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Effect of Temperature on Water Sorption Behavior and Crystallization of Amorphous Sucrose

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Introduction

- Physical state of amorphous carbohydrates affects their stability during storage.
- When amorphous carbohydrates are stored at temperatures which are higher than their glass transition temperature, various changes, such as crystallization, may occur.
- The rate of such changes often increases with increasing temperature difference between storage temperature and glass transition temperature ($T - T_g$).



Aims

- To study the effect of temperature ranging from 15 to 35°C on water sorption behavior and water plasticization of freeze-dried sucrose.
- To investigate the effect of various storage conditions (T , RH) on occurrence and kinetics of crystallization of freeze-dried sucrose.
- To relate the observed crystallization behavior to the physical state and glass transition of amorphous sucrose.



Materials and methods (1/2)

- A solution containing 15% (w/w) sucrose and 85% (w/w) distilled water was frozen and freeze-dried (Lyovac GT2, Amsco Finn-Aqua GmbH).
 - Further dehydration was carried out in vacuum desiccators over P_2O_5 at room temperature for at least one week.
- Water sorption behavior of freeze-dried sucrose was determined gravimetrically using samples which were stored in vacuum desiccators over saturated solutions of LiCl, CH_3COOK , $MgCl_2$, K_2CO_3 and $Mg(NO_3)_2$ at 15, 20, 25, 30 and 35°C.



Relative humidities (*RH*) at various temperatures (*T*)

<i>T</i> (°C)	<i>RH</i> (%)				
	LiCl	CH ₃ COOK	MgCl ₂	K ₂ CO ₃	Mg(NO ₃) ₂
15	12.1 ⁽¹⁾ 10.9 ⁽²⁾	26.2 ⁽¹⁾ 23.1 ⁽²⁾	34.1 ⁽¹⁾ 32.9 ⁽²⁾	45.1 ⁽¹⁾ 43.4 ⁽²⁾	55.9 ⁽¹⁾ 56.1 ⁽²⁾
	11.30 ± 0.35 ⁽³⁾	23.40 ± 0.32 ⁽³⁾	33.30 ± 0.21 ⁽³⁾	43.15 ± 0.33 ⁽³⁾	55.87 ± 0.27 ⁽³⁾
20	11.8 ⁽¹⁾ 10.8 ⁽²⁾	24.9 ⁽¹⁾ 22.2 ⁽²⁾	33.4 ⁽¹⁾ 32.5 ⁽²⁾	44.7 ⁽¹⁾ 43.2 ⁽²⁾	54.7 ⁽¹⁾ 54.1 ⁽²⁾
	11.31 ± 0.31 ⁽³⁾	23.11 ± 0.25 ⁽³⁾	33.07 ± 0.18 ⁽³⁾	43.16 ± 0.33 ⁽³⁾	54.38 ± 0.23 ⁽³⁾
25	11.4 ⁽¹⁾ 10.8 ⁽²⁾	23.7 ⁽¹⁾ 21.4 ⁽²⁾	32.9 ⁽¹⁾ 32.0 ⁽²⁾	44.3 ⁽¹⁾ 43.0 ⁽²⁾	53.6 ⁽¹⁾ 52.2 ⁽²⁾
	11.30 ± 0.27 ⁽³⁾	22.51 ± 0.32 ⁽³⁾	32.78 ± 0.16 ⁽³⁾	43.16 ± 0.39 ⁽³⁾	52.89 ± 0.22 ⁽³⁾
30	11.1 ⁽¹⁾ 10.7 ⁽²⁾	22.6 ⁽¹⁾ 20.6 ⁽²⁾	32.3 ⁽¹⁾ 31.6 ⁽²⁾	44.0 ⁽¹⁾ 42.8 ⁽²⁾	52.5 ⁽¹⁾ 50.5 ⁽²⁾
	11.28 ± 0.24 ⁽³⁾	21.61 ± 0.53 ⁽³⁾	32.41 ± 0.11 ⁽³⁾	43.17 ± 0.30 ⁽³⁾	51.40 ± 0.24 ⁽³⁾
35	10.8 ⁽¹⁾ 10.7 ⁽²⁾	21.6 ⁽¹⁾ 19.9 ⁽²⁾	31.8 ⁽¹⁾ 31.1 ⁽²⁾	43.6 ⁽¹⁾ 42.6 ⁽²⁾	51.5 ⁽¹⁾ 48.9 ⁽²⁾
	11.25 ± 0.22 ⁽³⁾	— ⁽³⁾	32.05 ± 0.13 ⁽³⁾	— ⁽³⁾	49.91 ± 0.29 ⁽³⁾

¹⁾ Values calculated using the equations from Labuza *et al.* (1985)

²⁾ Values calculated using the equations obtained in the present study

³⁾ Values from Greenspan (1977)



Materials and methods (2/2)

- Glass transition temperatures of freeze-dried sucrose stored under the same storage conditions were determined using differential scanning calorimeter (DSC-30, Mettler-Toledo AG).

- Crystallization of amorphous sucrose was followed
 - gravimetrically
 - using X-ray powder diffractometry (XRPD, Philips).

