Crystallization in “Tarassaco" (*Taraxacum officinale* Weber) Italian honey studied by Differential Scanning Calorimetry

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HONEY: highly concentrated (supersaturated) sugar solution

AVERAGE COMPOSITION

Moisture	13%-23%
Glucose	22%-41%
Fructose	27%-45%
Sucrose	0.25%-7.6%
Maltose	2.7%-16%
Higher sugars	0.13%-8.5%
Total Carbohydrates	75-80%

- a_w = 0.55-0.68

OTHER COMPONENTS

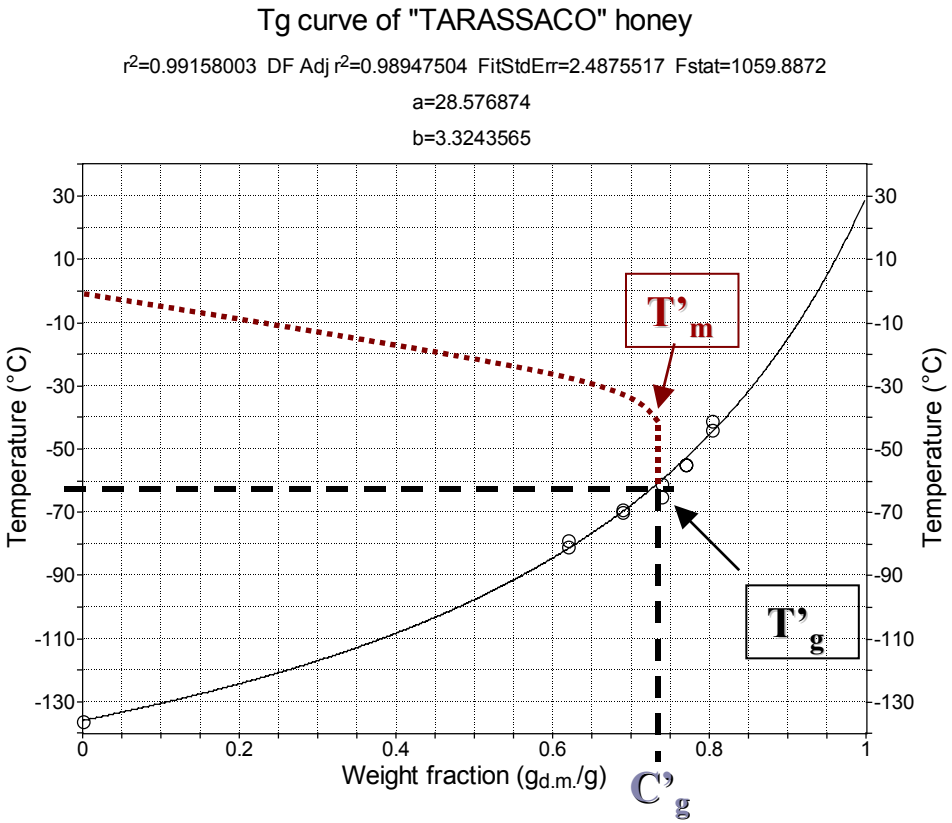
- Organic acids
- Aminoacids
- Enzymes
- Vitamins
- Inorganic substances
- Volatiles
- Pigmens

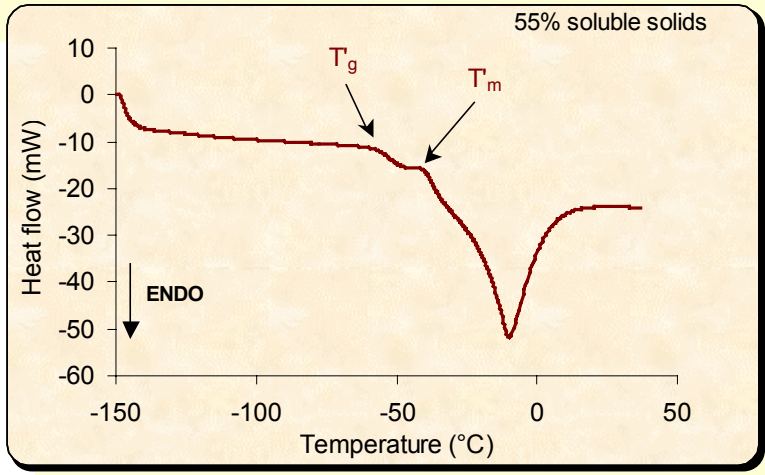
Physical properties and chemical composition of the "Tarassaco" Honey (liquid)

