QUICK RÉSUMÉ:

- Laboratory ice nucleation research 1962-1976   (McGill and U. Wyoming)

- Cloud microphysics. Origin of ice in clouds. Marine stratocumulus.
    - Elk Mountain Observatrory
    - Queen Air
    - King Air
    - Wyoming Cloud Radar (WCR) on aircraft.

- Retired in 2006.
    - Return to nucleation topics after 30 years.

In pursuit of sites

What do we know about ice nucleation sites?

My definition: “An ice nucleation site, INS, is the particular place on a surface where ice nucleation takes place. It is a part of an ice nucleating particle INP or entity.”

Outline of talk:

1. What is the evidence for INS of unique properties?
2. What are these sites?
3. What is the nucleation rate *j(T)* on these sites?

The character of this talk:

- Bits of history, revisiting ideas.
- No new results of my own.
-

Bounds for the talk:

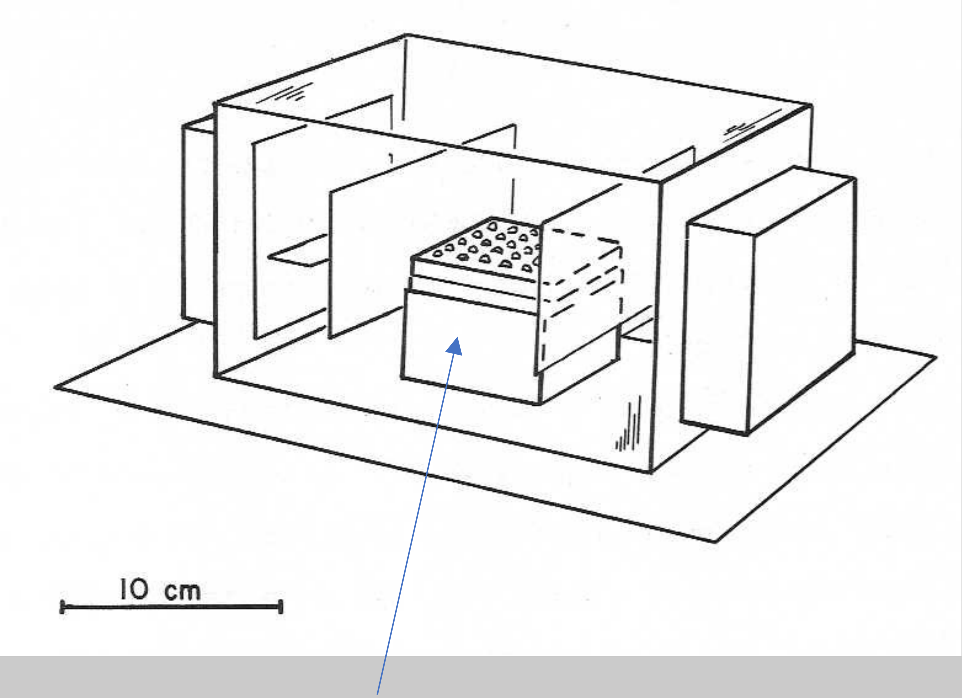
- Consider immersion freezing only
- Freezing at temperatures to about -25^{o}C
- Results from laboratory experiments

The beginning:

1962 drop freezer with good control of cooling-rate

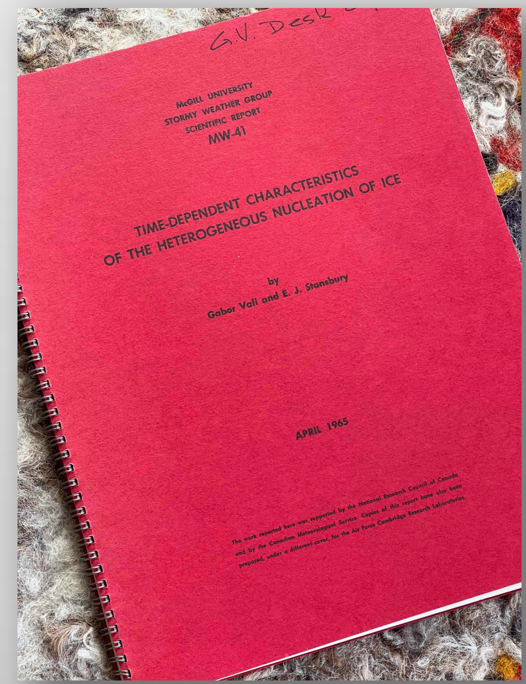
McGill University
Physics Dept.
Stormy Weather Group

Prof. Stewart Marshall
Prof. E. J. Stansbury



Peltier cooling and analog control circuit

GV
Apr. 11, 2024



G.V. Desk

McGILL UNIVERSITY
STORMY WEATHER GROUP
SCIENTIFIC REPORT
MW-41

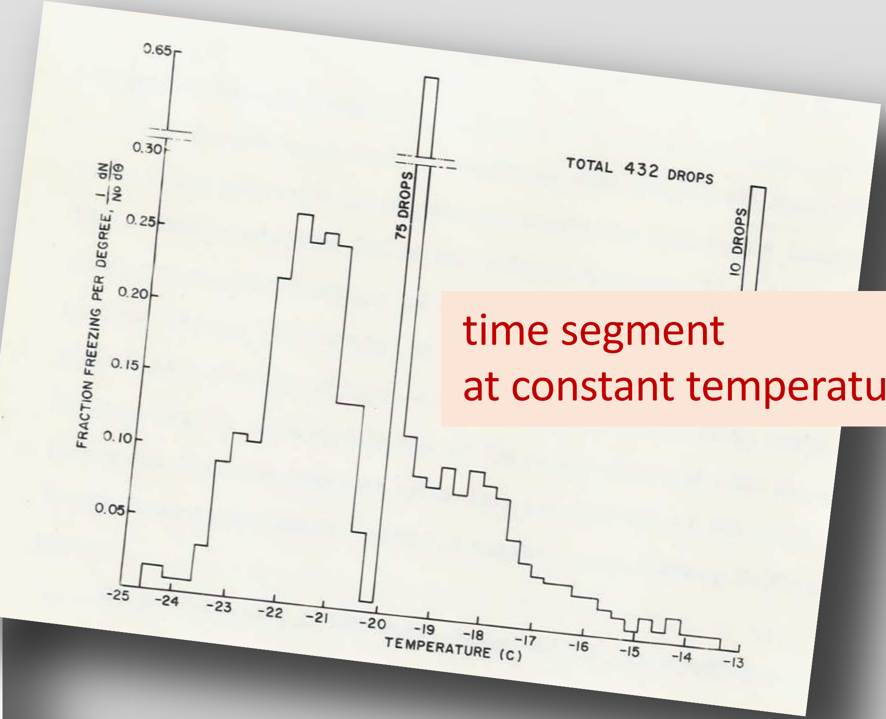
TIME-DEPENDENT CHARACTERISTICS
OF THE HETEROGENEOUS NUCLEATION OF ICE

by
Gabor Vali and E. J. Stansbury

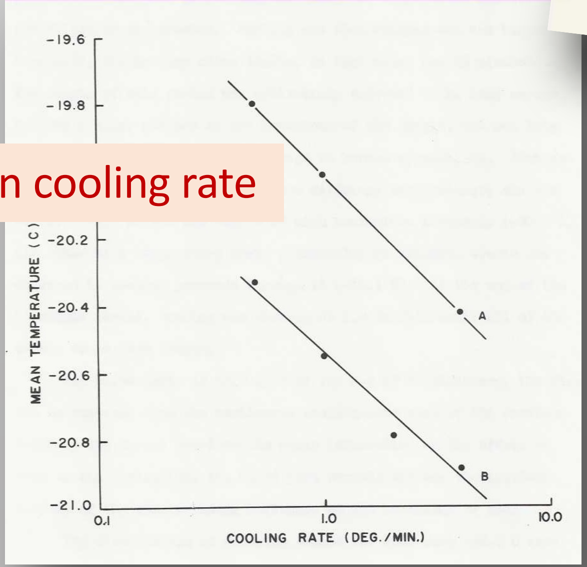
APRIL 1965

The work reported here was supported by the National Research Council of Canada and by the Canadian Meteorological Service. Copies of this report have also been prepared, under a different cover, for the Air Force Cambridge Research Laboratories.

M.Sc. thesis, at McGill U. 1964.



time segment
at constant temperature



dependence on cooling rate

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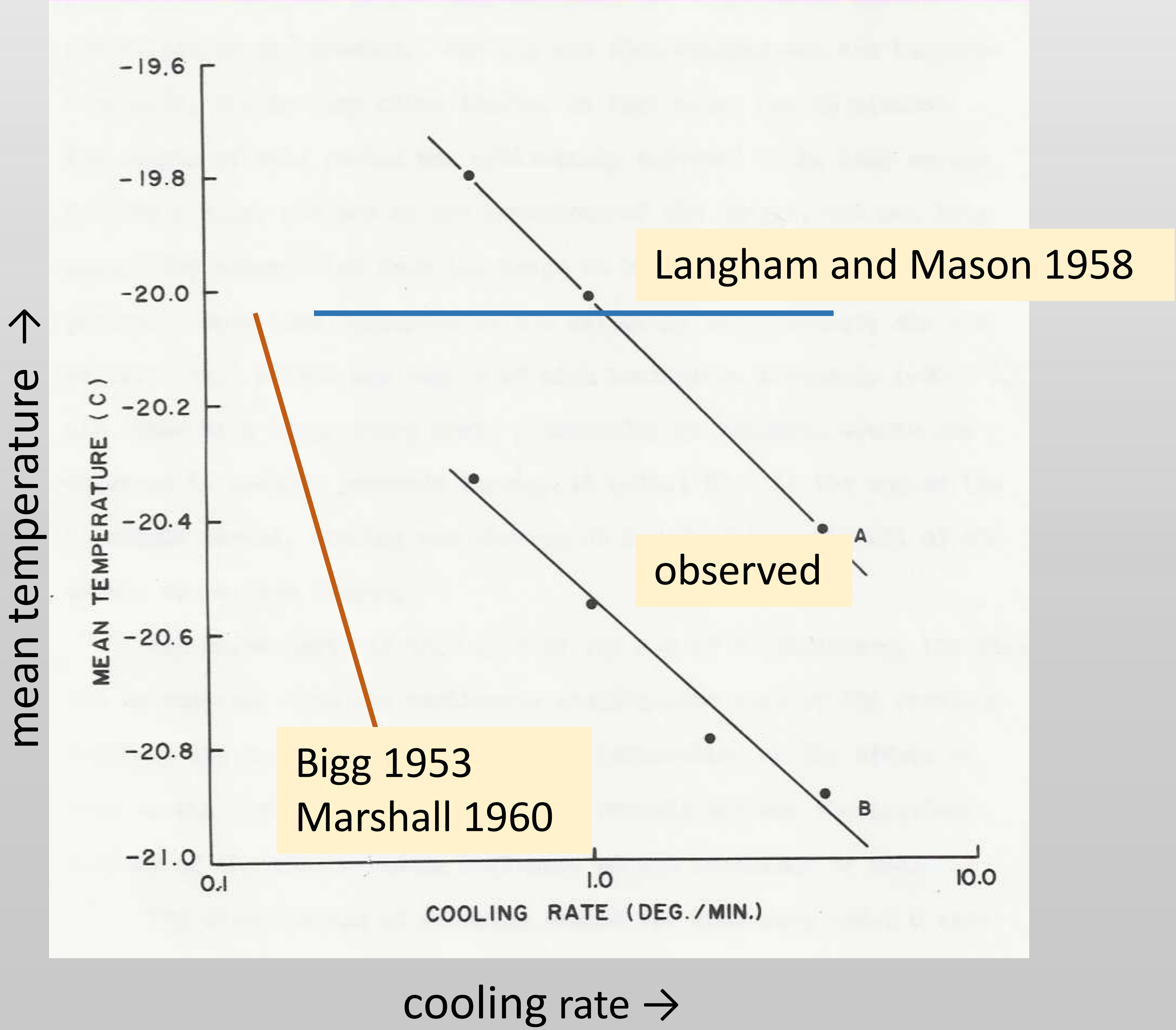


Langham and Mason 1958

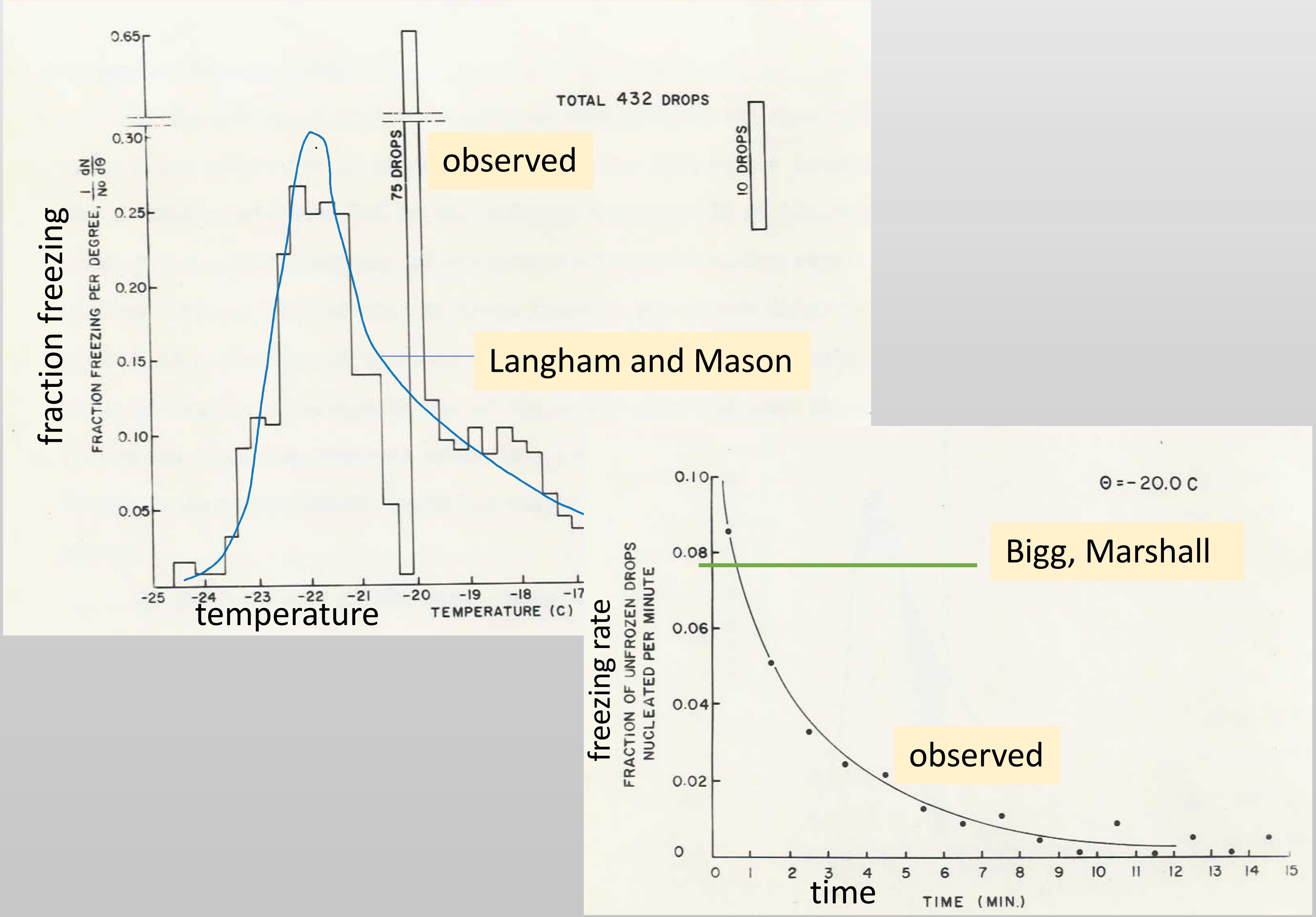
observed

Bigg 1953
Marshall 1960

mean temperature →

cooling rate →

Vali, 1964, M.Sc. thesis, McGill U.
Vali and Stansbury, 1966 Can. J. Phys.