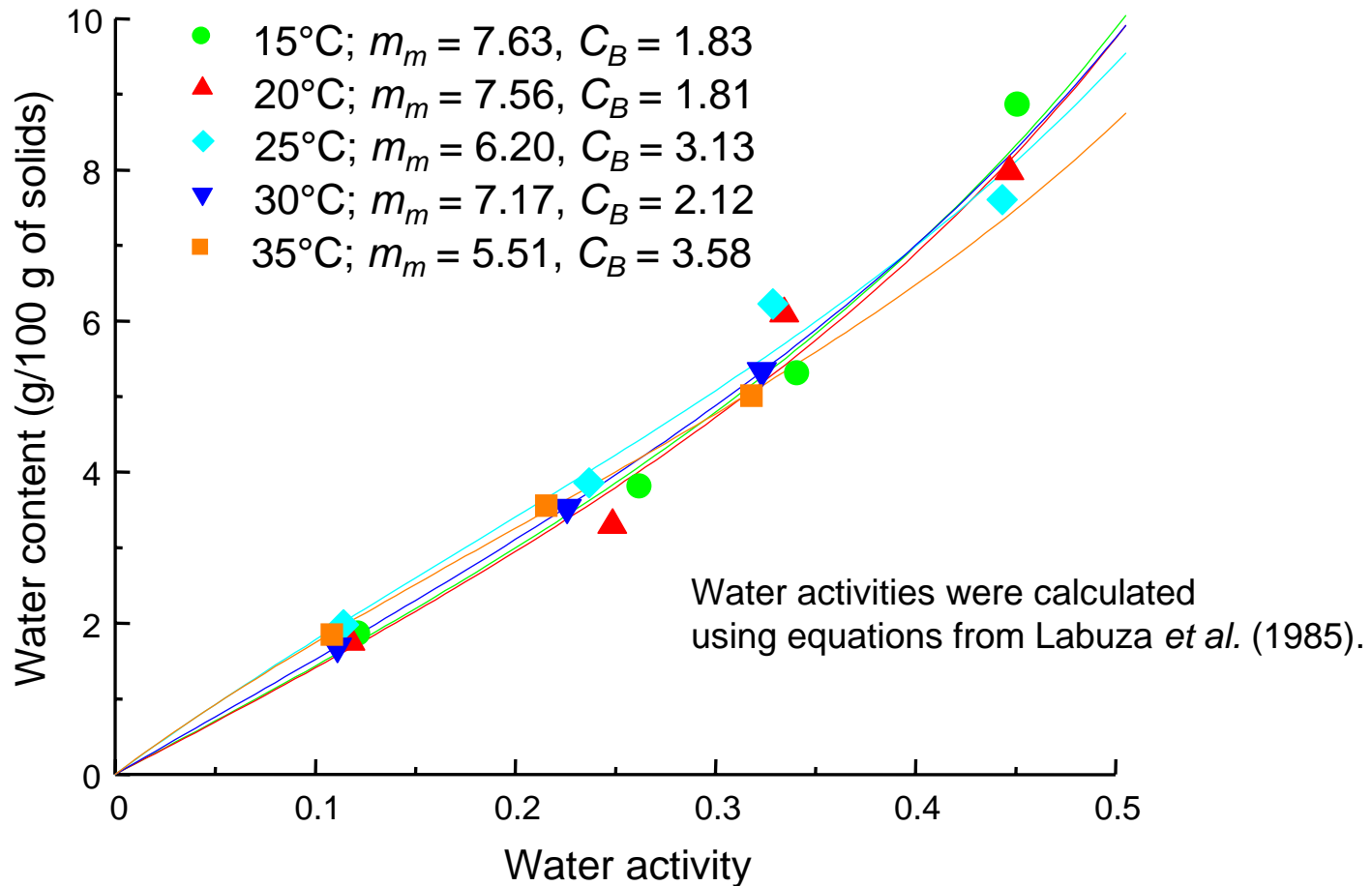


Results

- Water sorption isotherms for freeze-dried sucrose at various temperatures were obtained using BET modelling.
- Water plasticization of freeze-dried sucrose could be modelled using the Gordon-Taylor equation.
- Loss of sorbed water showed occurrence and kinetics of sucrose crystallization under various storage conditions.
- XRD data confirmed amorphous state of freeze-dried sucrose prior to crystallization study. Occurrence of sucrose crystallization could be observed from XRD patterns.