Moisture %	Solids %	T_g (°C)	a_w	Viscosity$_{20°C}$ Pa ·s (Newtonian)	Glucose %	Fructose %	Sucrose %
19.5 ± 0.3	80.5 ± 0.3	-42 ± 1	0.593 ± 0.007	6.59 ± 0.26	32.57 ± 1.33	37.40 ± 0.66	1.5 ± 0.8

Thermal properties (state diagram) of liquid "Tarassaco" honey

Gordon and Taylor fitting





$T_{gdry} \cong 29$ °C (extrapolated)

$K = 3.32$

$T'_g \cong -63$°C

$T'_m \cong -40$°C

$C'_g \cong 73\%$ s.s.

$UFW \cong 0.37 g_{H2O}/g_{d.m.}$

(T_g pure honey $\cong -42$ °C)

Crystallization of honey

- Homogeneous: desirable
  - fine crystals lead to creamed honey with spread behaviour
- Phase separated: undesirable
  - coarse crystals lead to water activity increase in the upper liquid phase (osmophylic yeasts may grow)

Crystallization of honey

- Time dependent related to
  - Presence, number and size of nucleation seeds (impurities, pollen, air bubbles…)
  - Concentration
  - Supersaturation of sugars (mainly glucose)
  - Viscosity

Temperature dependent

Glucose crystal forms

- α-D-glucose monohydrate
  → stable form at Temp. <50° C
- α-D- glucose anhydrous
  →stable form at Temp. >50° C
- At high fructose concentrations
  → hydrate/ anhydrous glucose transition at temperature <30°C according to Kelly 1954

Crystals separation and purification
(MATERIALS AND METHODS)

Crystallized honey (90 days at 15°C)

Washing with excess (1g:500mL) cooled (-20°C) ethanol,

Filtration,

Crystals recovery and

White, disaggregated crystals + ethanol

Evaporation of ethanol with dry nitrogen flow

Pure anhydrous honey crystals

Cooled ethanol allowed:

- Removal of amorphous phase
- Dehydration: avoided melting of crystals during filtration and allowed their retention (melting point: α-gluc. monohydr.= 83°C; α-gluc. anhydr.= 146°C; MERCK INDEX)

RESULTS

Composition of crystals (melt) g/100g (HPLC)