Vali, 1964, M.Sc. thesis, McGill U.

Vali and Stansbury, 1966 Can. J. Phys.

For a fixed rate of cooling, and with near-exponential number distribution of activity, the Bigg and the Langham-Mason equations are identical making the distinction difficult.
(cf. Appendix A in Vali, 2014 in ACP).

Observed cooling rate dependence, and freezing at constant temperature are incompatible with both the stochastic prediction and with the fixed temperature per particle assumption.

The fixed temperature assumption is a better approximation → “chracteristic temperature”; “singular hypothesis” (Levine, 1950) → nucleus spectra k(T), K(T).

But the time-dependence had to be accounted for.

First notion:

Vali, 1964, M.Sc. thesis, McGill U.
Vali and Stansbury, 1966 Can. J. Phys.

Freezing of a drop can be characterized by T^c and a time-dependent rate:

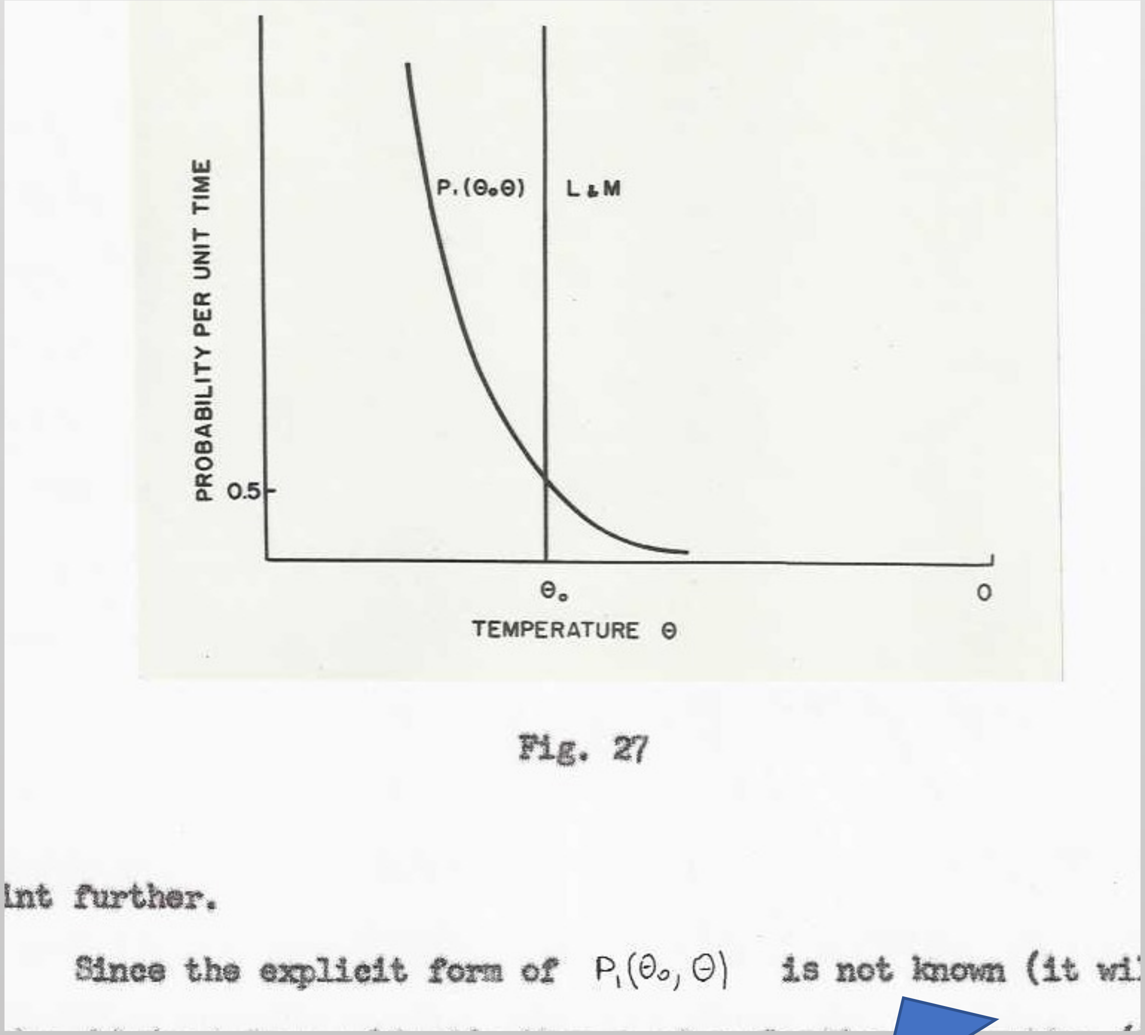
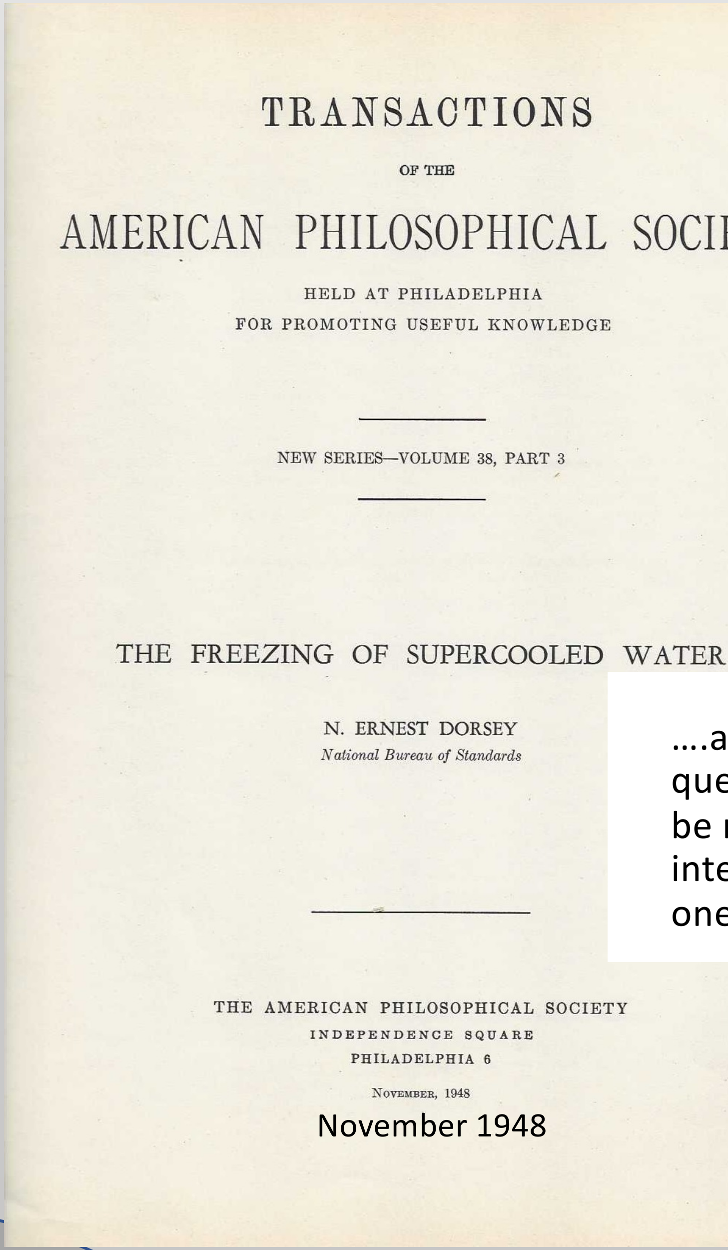


Fig. 27

int further.

Since the explicit form of $P_1(\Theta_0, \Theta)$ is not known (it wi

Evidence for characteristic temperature:



TRANSACTIONS

OF THE

AMERICAN PHILOSOPHICAL SOCIET

HELD AT PHILADELPHIA
FOR PROMOTING USEFUL KNOWLEDGE

NEW SERIES—VOLUME 38, PART 3

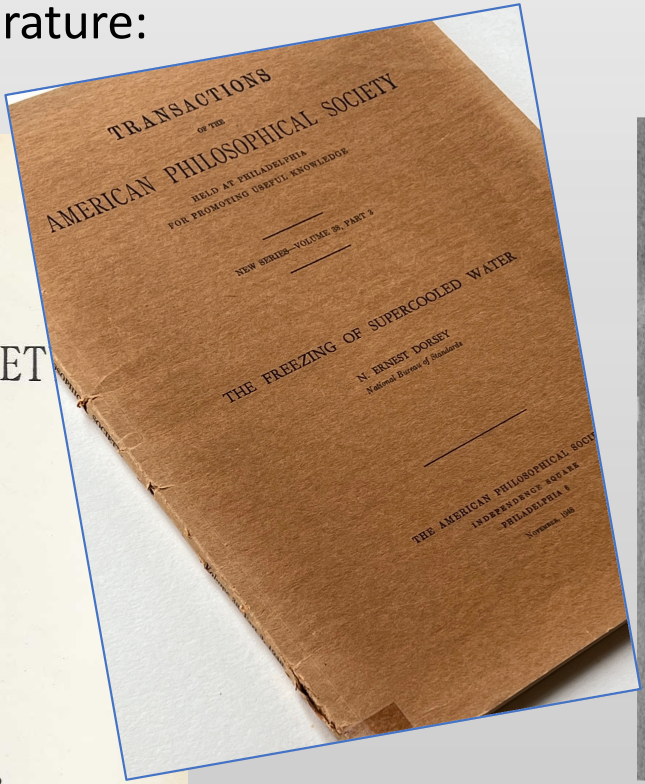
THE FREEZING OF SUPERCOOLED WATER

N. ERNEST DORSEY
National Bureau of Standards

THE AMERICAN PHILOSOPHICAL SOCIETY
INDEPENDENCE SQUARE
PHILADELPHIA 6

November, 1948

November 1948



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November, 1948

Noah Ernest Dorsey
1873 - 1959

….all these things aroused my curiosity and raised many questions. They invited an independent survey of the subject, to be made, not with the idea of obtaining data that may be interpreted by an accepted theory, but with the idea of seeing for one's self how water actually does behave when cooled …

"... at such odd times as were available from other and more immediately important work."

~ 12 years ; 80 pages

Preferred temperatures

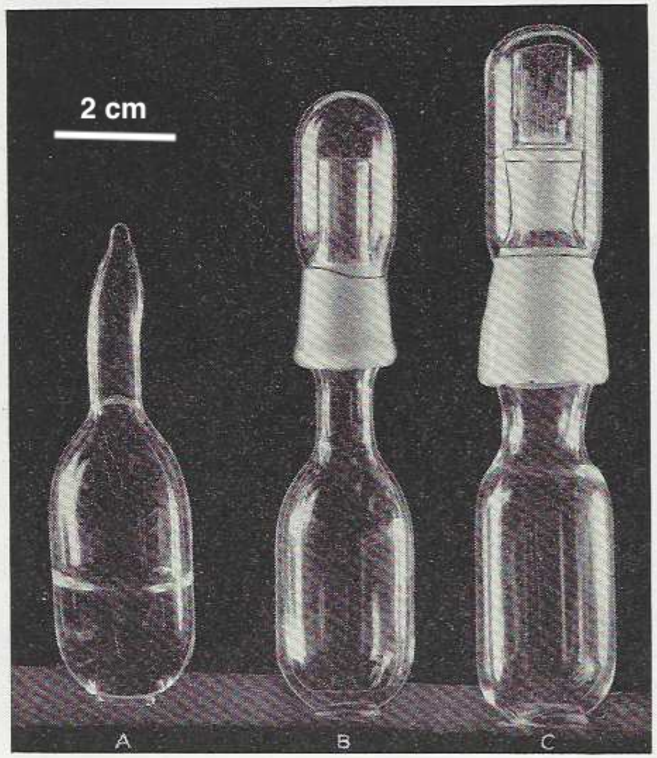


FIG. 1. Types of bulbs. *A*, sealed; *B*, capped; *C*, stoppered and capped.