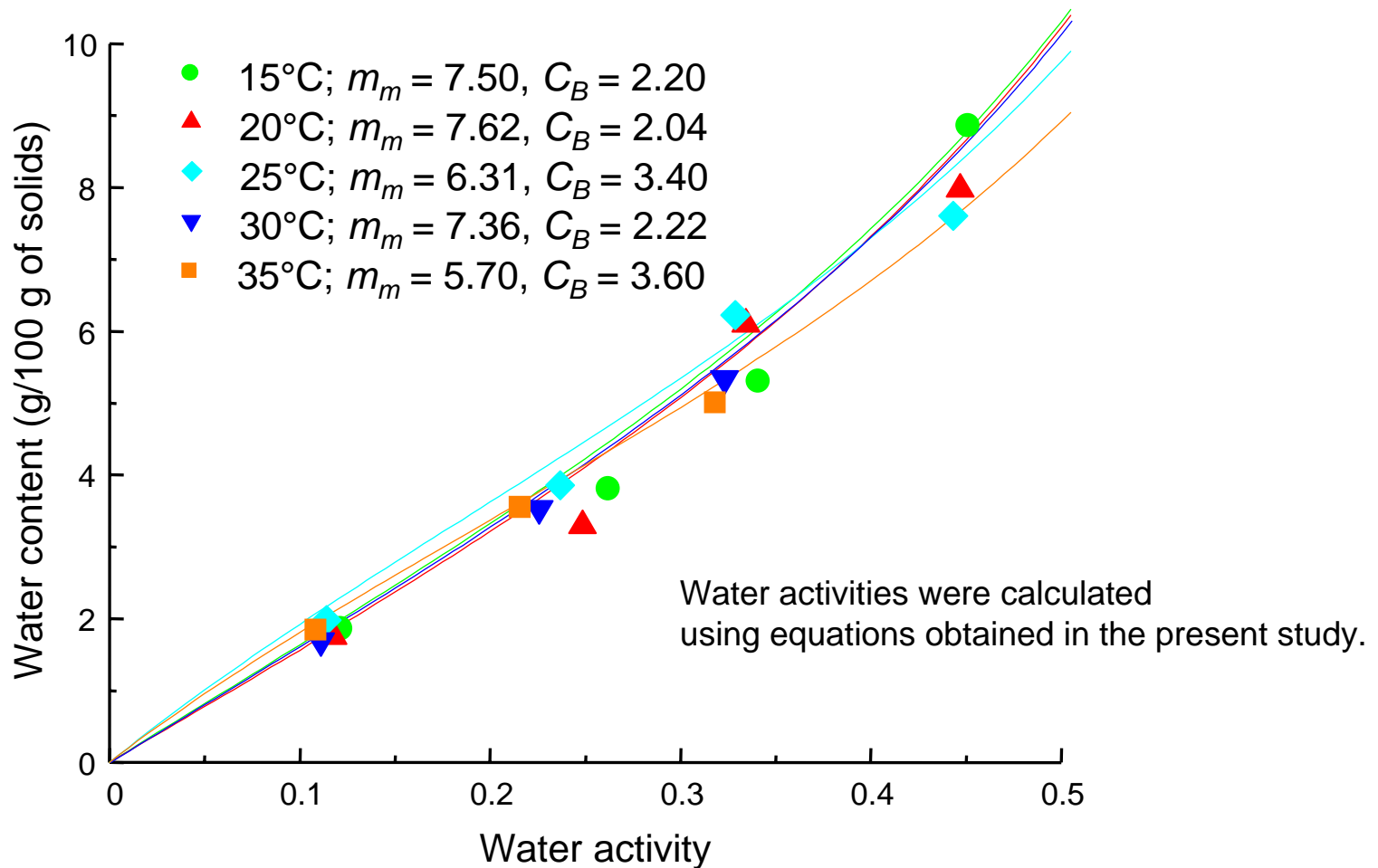


BET water sorption isotherms for freeze-dried sucrose at temperatures ranging from 15 to 35°C