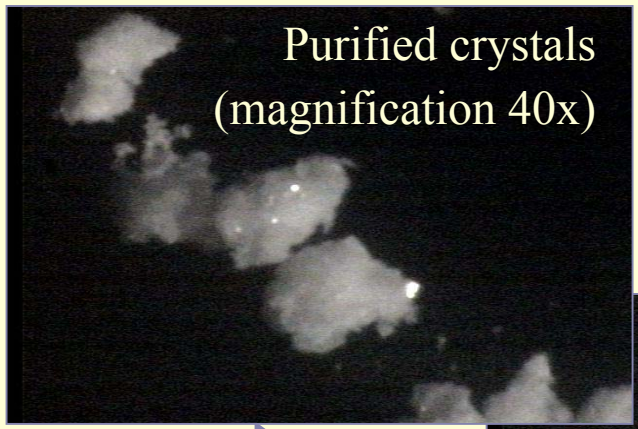
~ 2 % fructose

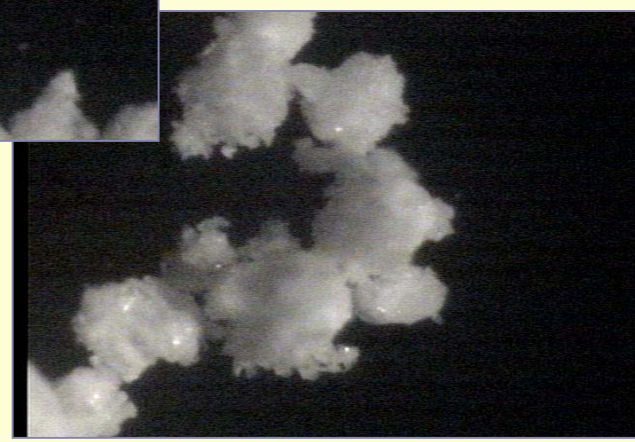
~ 73 % glucose

~ 7-9% water

~ 1.5% other sugars

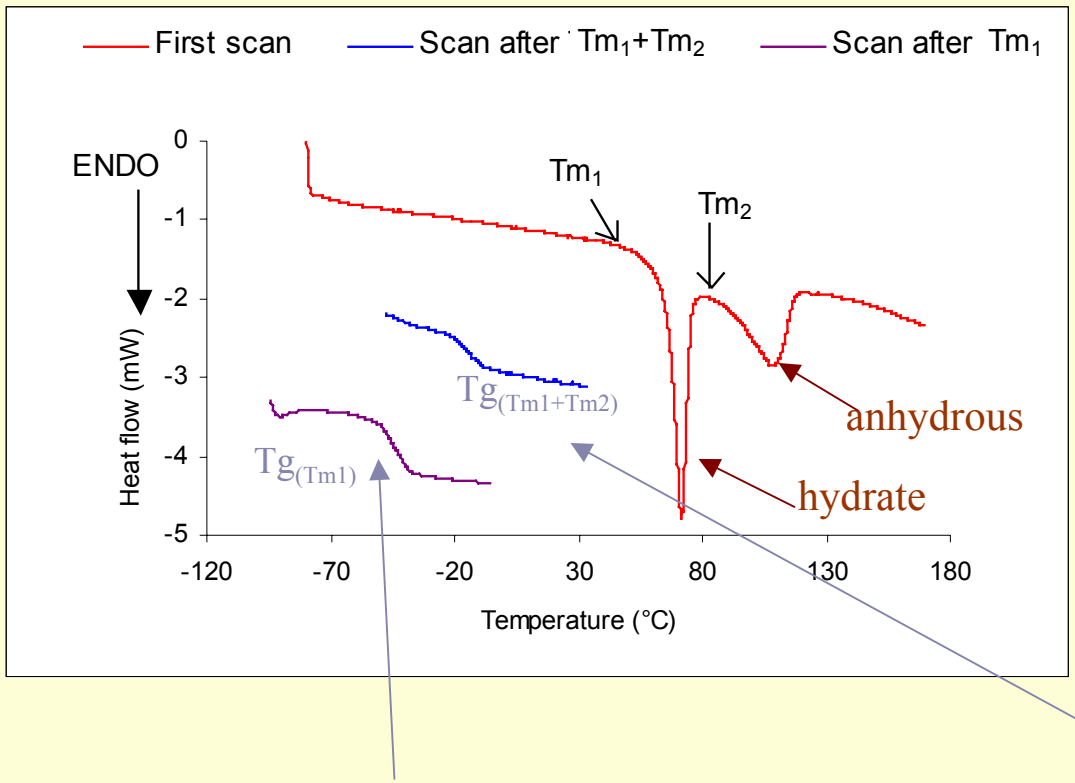
~ 14% others substances





DSC of purified crystals

(scan rate 5° C/min)



No detectable T_g at the first scan → no/negligible residual amorphous phase

$Tm_1 \cong 52$ °C (honey crystals)

Glucose monohydrate (Sigma grade)
$T_m = 56$°C (DSC determination)

$Tm_2 \cong 83$ °C

$\Delta H_{(Tm1+Tm2)} = 108.39 \pm 6.16$ J·g^{-1}

Rescan after $Tm_1 \rightarrow T_g \sim -50$ °C (congruous with 82% glucose solution according to glucose state diagram)