6-8 mL

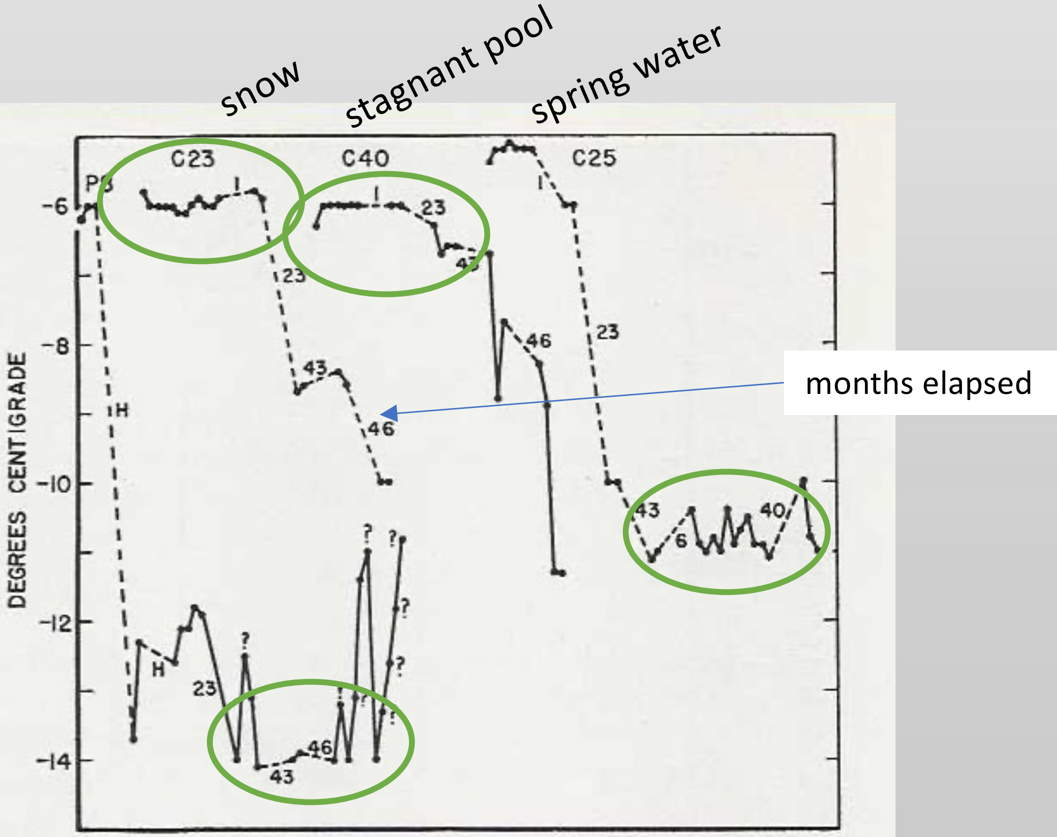
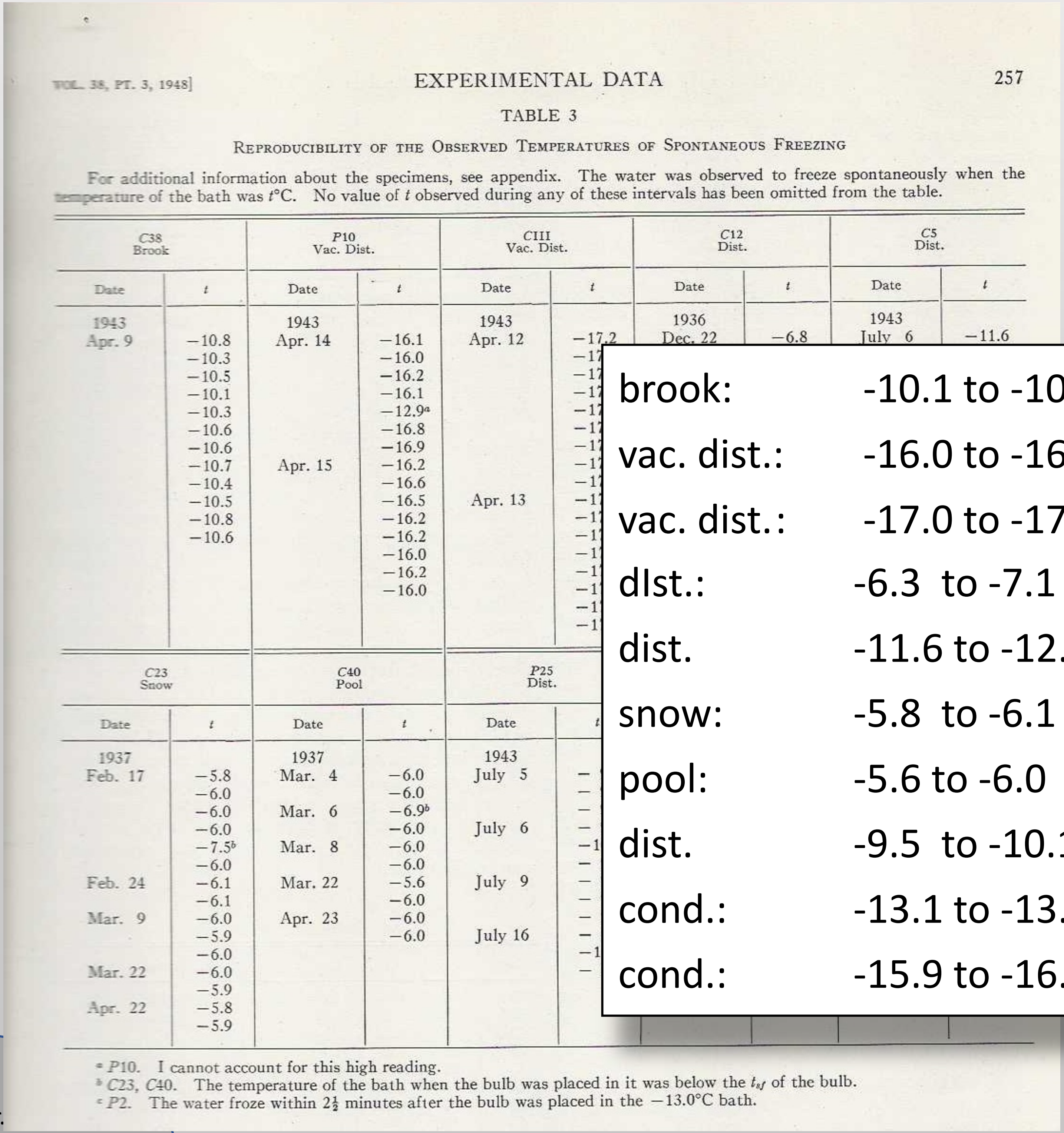


FIG. 4. Preferred temperatures: I. *P*8 cold faucet; *C*23 melted snow; *C*25 large spring; *C*40 surface of stagnant pool. Heatings (*H*), left to right: *P*8, 2 and 5.5 hours. See section B,I,1,*g*.



VOL. 38, PT. 3, 1948] EXPERIMENTAL DATA 257

TABLE 3

REPRODUCIBILITY OF THE OBSERVED TEMPERATURES OF SPONTANEOUS FREEZING

For additional information about the specimens, see appendix. The water was observed to freeze spontaneously when the temperature of the bath was t°C. No value of t observed during any of these intervals has been omitted from the table.

C38 Brook		*P10* Vac. Dist.		CIII Vac. Dist.		*C12* Dist.		*C5* Dist.	
Date	t	Date	t	Date	t	Date	t	Date	t
1943 Apr. 9	−10.8	1943 Apr. 14	−16.1	1943 Apr. 12	−17.2	1936 Dec. 22	−6.8	1943 July 6	−11.6
	−10.3		−16.0		−17				
	−10.5		−16.2		−17				
	−10.1		−16.1		−17				
	−10.3		−12.9[a]		−17				
	−10.6		−16.8		−17				
	−10.6		−16.9		−17				
	−10.7	Apr. 15	−16.2		−17				
	−10.4		−16.6		−17				
	−10.5		−16.5	Apr. 13	−17				
	−10.8		−16.2		−1				
	−10.6		−16.2		−1				
			−16.0		−1				
			−16.2		−1				
			−16.0		−1				
					−1				
					−1				

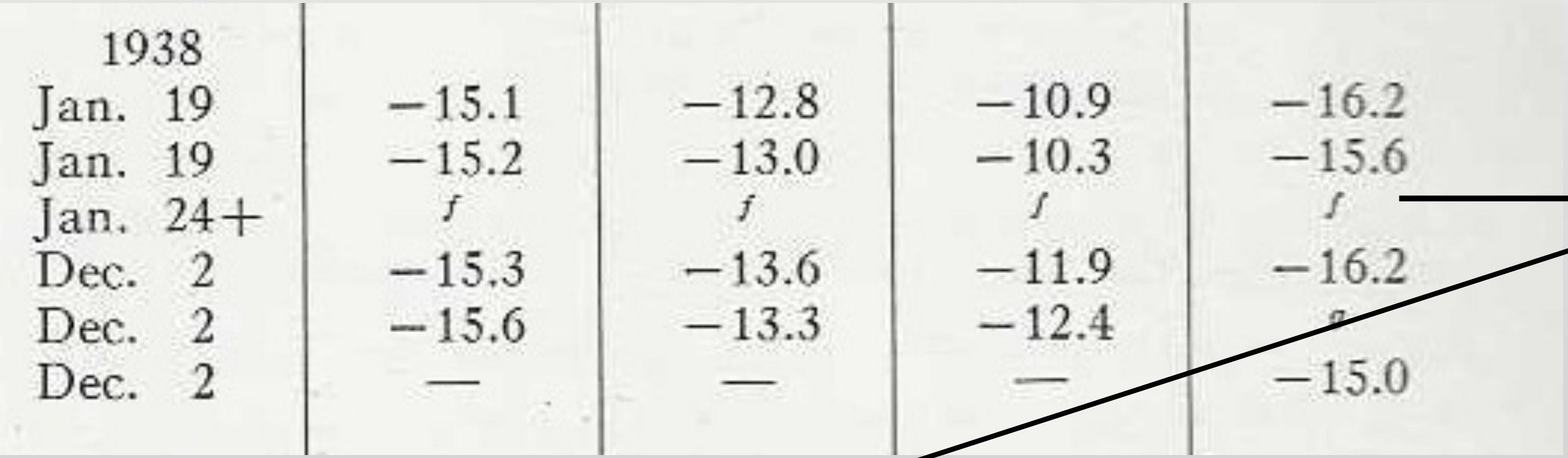
C23 Snow		*C40* Pool		*P25* Dist.	
Date	t	Date	t	Date	t
1937 Feb. 17	−5.8	1937 Mar. 4	−6.0	1943 July 5	−
	−6.0		−6.0		−
	−6.0	Mar. 6	−6.9[b]		−
	−6.0		−6.0	July 6	−
	−7.5[b]	Mar. 8	−6.0		−1
	−6.0		−6.0		−
Feb. 24	−6.1	Mar. 22	−5.6	July 9	−
	−6.1		−6.0		−
Mar. 9	−6.0	Apr. 23	−6.0		−
	−5.9		−6.0	July 16	−
	−6.0				−1
Mar. 22	−6.0				−
	−5.9				
Apr. 22	−5.8				
	−5.9				

[a] *P10*. I cannot account for this high reading.

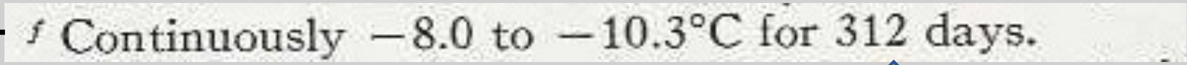
[b] *C23*, *C40*. The temperature of the bath when the bulb was placed in it was below the t_{sf} of the bulb.

[c] *P2*. The water froze within 2½ minutes after the bulb was placed in the −13.0°C bath.

brook:	-10.1 to -10.8	same day
vac. dist.:	-16.0 to -16.9	2 days
vac. dist.:	-17.0 to -17.8	2 days
dIst.:	-6.3 to -7.1	14 days
dist.	-11.6 to -12.2	10 days
snow:	-5.8 to -6.1	63 days
pool:	-5.6 to -6.0	50 days
dist.	-9.5 to -10.1	11 days
cond.:	-13.1 to -13.8	50 days
cond.:	-15.9 to -16.0	48 days

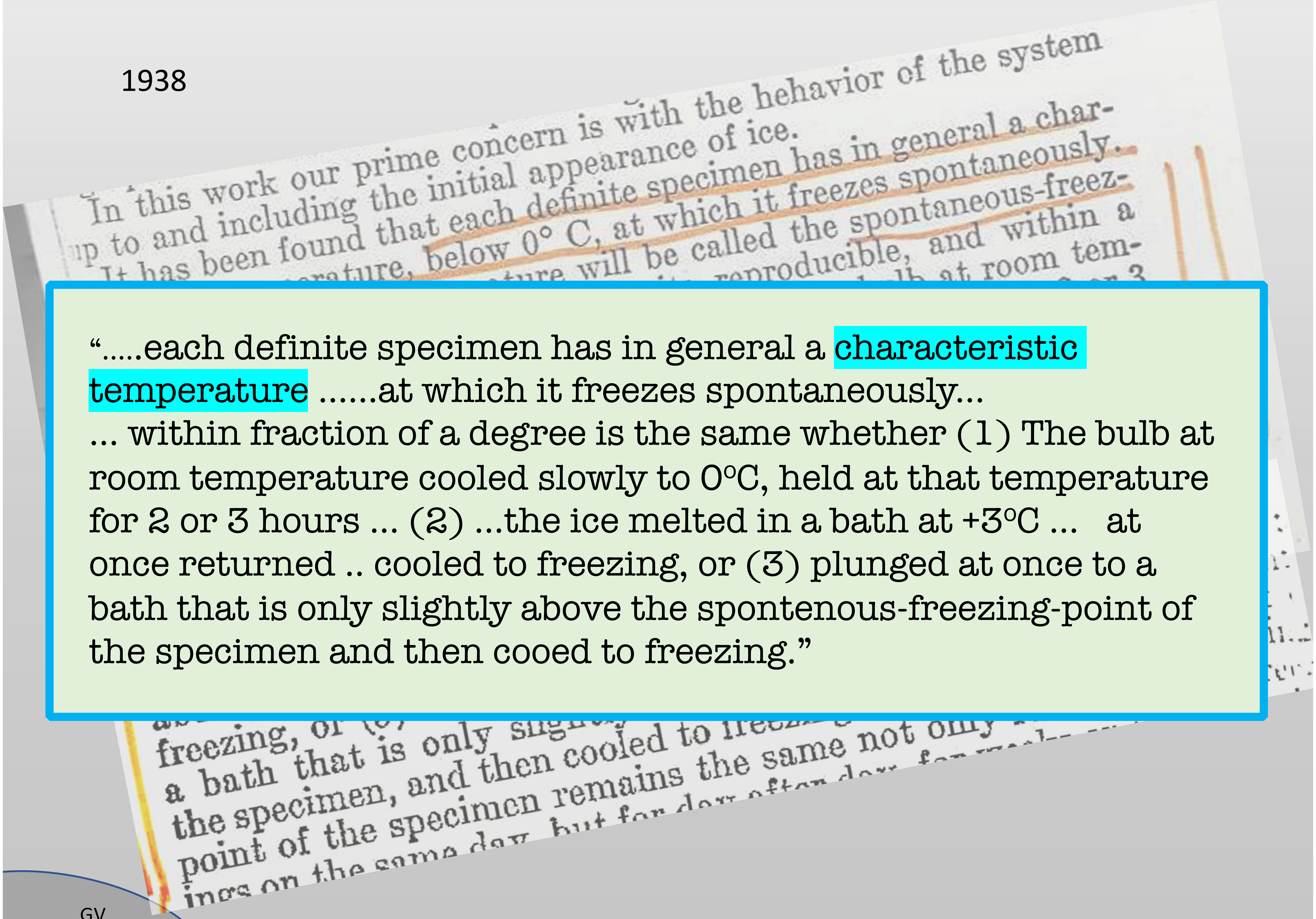


Bulb #	C11	*C*35	*C*49	*P*10
1938				
Jan. 19	−15.1	−12.8	−10.9	−16.2
Jan. 19	−15.2	−13.0	−10.3	−15.6
Jan. 24+	[f]	[f]	[f]	[f]
Dec. 2	−15.3	−13.6	−11.9	−16.2
Dec. 2	−15.6	−13.3	−12.4	[f]
Dec. 2	—	—	—	−15.0



[f] Continuously −8.0 to −10.3°C for 312 days.

1938

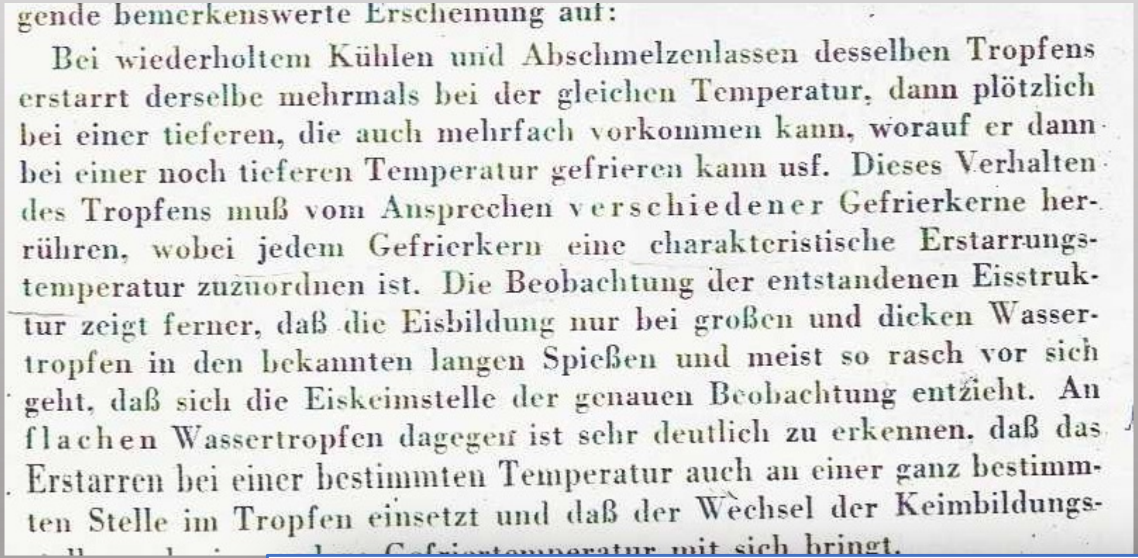


In this work our prime concern is with the behavior of the system
p to and including the initial appearance of ice.
It has been found that each definite specimen has in general a char-
erature, below 0° C, at which it freezes spontaneously.
ture will be called the spontaneous-freez-
reproducible, and within a
ulb at room tem-

freezing, or (
a bath that is only sligh
the specimen, and then cooled to freez
point of the specimen remains the same not only
ings on the same day, but for day after day

"…..each definite specimen has in general a characteristic temperature ……at which it freezes spontaneously…
… within fraction of a degree is the same whether (1) The bulb at room temperature cooled slowly to 0°C, held at that temperature for 2 or 3 hours … (2) …the ice melted in a bath at +3°C … at once returned .. cooled to freezing, or (3) plunged at once to a bath that is only slightly above the spontenous-freezing-point of the specimen and then cooed to freezing."