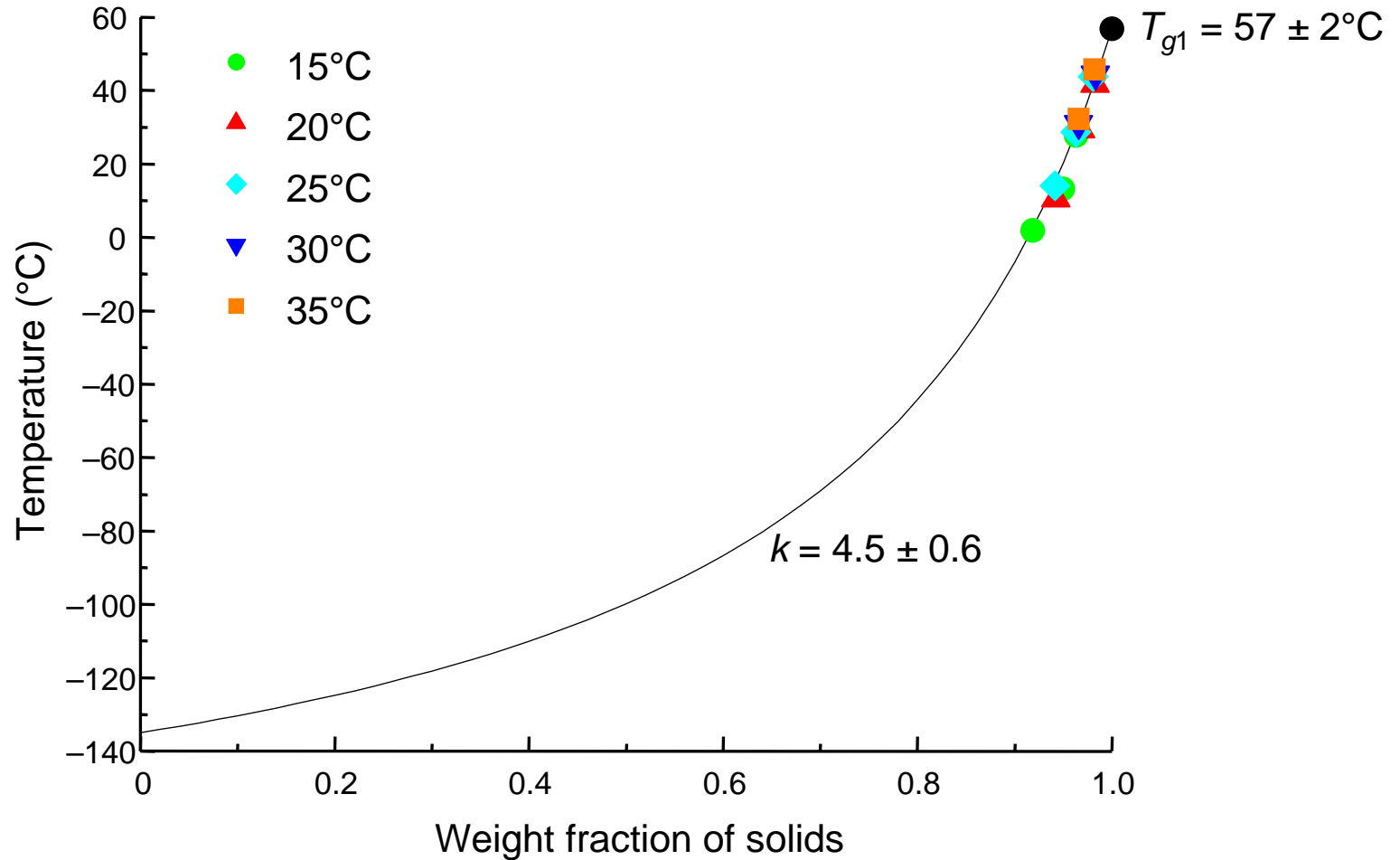


BET water sorption isotherms for freeze-dried sucrose at temperatures ranging from 15 to 35°C