Rescan after $Tm_1+Tm_2 \rightarrow T_g \sim$ -20 °C (congruous with 90% glucose solution)

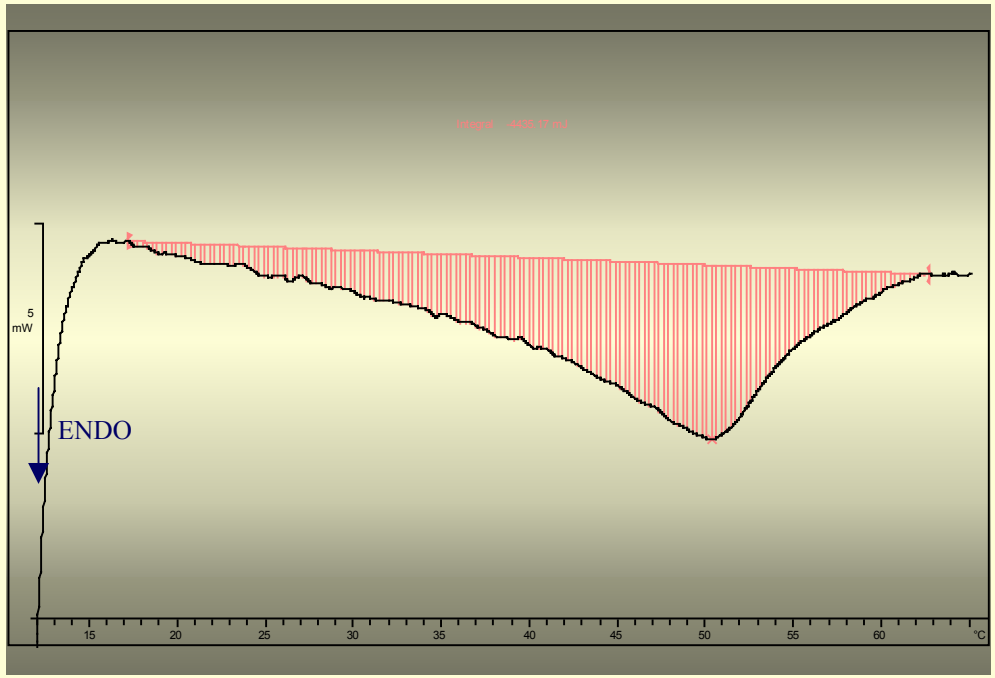
Samples of liquid honey were stored into 80 g pots up to 222 days at:

- 5° C
- 10° C
- 15° C
- 20° C
- 25° C

DSC analysis performed at time intervals; determinations of T_g, T_m and ΔH

Crystals melting enthaply in granulated honey

$$\frac{\Delta H \text{ honey (J)}}{108.39\ (Jg^{-1})} = g_{\text{ crystals}}$$



Example. 222 days at 15°C

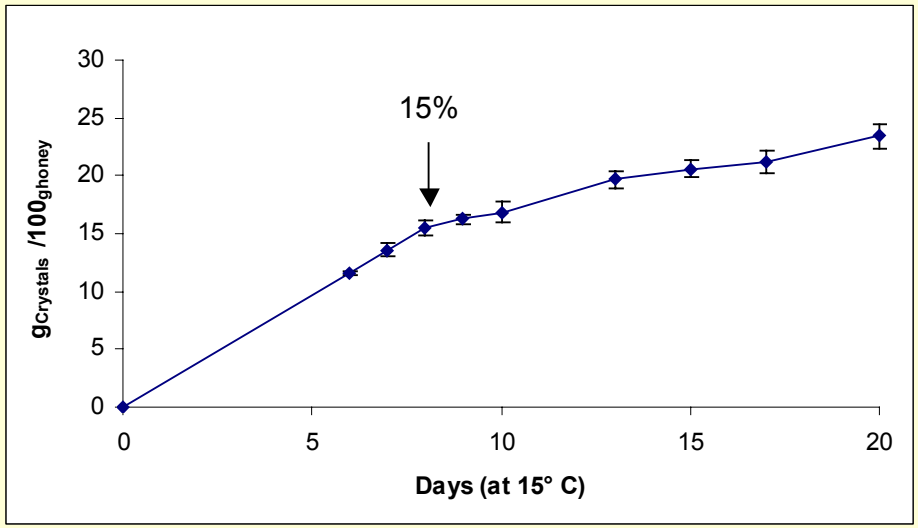
$$g_{\text{ crys.}}/g \text{ honey x } 100 = g_{\text{ crys.}}\%$$