W. Rau, 1944 Schriften deutsche. Akad. Luftfahrforsch. 8, 65-84



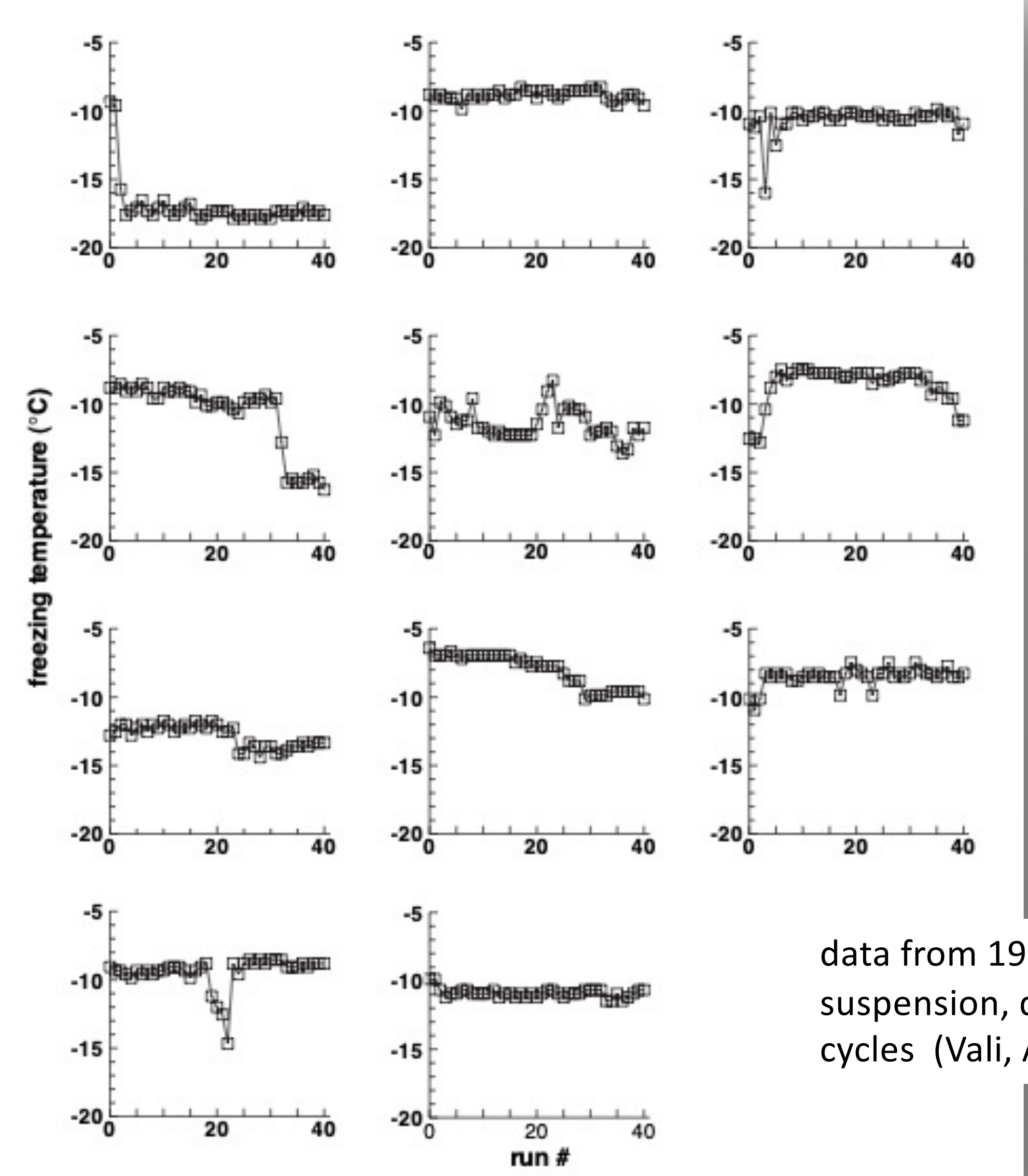
gende bemerkenswerte Erscheinung auf:

Bei wiederholtem Kühlen und Abschmelzenlassen desselben Tropfens erstarrt derselbe mehrmals bei der gleichen Temperatur, dann plötzlich bei einer tieferen, die auch mehrfach vorkommen kann, worauf er dann bei einer noch tieferen Temperatur gefrieren kann usf. Dieses Verhalten des Tropfens muß vom Ansprechen verschiedener Gefrierkerne herrühren, wobei jedem Gefrierkern eine charakteristische Erstarrungstemperatur zuzuordnen ist. Die Beobachtung der entstandenen Eisstruktur zeigt ferner, daß die Eisbildung nur bei großen und dicken Wassertropfen in den bekannten langen Spießen und meist so rasch vor sich geht, daß sich die Eiskeimstelle der genauen Beobachtung entzieht. An flachen Wassertropfen dagegen ist sehr deutlich zu erkennen, daß das Erstarren bei einer bestimmten Temperatur auch an einer ganz bestimmten Stelle im Tropfen einsetzt und daß der Wechsel der Keimbildungs-

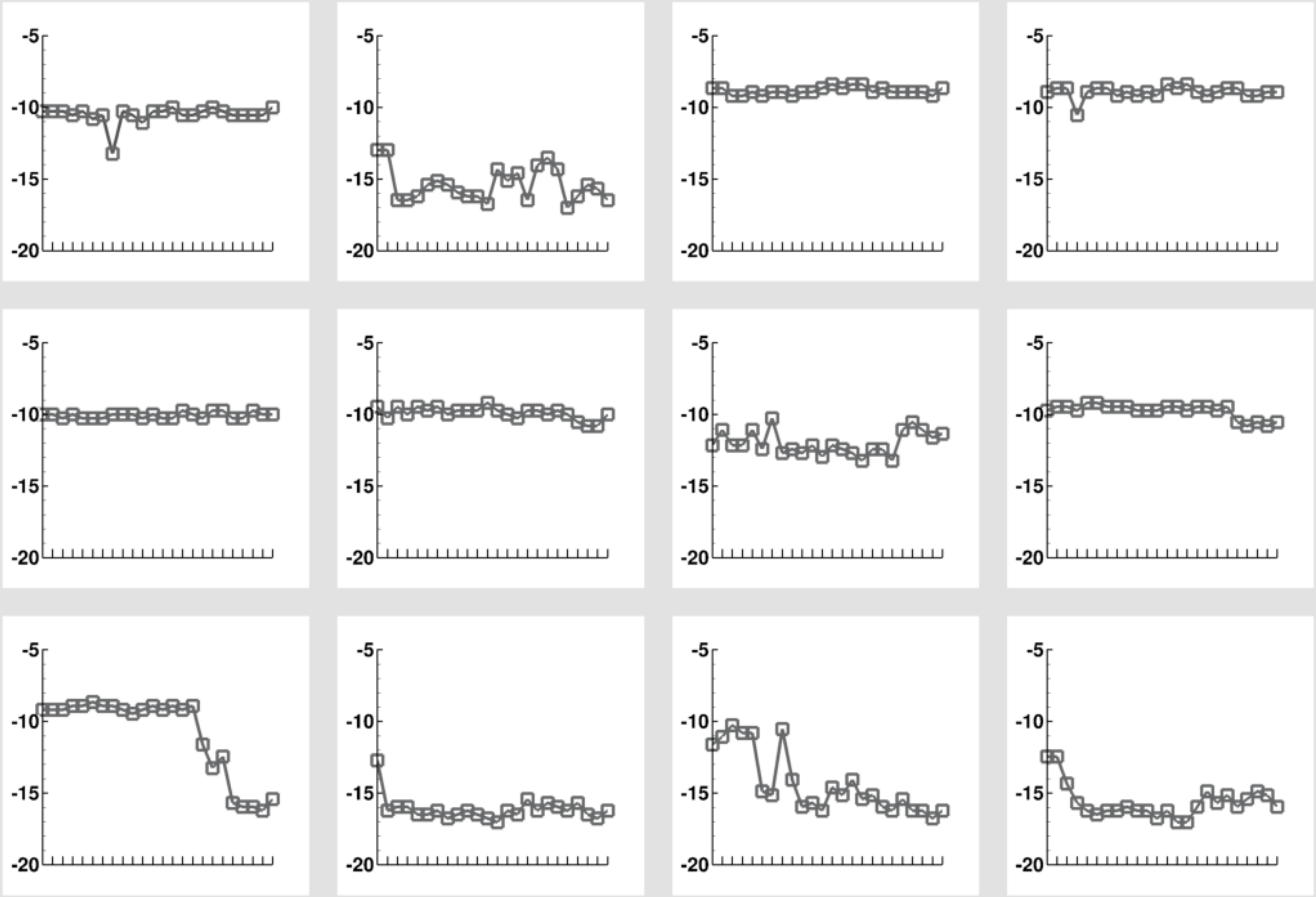
Gefriertemperatur mit sich bringt.

With reapeted cooling and melting, given drops frequently <u>freeze at the same temperature</u>, then suddenly at a lower one which also can be repeated several times, then to a yet lower freezing temperature, and so on. This behavior of the drops must arise from various Gefrierkerne, with each Gefrierkerne having a ***characteristic freezing temperature***.

More evidence for repeated freezing temperatures:



data from 1967 experiment with soil suspension, drop array; repeated cooling cycles (Vali, ACP 2008)



selection from the 56 drops frozen at –13°C in run 19, aug 22-24/67 experiment

runs 19-42; drops 24 - 35 of the ttcv subset

drop_seq2.bmp 17 Dec 2023

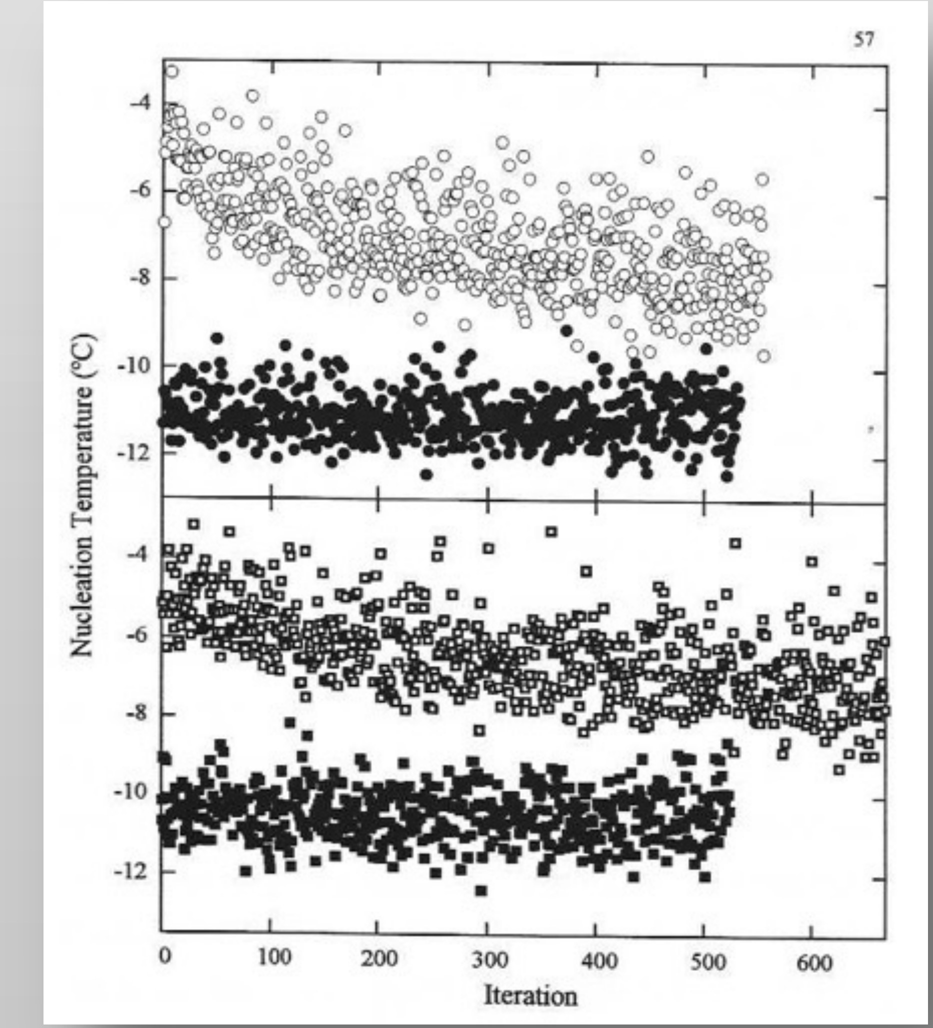
More re-freezing experiments:

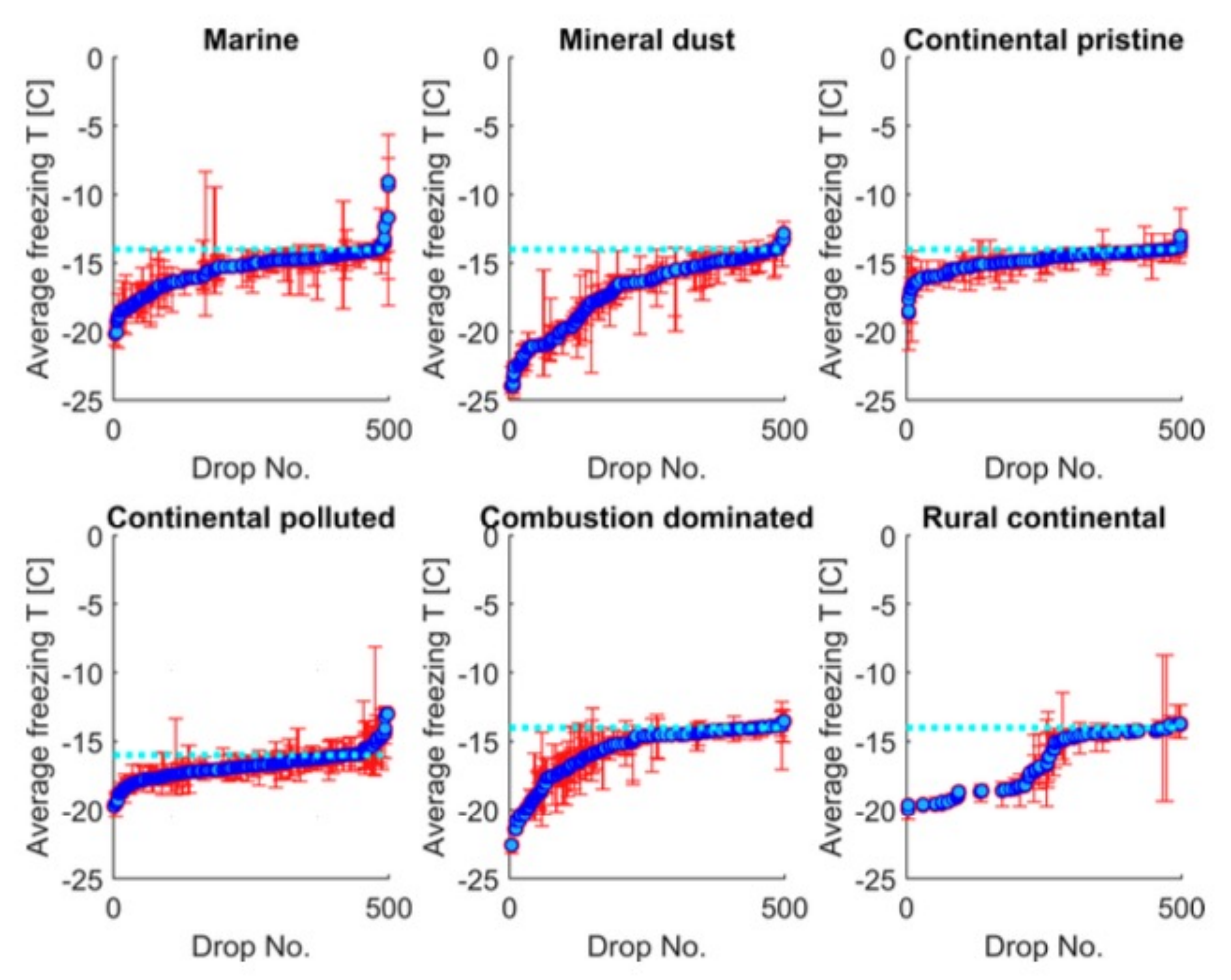
Brewer and Palmer, 1951
Bayardelle, 1954 Carte, 1956
Roulleau, 1957 Salt, 1966
Salt, 1966 Levkov and Genadiev, 1966
Seeley and Seidler, 2001
Henegahn et al, 2002, Shaw et al., 2005
Zobrist et al., 2007, Vali, 2008, Fornea et al. 2009
Hoyle et al. 2011 Pinti et al., 2012
Wright and Petters, 2013
Kaufmann et al. 2027 Jakobsson et al., 2022

Run-to-run variations of about 1^{o}C; much less than spread in temperatures over set of drops. Occasional other changes

Seeley, 2001 PhD dissertation

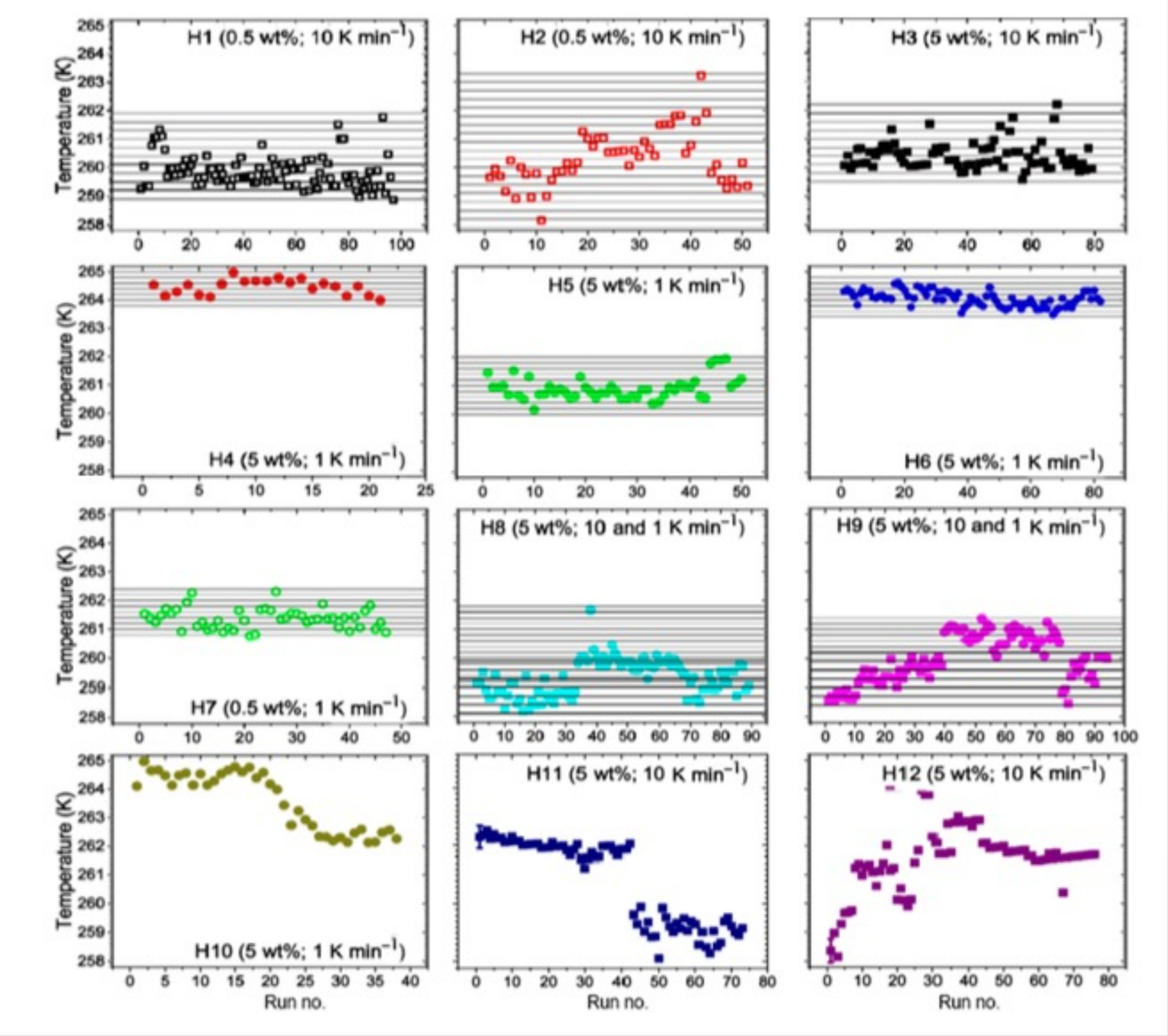
alcohol monolayers on single drop; cooling cycles





Jakobsson et al. 2022 Constant cooling rate exp.

Temperature ranges for individual drops: 0.53-0.93 K in samples with spread of 8 to 12 K among drops



Kaufmann et al., 2017

A single particle in a drop; repeated cycles of freezing.
Fornea et al. 2009

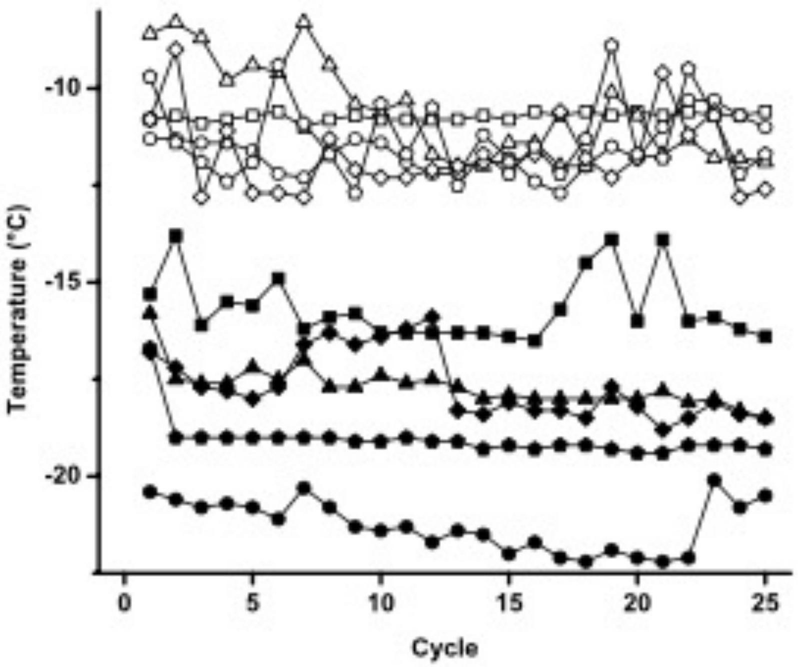


Figure 5. Observed freezing temperatures are shown for immersion (solid symbols) and contact freezing experiments (open symbols) on volcanic ash. Each data series represents measurements conducted using a unique ash particle.

it can be this reproducible

The five ash particles show different preferred freezing temperatures. The best site on each particle is detected.

1. Why would given drops freeze repeatedly at the same temperature, when other drops with INPs of the same origin freeze at varying temperatures over a large range?
2. Why would freezing occur at the same temperature on a particle that is infinitely larger than the critical embryo?

CNT based answer(s):

Drops contain different amount of the substrate.

Variations in the composition of the substrate.

Many locations on the surface can serve for embyro to grow on

Random effects.

1. Why would given drops freeze repeatedly at the same temperature, when other drops with INPs of the same origin freeze at varying temperatures over a large range?

2. Why would freezing occur at the same temperature on a particle that is infinitely larger than the critical embryo?

Add: The probability of chance repetition of the kind observed is minimal without something very specific on the INP involved for the embryo to form on.

A plausible answer:

INPs with different active sites are allocated to different drops.

Most active INP in each drop has unique site on it.

Repetition demonstrates that active sites have remarkable resistance to lapse of time time, ice formation, dissolution, adherence of other molecules, ...

Repetition within small temperature range shown specific interaction energy with embryo.

But, reproducibility is not total.

"Sites versus surfaces" - Vali 2008 and 2014 in ACP

What are sites? cf. Molinero, Virtual INP Colloguium, Feb 03 2022

* Direct (approximate) observations:

Surface features on minerals: Whale et al., 2017; Holden et al. 2019 !!!
Controlled pore size: Nandy, Fenton and Freedman
Aggregates of lipoglycoprotein complexes: Lindow, Kozloff
Promoter region, cell-free INPs <0.2 um: Tegos et al., 2000
Cell membrane around site: Schwidetzky et al 2021a; Lukas et al. 2022
Aggregate size: Qiu, Hudait and Molinero, 2019
ESEM (promise): Pach and Verdauger, 2019, 2022

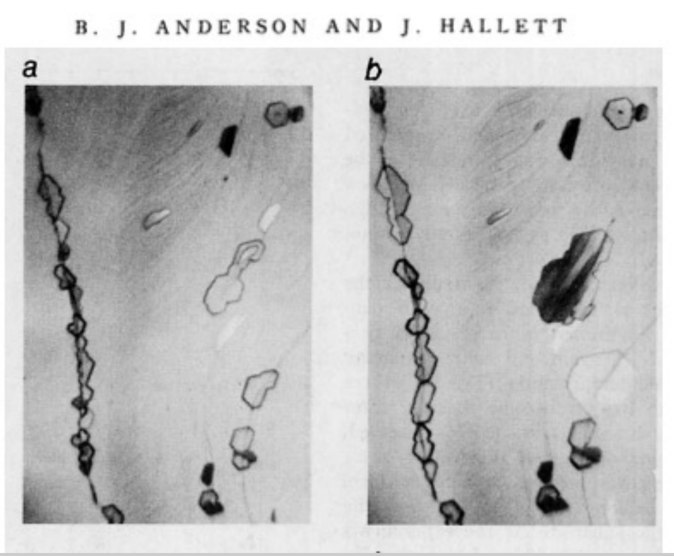
how permanent are these ????

* Surfaces: Numerous studies of surface characteristics vs. nucleating ability

how do these relate to specific sites ?

Direct observartions of active sites

deposition nucleation


B. J. ANDERSON AND J. HALLETT

1976

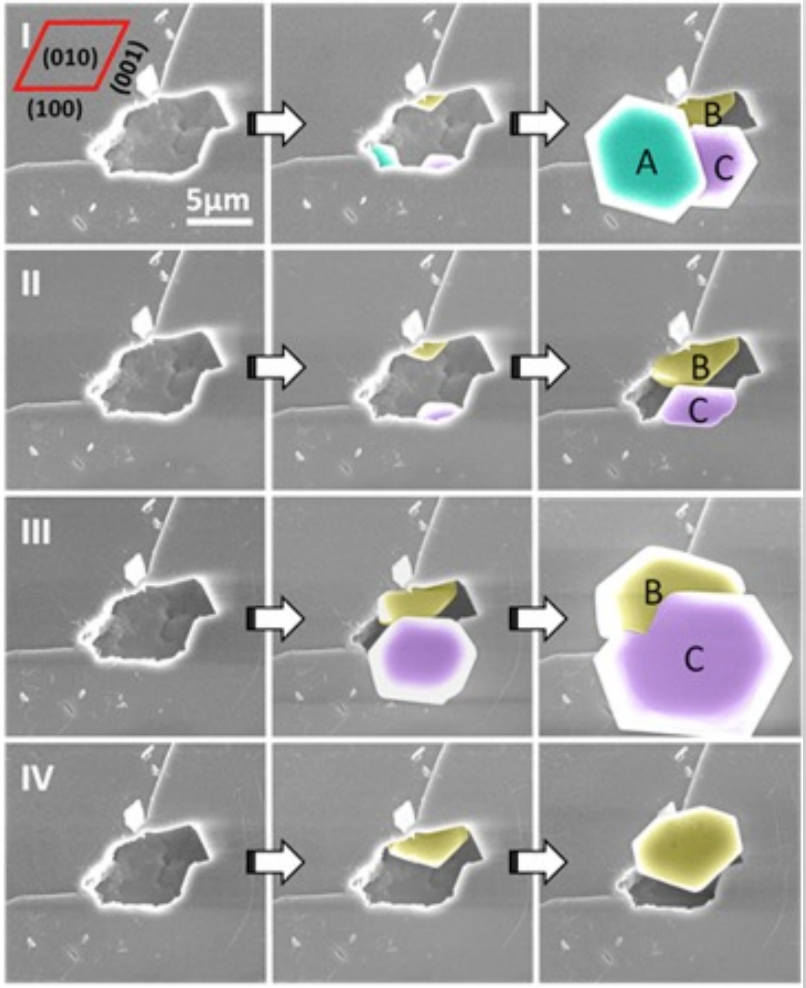
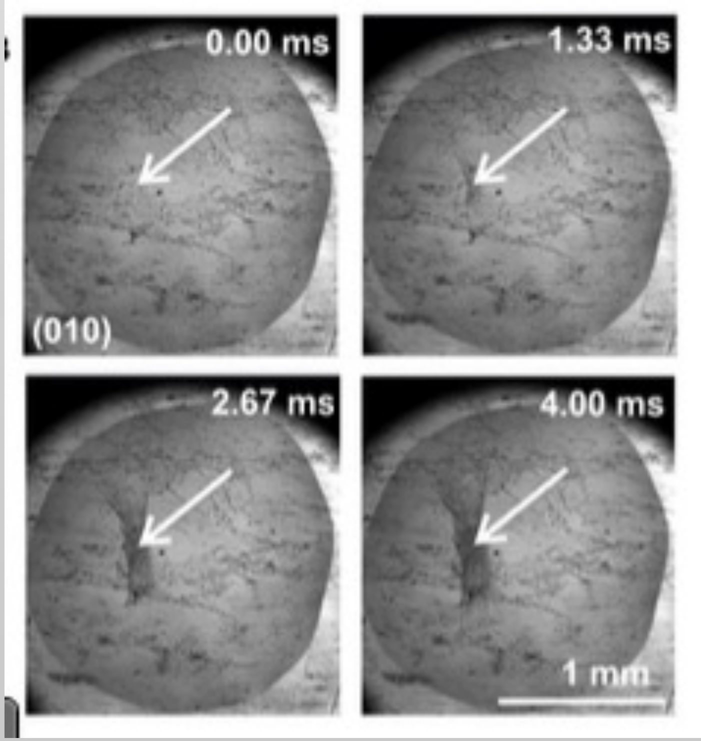


Figure 6. ESEM images of four nucleation cycles (I–IV) from a single pore

Pach and Verdaguer, 2019, 2022

Direct observartions of active sites

freezing nucleation



Holden et al. 2019

Time dependence

examined via varying the cooling rate or by holding a set of drops at a fixed temperarture.