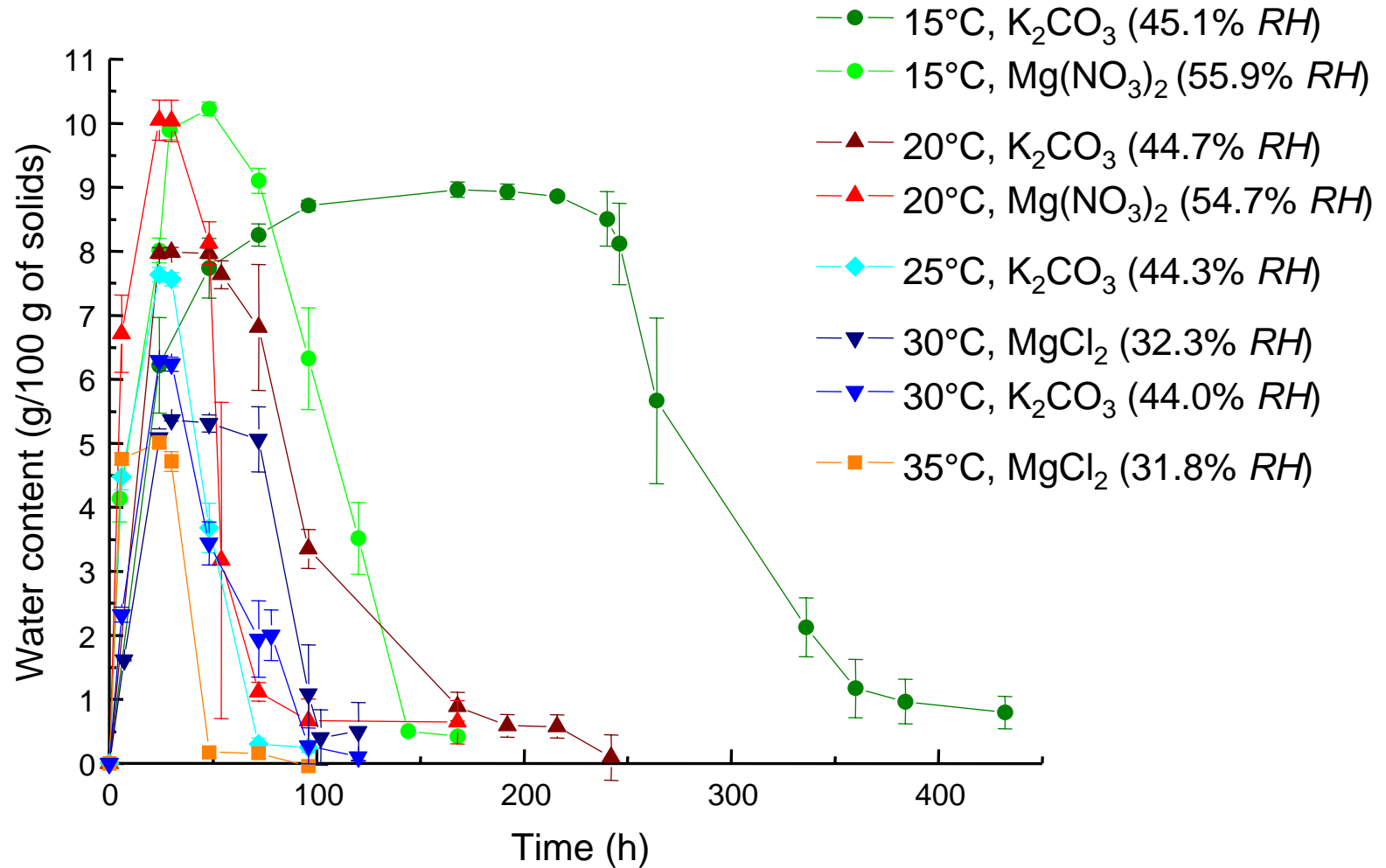


State diagram of freeze-dried sucrose



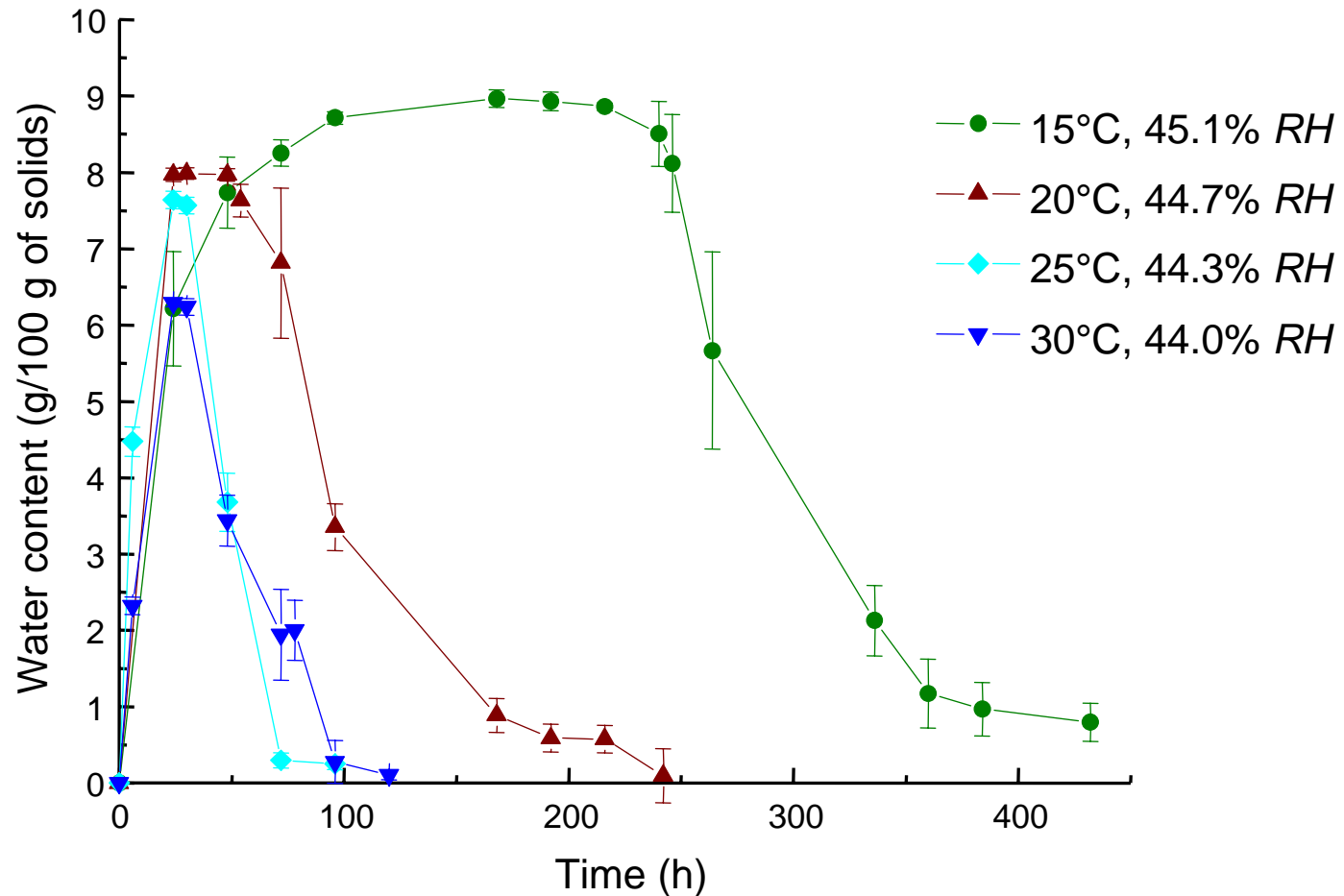


Water sorption behavior of freeze-dried sucrose