RESULTS

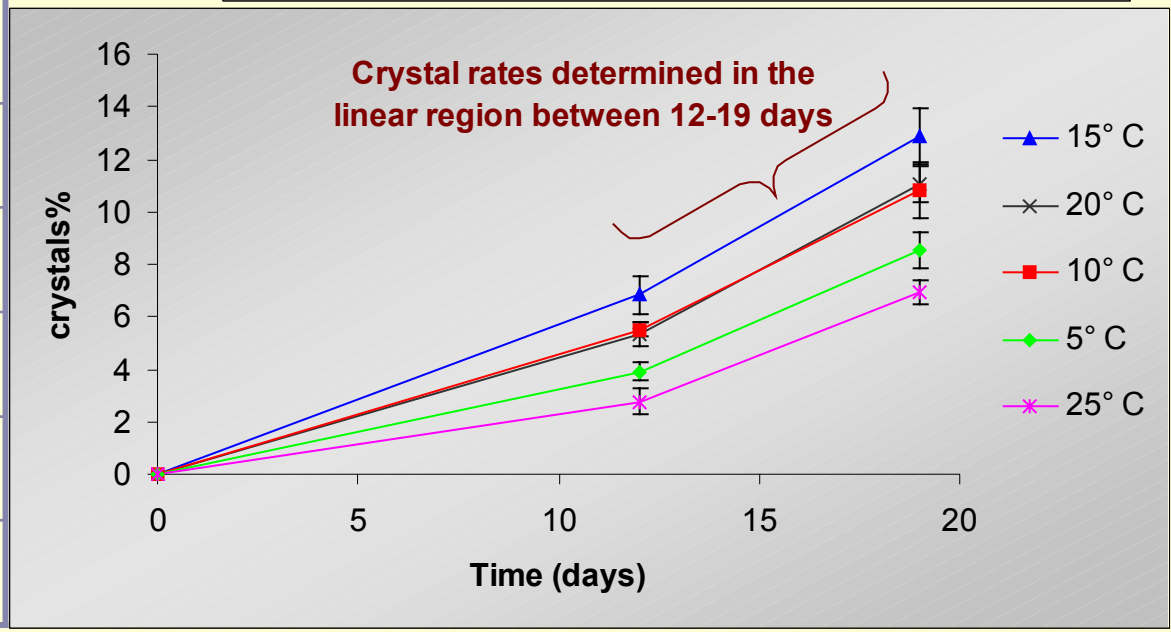
Crystallization rates

Linear growth up to 15%

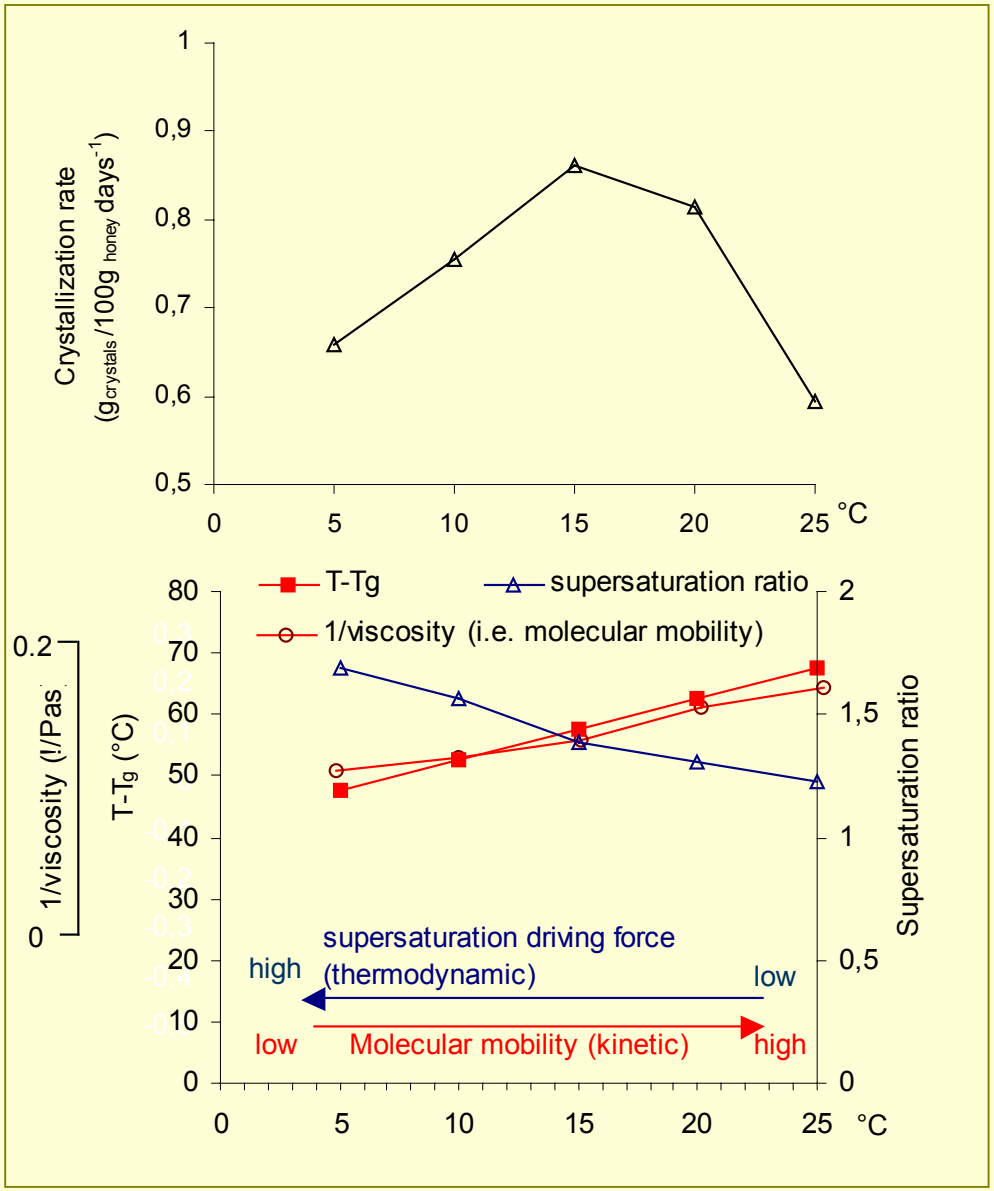
after crystallization induced by thermal shock



Temp. (°C)	Crystallization rates ($g_{Cry} \cdot 100g_{honey}^{-1} \cdot days^{-1}$)
5	0.659
10	0.755
15	0.861
20	0.815
25	0.593