Vonnegut, 1948 – const. T with many separate sample drops
Vali, 1966 – const. T with multiple separate sample drops
Vonnegut and Baldwin, 1984 – multiple freezes of same sample
Wang and Vonnegut, 1984 - multiple freezes of same sample
Heneghan et al., 2001 - multiple freezes of same sample
Wright and Petters, 2013

MORE

All these results refer to populations of drops and/or drops with multiple partilces suspended.

There is NO data on time to freeze on given site.

B

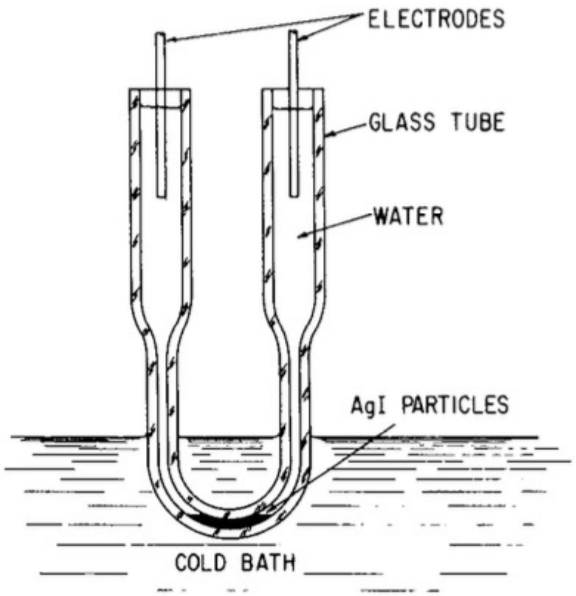
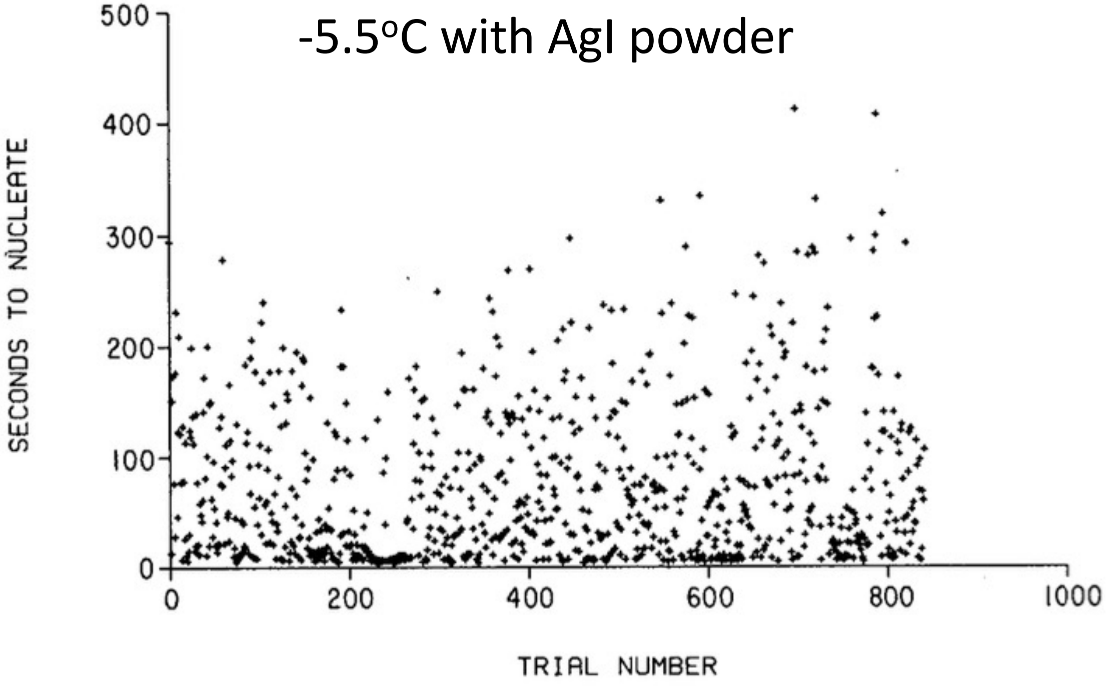


FIG. 1. Schematic diagram of glass capillary U-tube used fo experiments. The glass capillary tube is approximately 0. diameter, and is submerged to a depth of 10 mm.

Vonnegut and Baldwin, 1984

J. Clim. Appl. Meteor., 23, 486-490



-5.5^{o}C with AgI powder

FIG. 2. Time intervals that elapsed before nucleation took place at −5.5°C.

Vonnegut, 1948
(dilatometer)

BERNARD VONNEGUT

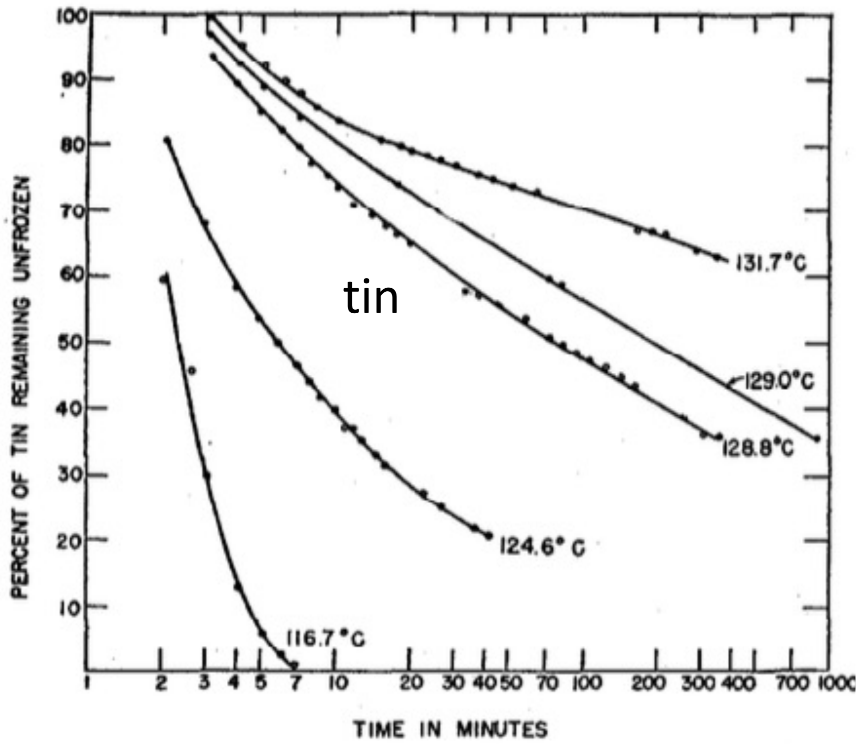


FIG. 3. Fraction of tin drops remaining unfrozen as a functi
of time from dilatometer data.

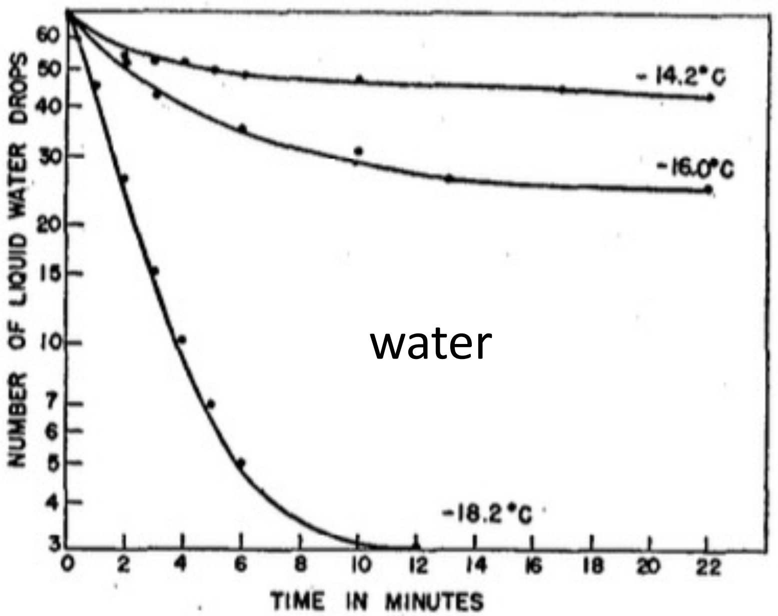


FIG. 5. Fraction of water drops remaining unfrozen as a function of time.

rate slows down with time, many drops remain unfrozen

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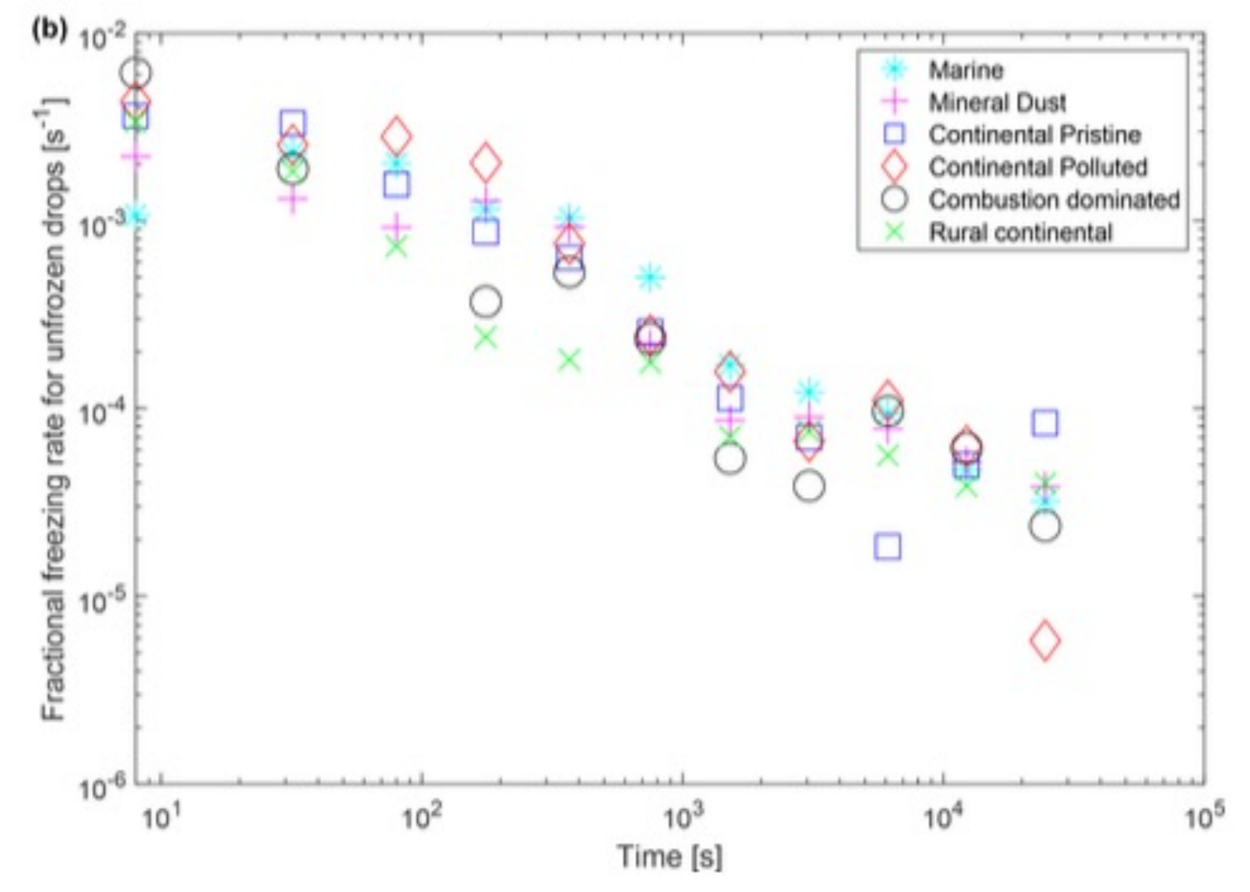
Apr. 11, 2024

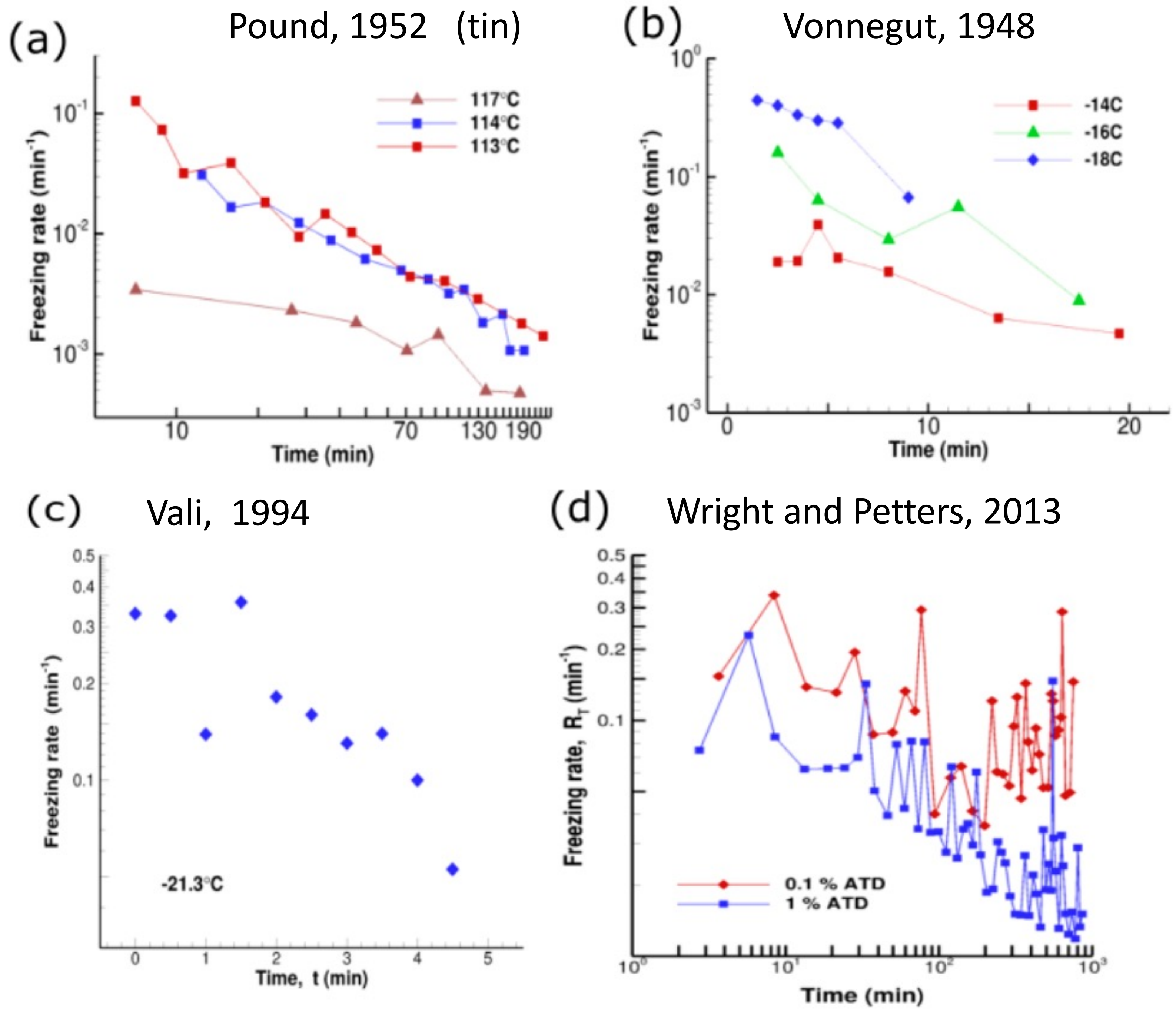


Jakobsson et al. 2022 Constant temperature exp.