stored under various conditions



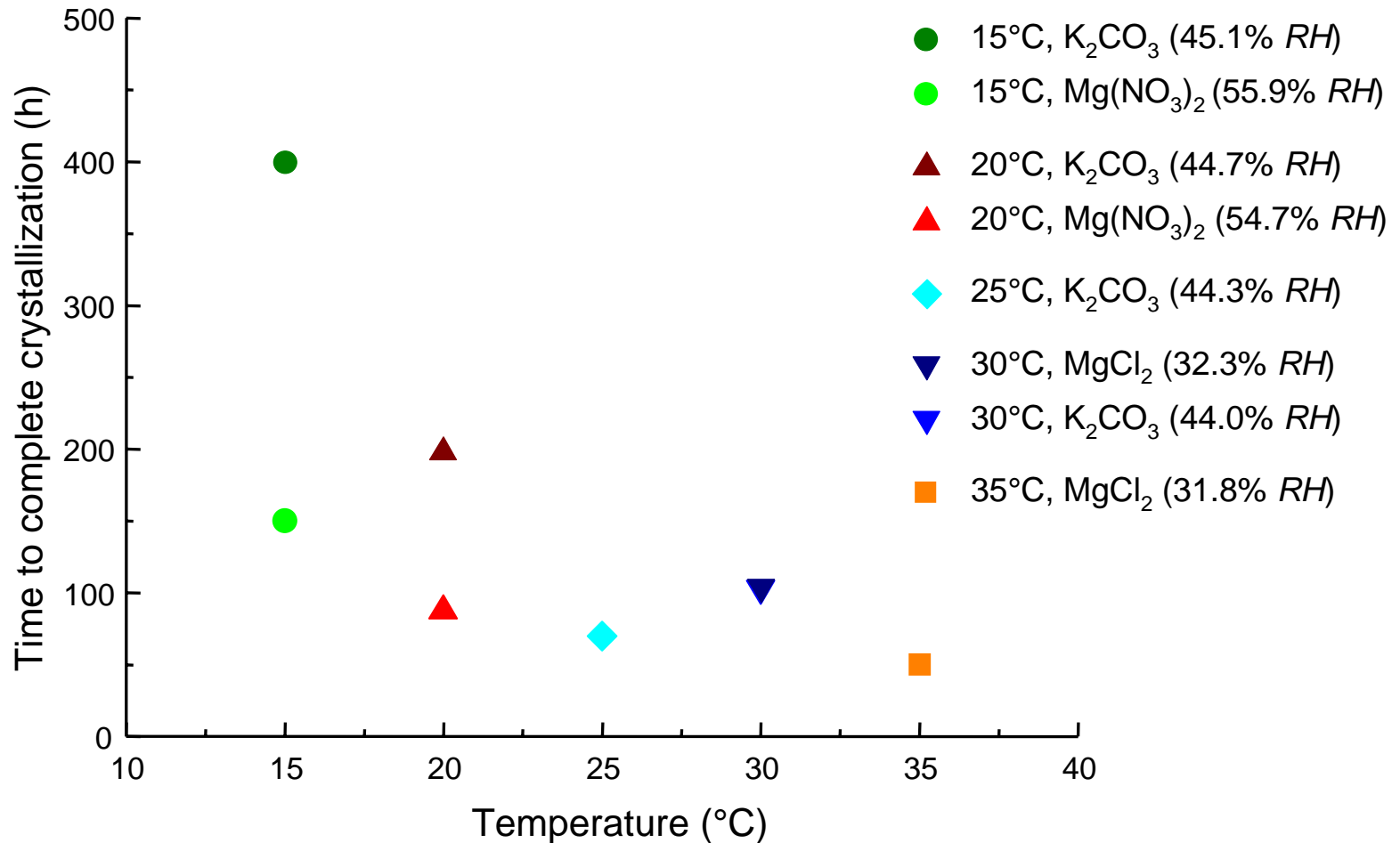


Water sorption behavior of freeze-dried sucrose stored over saturated K_2CO_3 solution



