branches grew with time elapsed (h).

The morphology of ice crystals grown in sucrose solution is considerably different from that in pure water. Moreover, it was found that the transition from a round shape to a faceted shape depended on supercooling, sucrose concentration and crystal size.

3.3 Growth rate of ice crystals

Figure 5 shows the relationship between the growth rate of ice crystals grown in pure water and in aqueous sucrose solution of 41.5 % and the supercooling. The growth rate of ice crystals grown in pure water increases linearly with increasing supercooling. Moreover, the growth rate of ice crystals grown in aqueous sucrose solution is small by a digit than that in pure water, and slightly increases with increasing supercooling.

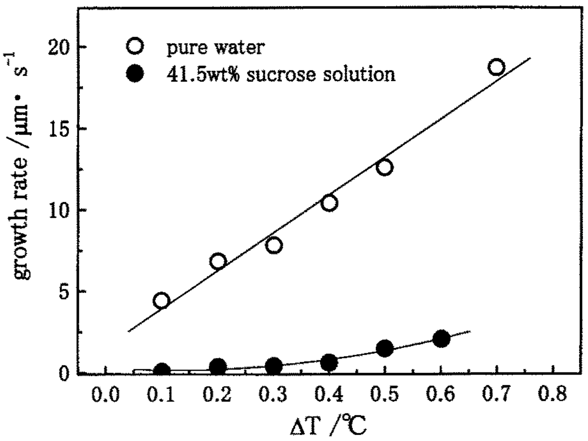

Fig. 5. Growth rate of ice crystals grown from pure water and in aqueous sucrose solution of 41.5 wt % versus supercooling.

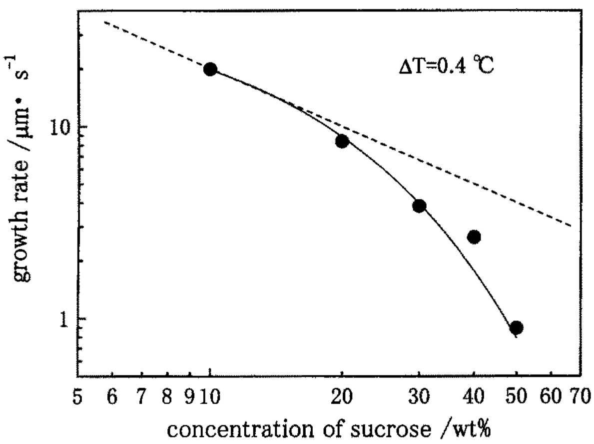

Fig. 6. Growth rate of ice crystals grown at a constant supercooling (0.4 °C) versus sucrose concentration.

Figure 6 shows the relationship between the growth rate of ice crystals grown under constant supercooling (0.4°C) and the sucrose concentration. It is seen that the growth rate of ice crystals rapidly decreases with increasing sucrose concentration under a constant supercooling

4. Discussion

It is known that the freezing of plant cells is protected by the sugar stored in the cells when the plant tissue cells were encountered at low temperature. One of the mechanisms of freezing tolerance of plant cells is the problems of the melting point depression, the freezing point depression and the constitutional supercooling, depending on sugar concentration. However, we do not discuss these problems in this paper. In the present experiments, it was found that the growth rate of ice crystals in aqueous sucrose solution was small by a digit than that in pure water. Moreover, it was also found that the growth rate of ice crystals rapidly decreased with increasing sucrose concentration. The mechanism to suppress the growth rate of ice crystals due to the sugar is as described below. As shown in Fig. 2, when an ice crystal grows in aqueous sucrose solution at small supercooling, the prismatic facets were formed at the periphery of the ice crystal in the stage of small crystal size (about 18 μm). This fact means that sucrose molecules hydrated by many water molecules (dynamic hydration number is 36.8 (Kawai *et al.*, 1992)), giant clusters adhere on the crystal surface and the prismatic facets are formed. That is, under small supercooling, the growth rate of the ice crystal growing in sucrose solution is reduced by the adhesion of hydrated sucrose molecules on the prismatic surface.

Second, as shown in Fig. 3, when an ice crystal grows in aqueous sucrose solution of relatively small supercooling, the shape instability at the periphery began to occur in the stage of small crystal size (about 26 μm). In this case, though there exists the resistance of the surface kinetics, which depends on hydrated sucrose molecules, Fig. 3 shows that the resistance of the volume diffusion of H_2O clusters began to produce when H_2O clusters diffuse among many hydrated sucrose molecules. Thirdly, as shown in Fig. 4, when an ice crystal grows in sucrose solution of high concentration, a dendritic ice crystal with many side branches was formed in the stage of small crystal size. This fact means that the resistance of the volume diffusion of H_2O clusters became prominent with increasing sucrose concentration. In order to study precisely the mechanism to suppress the growth rate of ice crystals due to the sugar stored in plant cells, we are necessary to clarify the structure of aqueous sugar solution and the solid-liquid interface of growing ice crystal using another experimental technique.

5. Concluding remarks

In order to study the mechanism to suppress the intracellular freezing due to the sugar stored in the cells at low temperature, the experiments of ice crystal growth in aqueous sucrose solution were carried out. The growth rate of ice crystals in aqueous sucrose solution is small by a digit than that in pure water. The growth rate of ice crystals rapidly decreases with increasing sucrose concentration at a constant supercooling. By precisely comparing the change in growth rate with the morphological change of ice crystals, it was found that there existed three mechanisms to suppress the growth rate of ice crystals growing in sucrose solution, depending on supercooling and sucrose concentration.

References

Kawai, H., Sakurai, M., Inoue, Y., Shujo, R. and Kobayashi, S. (1992): Hydration of Oligosaccharides: Anomalous hydration ability of Trehalose. Cryobiology, **29**, 599-606.

Knight, C. A. and Devries, A. L. (1994): Effects of polymeric, nonequilibrium "antifreeze" upon ice growth from water. J. Crystal Growth, **143**, 301-310.

Levitt, J. (1971): "Responses of plant to Environmental Stresses" Academic Press, New York and London, pp. 697.

Mackenzie, A. P. and Rapatz, G. L. (1968): Transition from polyhedral to spheroidal ice crystals and vice versa, in partly frozen aqueous systems. Biodynamica, **10**, 219-227.

Muhr, A. H. and Blanshard, J. M. V. (1986): Effect of polysaccharide stabilizers on the rate of growth of ice. J. Food Technology, **21**, 683-710.

Sei, T. and Gonda, T. (1992): Faceted growth of ice crystals growing at temperature just below the melting point. Physics and Chemistry of ice, Hokkaido University Press, 349-356.

Shimada, W. and Furukawa, Y. (1997): Pattern formation of ice crystals during free growth in supercooled water. J. Phys. Chem B. **101**, 6171-6173.

Tirmizi, S. H. and Gill, W. N. (1987): Effect of natural convection on growth velocity and morphology of dendritic ice crystals. J. Crystal Growth, **85**, 488-502.

Tirmizi, S. H. and Gill, W. N. (1989): Experimental investigation of the dynamics of spontaneous pattern formation during dendritic ice crystal growth. J. Crystal Growth, **96**, 277-292.