→ Freezing rate decreases with time

GV
Apr. 11, 2024

GV comment; https://doi.org/10.5194/acp-2021-830-CC1


(a) Pound, 1952 (tin)

(b) Vonnegut, 1948

(c) Vali, 1994

(d) Wright and Petters, 2013

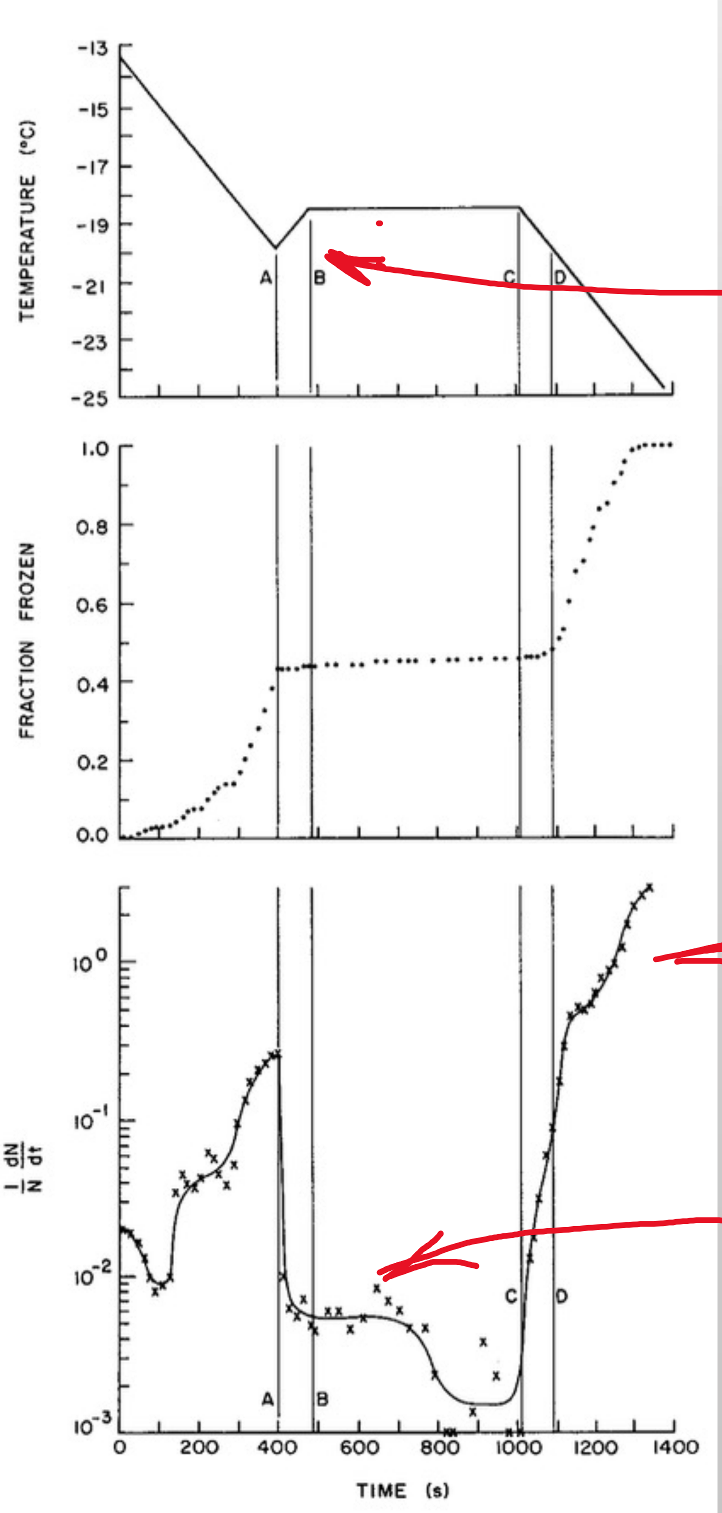
At a constant temperature the number of freezing events decreases exponentially with time.

Inconsistent with CNT-based explanations.

In terms of VS66 model, this reflects the long tail of the probability for freezing to occur at temperature above the characteristic temperature, with the probability distribution resulting from a nucleation rate function associated with each site, $j_x(T)$.

But, there is no data on the time to freeze on given site.

Vali, 1994

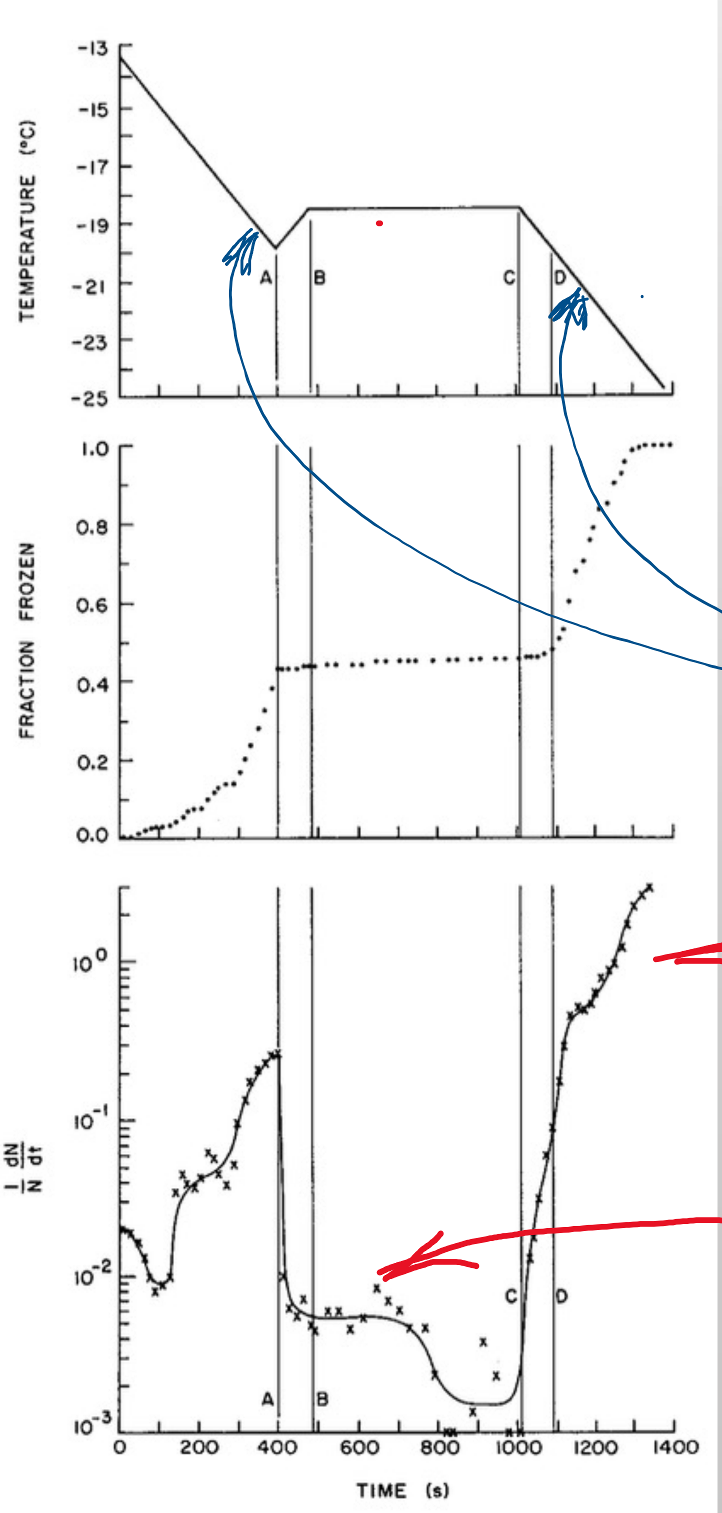


overshoot in cooling followed by constant temperature

freezing rate goes to zero for 10 minutes at -19°C with 60% of sample unfrozen

then pick up when cooling is resumed

Vali, 1994



overshoot in cooling followed
by constant temperature

points to qualitative difference in nucleating probablity between drops freezing with only 1-2°C difference; different INP

freezing rate goes to zero
for 10 minutes at -19°C
with 60% of sample unfrozen

then pick up when cooling is
resumed

Consistent with the VS66 explanation:

The temperature overshoot pre-empts events that would otherwise occur if the temperature were held constant. A good indicator for the relevant range (width) of $j_x(T)$.

Site nucleation rate, $j_x(T)$

An expression of the probability of nucleation per unit time near the characteristic temperature T^c for site x.

Expect the temperature dependence of $j_x(T)$ to be something similar to the homogeneous nucleation rate and reasonable fit to CNT.

First notion:

Vali, 1964, M.Sc. thesis, McGill U.
Vali and Stansbury, 1966 Can. J. Phys.

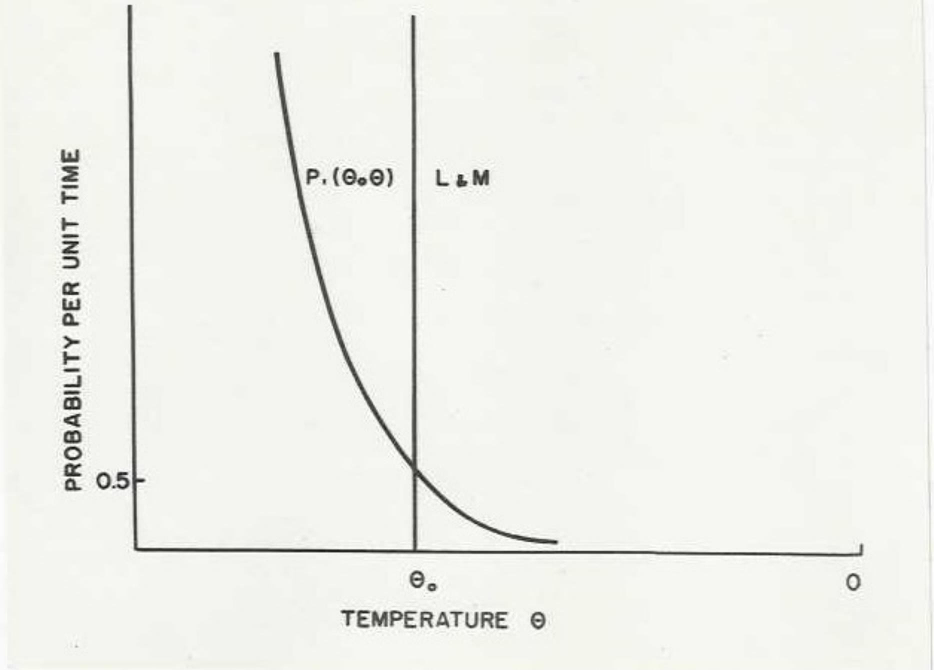


Fig. 27

int further.

Since the explicit form of $P_1(\Theta_0, \Theta)$ is not known (it wi

Vali, 1964, M.Sc. thesis, McGill U.
Vali and Stansbury, 1966 Can. J. Phys.

first notion:

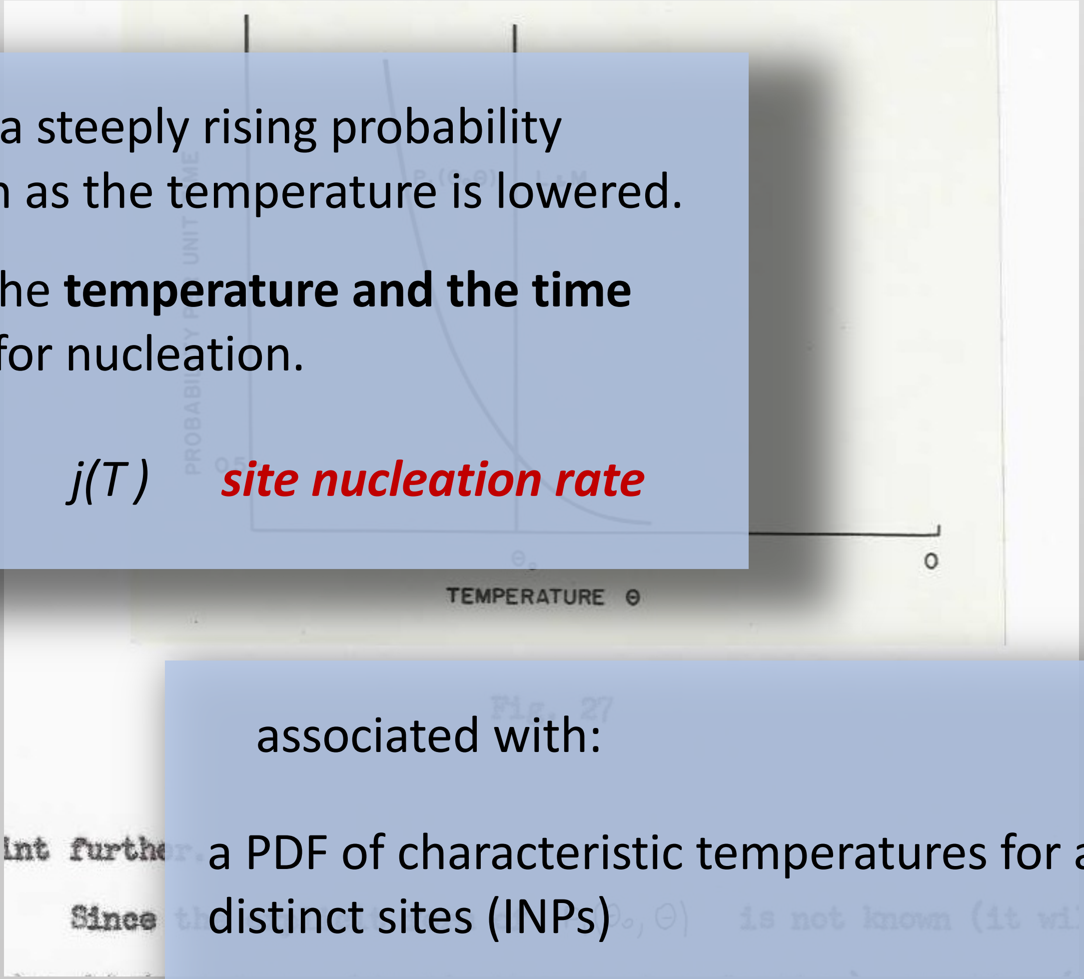


Fig. 27

int further.

Since th … (θ_o, Θ) is not known (it wi

Each site has a steeply rising probability for nucleation as the temperature is lowered.

This defines the **temperature and the time** dependence for nucleation.