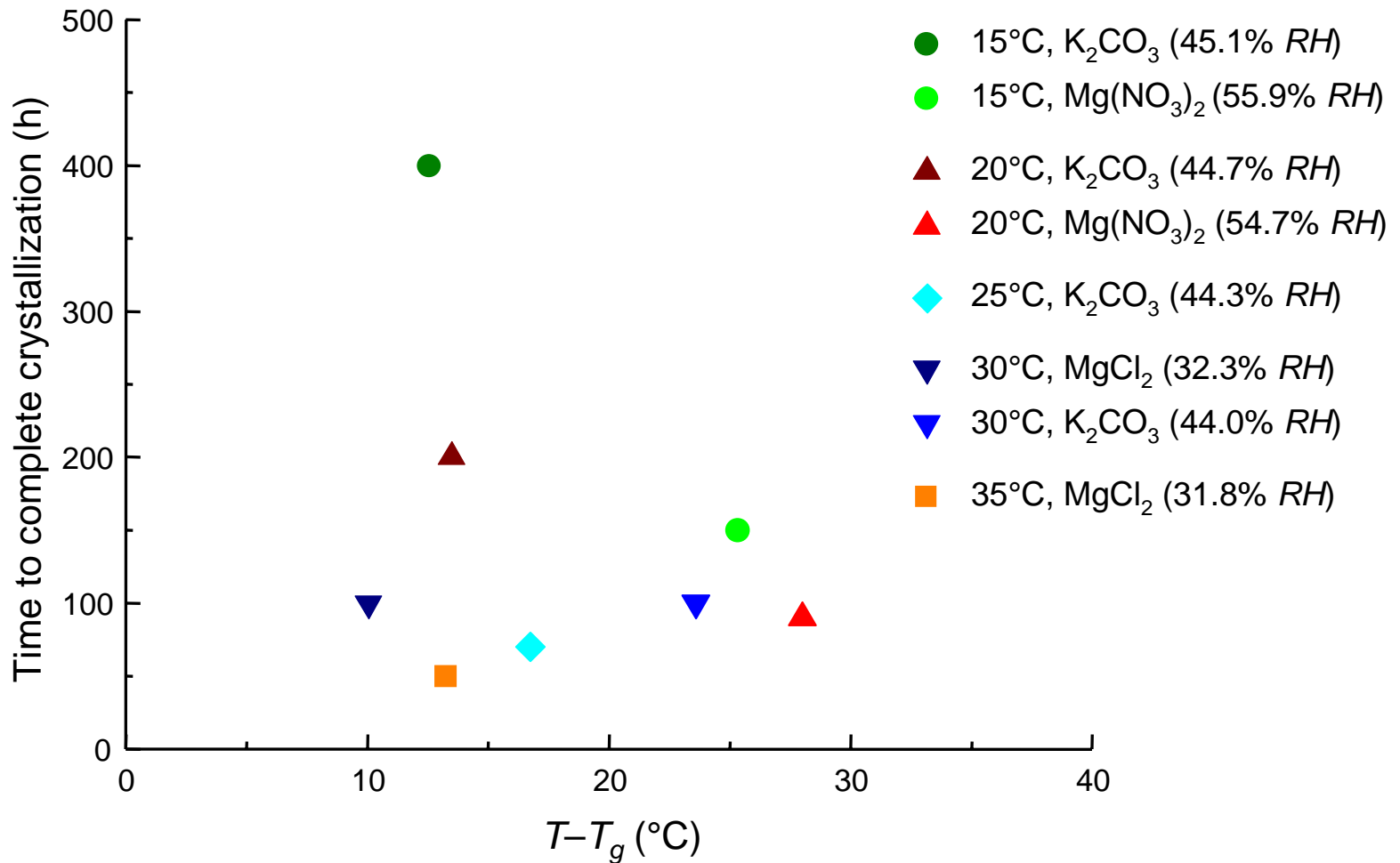


Crystallization kinetics, as observed from the loss of sorbed water, vs. temperature