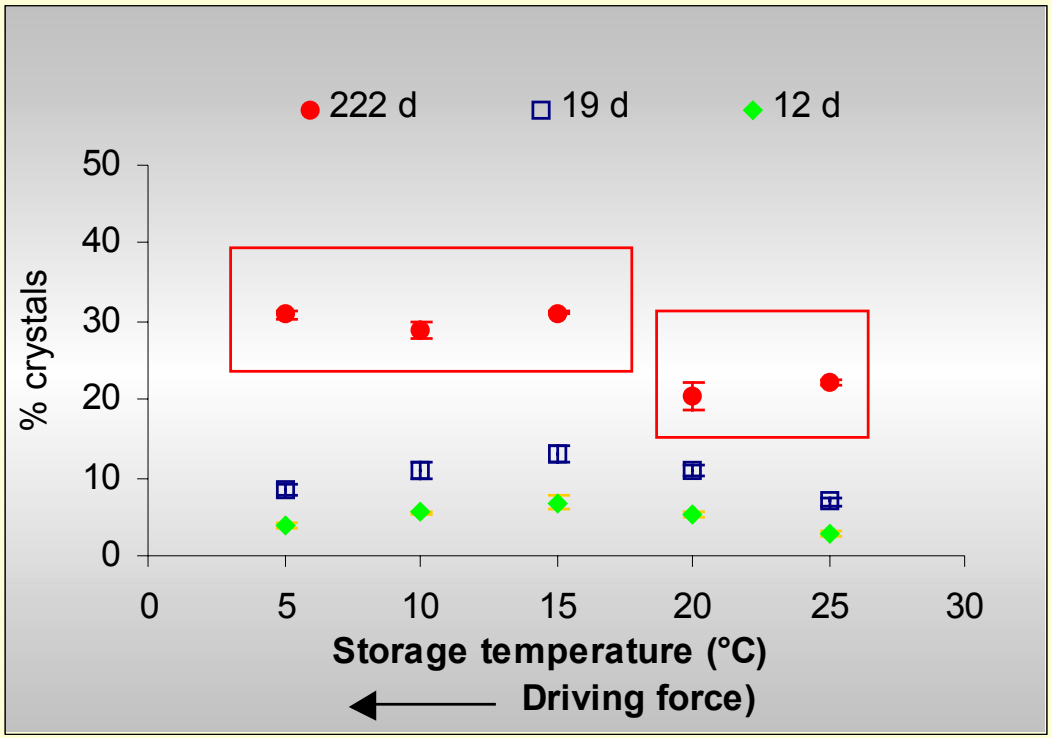
Maximum crystallization rate at 15°C



Factors affecting crystallization

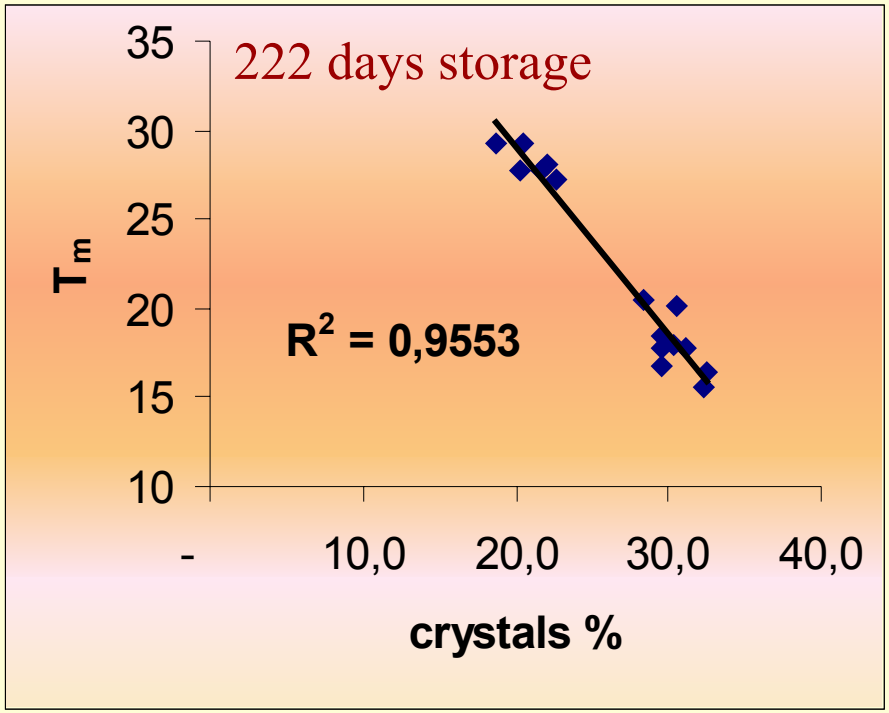
- Supersaturation ratio= thermodynamic driving force
- Viscosity/ $(T-T_g)$= mobility kinetic driving force