Crystallization kinetics, as observed from the loss of sorbed water, vs. $T-T_g$



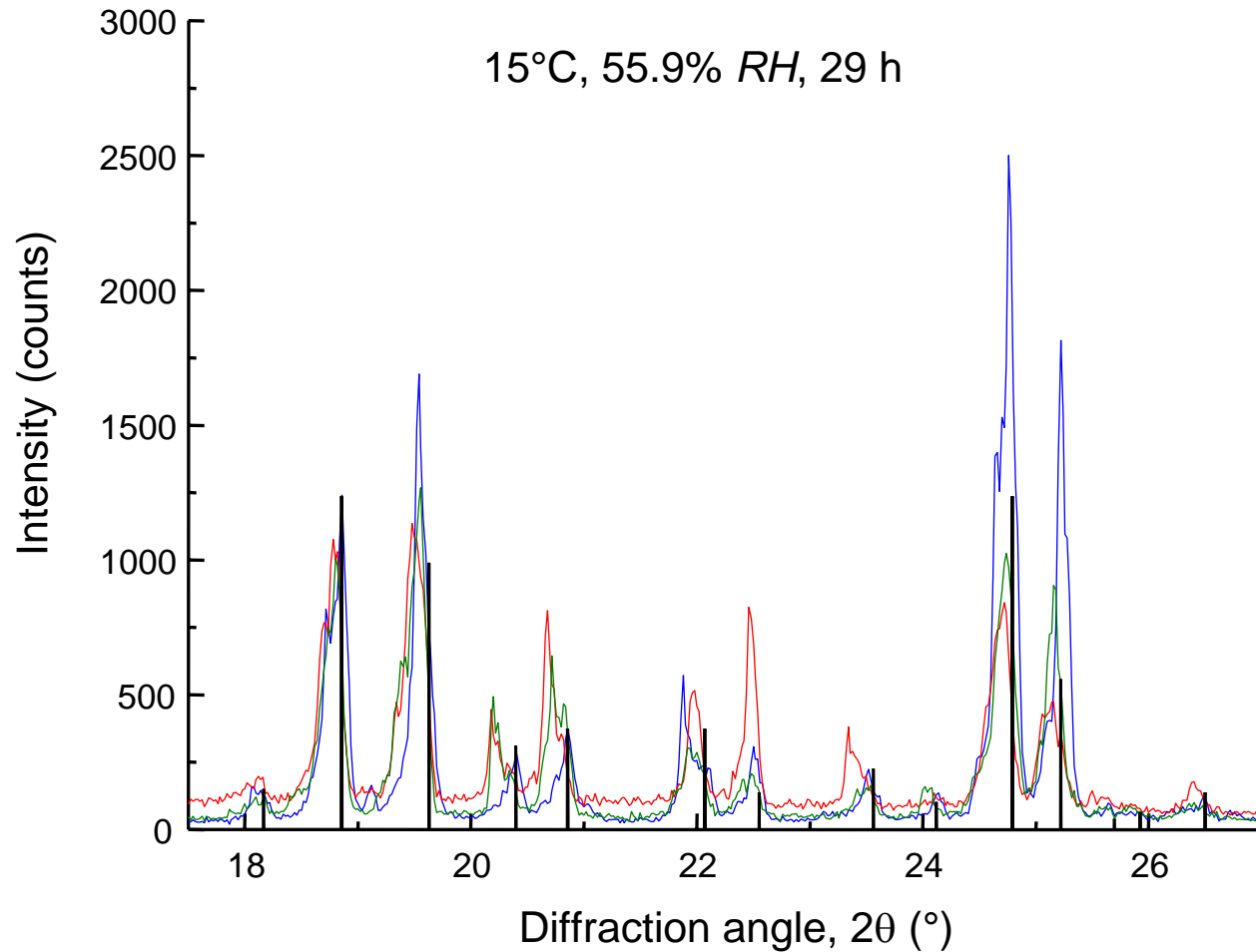


Time to complete crystallization (t_{cc}) for various dehydrated sucrose samples

Material (reference)	T (°C)	RH (%)	t_{cc}
Freeze-dried sucrose (Mathlouthi, 1995)	20	44	80 h (3.3 d)
Spray-dried sucrose (Elamin <i>et al.</i> , 1995)	21	57	35 h (1.5 d)
Freeze-dried sucrose (the present study)	20	44.7	200 h (8.3 d)
		54.7	90 h (3.8 d)
Spray-dried sucrose (Makower & Dye, 1956)	25	33.6	< 48 h (< 2 d)
Spray-dried sucrose (Palmer <i>et al.</i> , 1956)	24	32.5	96 h (4 d)
		33.5	< 48 h (< 2 d)
Freeze-dried sucrose (the present study)	25	44.3	70 h (2.9 d)
Freeze-dried sucrose (Saleki-Gerhardt & Zografis, 1994)	30	32.4	10 h
Freeze-dried sucrose (the present study)	30	32.3	100 h (4.2 d)
Freeze-dried sucrose (Iglesias & Chirife, 1978)	35	54	25 h
Freeze-dried sucrose (the present study)	35	31.8	50 h (2.1 d)

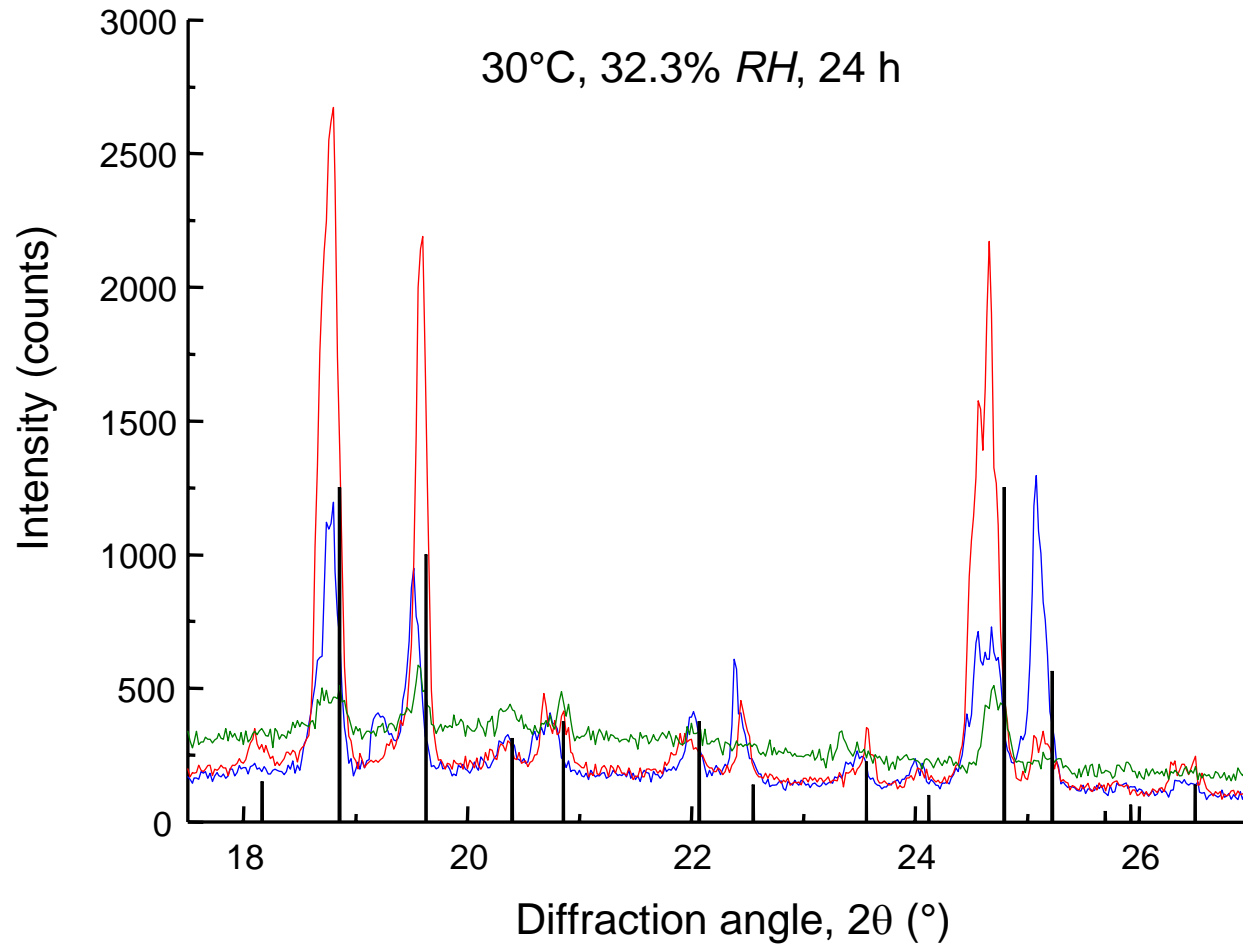


XRD patterns for crystallized sucrose samples (1/2)





XRD patterns for crystallized sucrose samples (2/2)





Conclusions

- Water sorption isotherms for freeze-dried sucrose at various temperatures were almost identical.
- Both temperature and water content affected occurrence and kinetics of sucrose crystallization.
- Knowledge of the effects of temperature and water content on changes occurring in amorphous carbohydrates is important in selection of proper processing and storage conditions in order to maintain desired properties of food products containing amorphous carbohydrates.



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