Crystallization degree at extended storage time
(222 days storage)



- A thermodynamic equilibrium is reached at extended storage times
- Maximum crystallization degrees= 22-32%

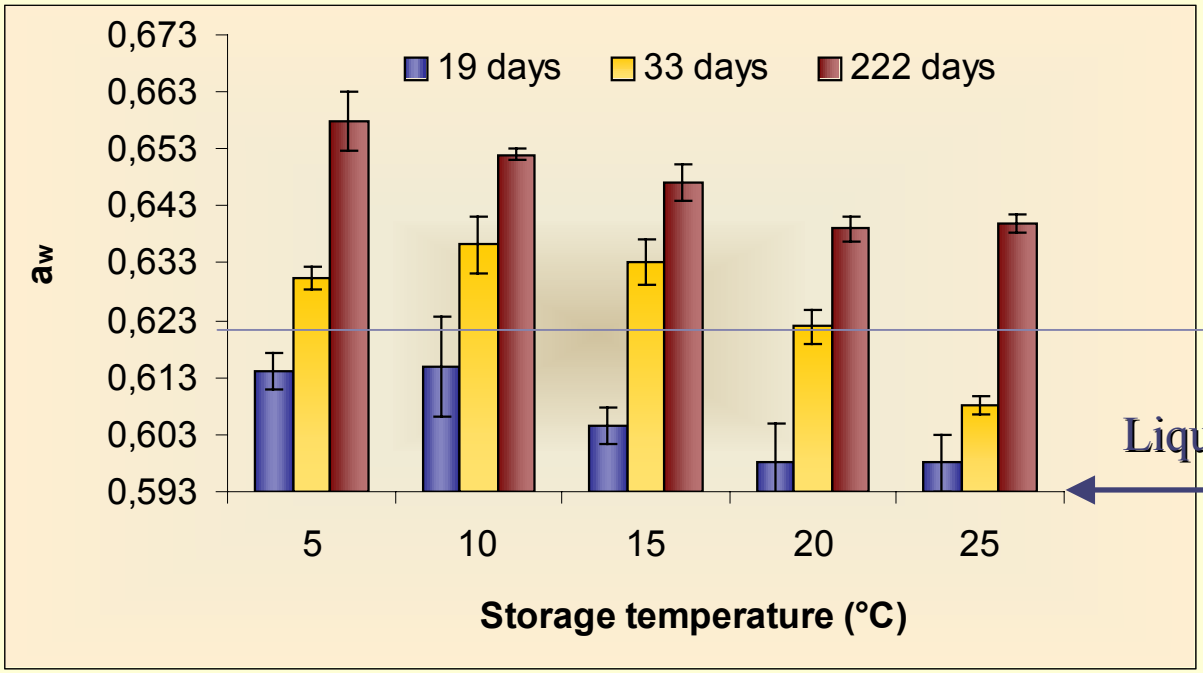
Crystals melting temperature (T_m)



melting temperature approximatively related to the degree of crystallization in agreement with solubility curve, i.e. the higher the crystallization degree the lower the T_m

RESULTS

a_w



- a_w increased with increasing crystallization degree

-After 33 days storage most samples showed aw> 0,62 which could be congruous with yeasts growth

- Fermentation aroma at 222 days storage was perceived in samples stored at temperatures higher than 15°C. In such samples a sedimentation of separated crystals was also observed.

Conclusions

- Crystals from “Tarassaco” honey were mainly composed by glucose
- Two crystal forms: hydrated glucose and anhydrous glucose
- Melting enthapy of pure crystals = 108.39 J/g
- Maximum crystallization rate occurred at 15° C as a result of opposite thermodynamic and kinetic driving forces
- Maximum observed crystallization degree (after experimental time 222 days) ≅32%
- The increase of a_w was associated with crystallization.
- Critical threshold for osmophylic yeasts growth (~ 0.62) was reached at faster rate at intermediate temperatures. After extended storage time all samples showed a_w >0.62, fermentation flavour was perceived in samples stored at temperatures >15°C where a phase separation also occurred.