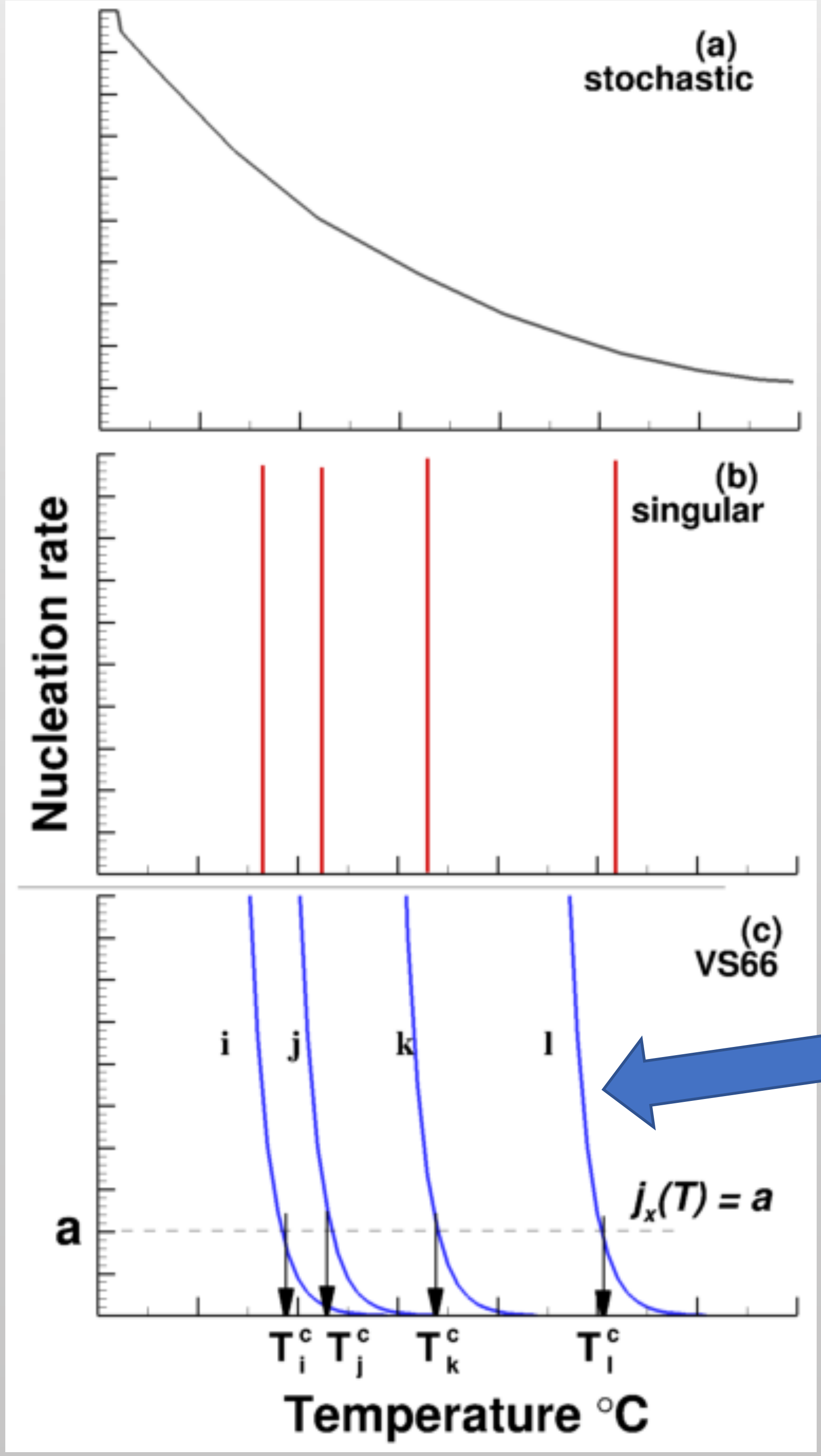
$P_1(\theta_o\theta)$ *j(T)* ***site nucleation rate***

associated with:

a PDF of characteristic temperatures for a population of distinct sites (INPs)

GV
Apr. 11, 2024

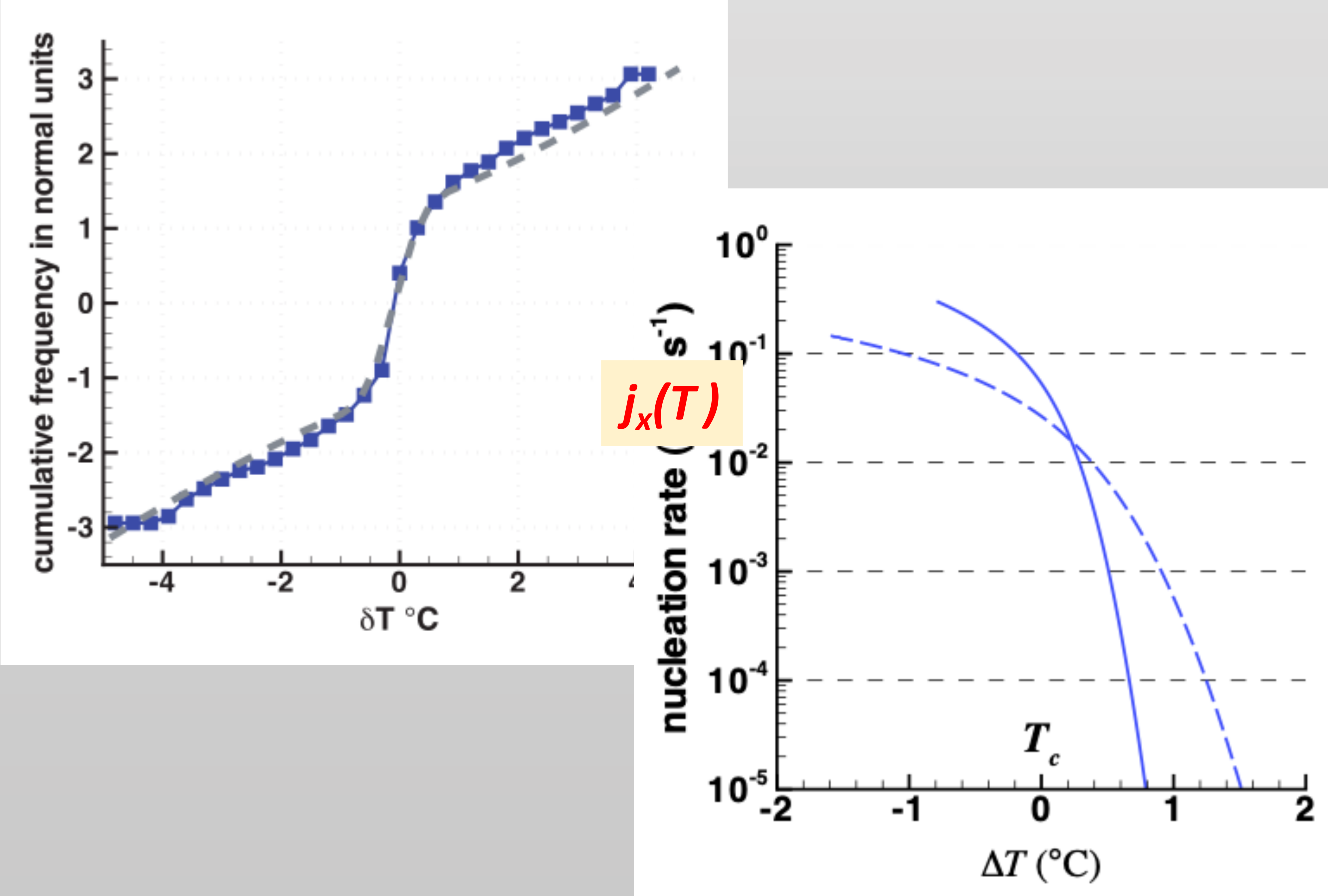
VS66 model



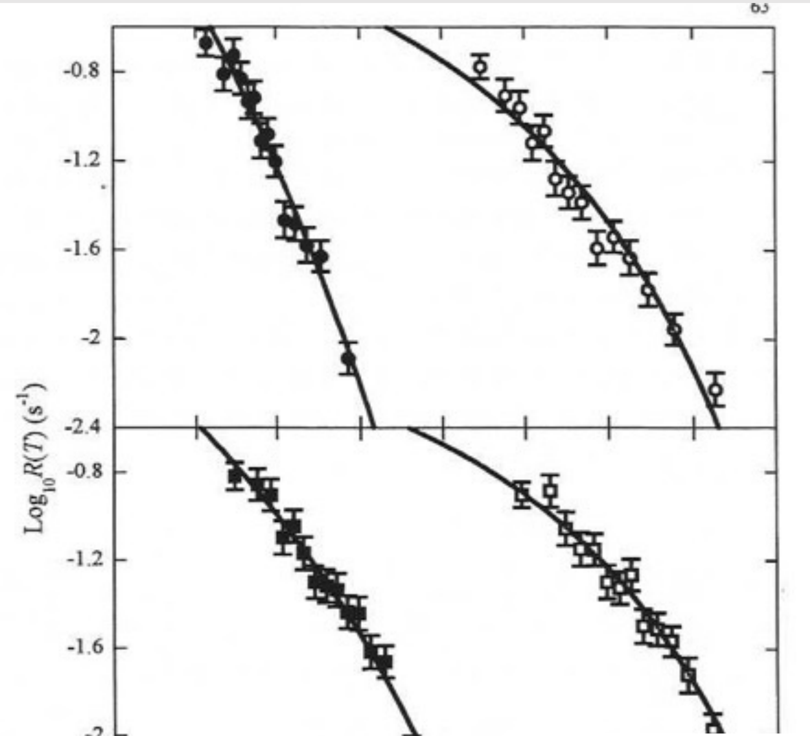
Characteristic temperature, $\mathbf{T^c}$
Site nucleation rate, $j_x(T)$

Vali 2014 in ACP

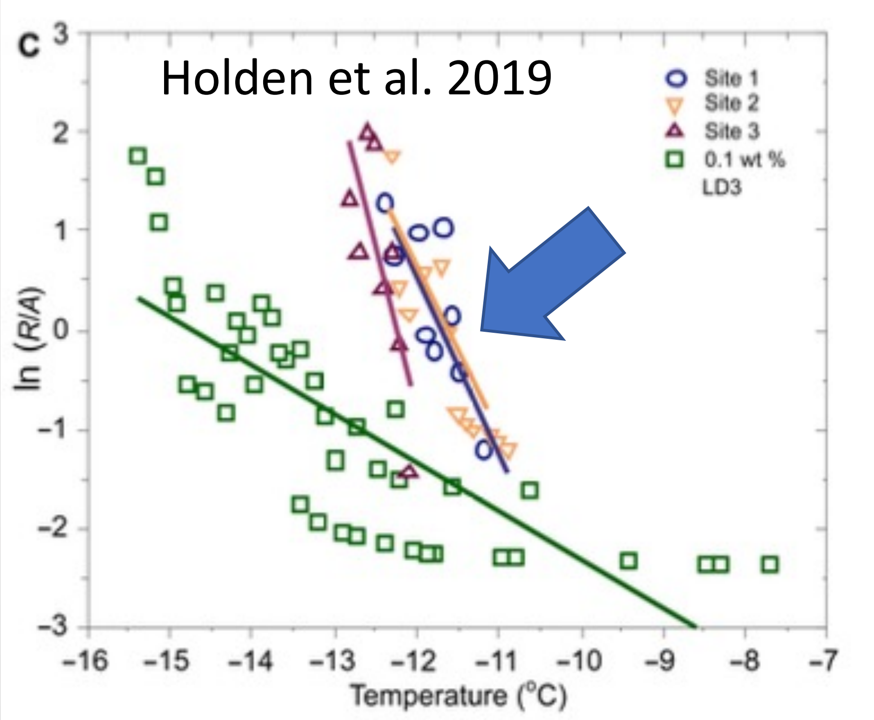
Vali (2008): An attempt to determine ***$j_x(T)$*** from repeated freezing data. Assumes that the PDF of freezing temperature fluctuations (not distinct changes) derive from the stochastic variation resulting from ***$j_x(T)$*** for the cooling rate applied.



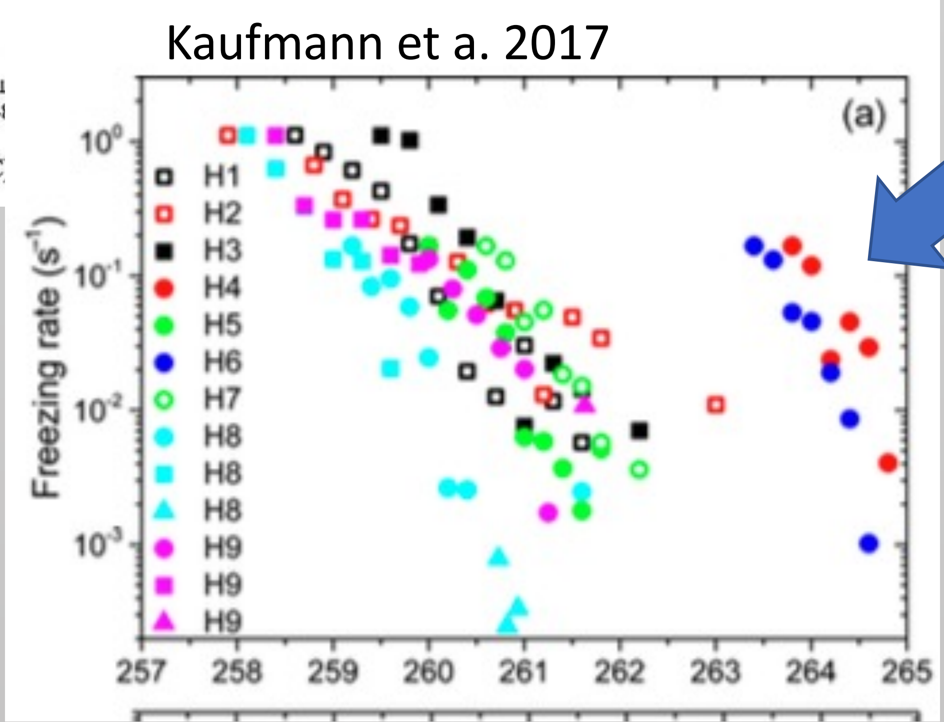
form is tentative; rise of 10^4 in ~2°C is about right.



Seeley, 2001



Holden et al. 2019



Kaufmann et a. 2017

My view (1):

Sites of particular surface configurations lead to nucleation at some corresponding temperature.

The high specificity of sites (characteristic temperature) is amazing when one thinks of the large number of molecules forming critical embryo and the large site area on the molecular scale required to anchor it.

Fundamental questions about heterogeneous ice nucleation:

1. how abundant sites are for given substances/materials,
2. what consitututes the sites on different substrates and for different T^c values
3. how can $j_x(T)$ be related to the morphologies of different sites

Much is, and will be, learned about 1 and 2 from direct observations and from molecular simulations. Yet, it will be very difficult to incorporate the answers into weather and climate models, or predictions of plant and animal freeze resistance. Artificial enhancement of sites may become possible.

Question 3 may not be important for most purposes, due to time dependence being minor, but, it is a basic question for fuller understanding of heterogeneous ice nucleation.

My view (2):

- we know what materials are effective ice nucleators
- we know which surfaces are more effective
- we know that preferred locations, sites, exist on surfaces of ice nucleators
- we have some ideas of what the sites ar

$j_x(T)$ may be determined from theory or molecular simulation after structure of sites is determined in sufficient detail

in the meantime, resort to use of empirically determined R, K or k, elaborated as needed with physico-chemical information

Limitations to the site and site nucleation rate concepts :

- may not applicable to dissolved macromolecules, monolayers, ….
- changes arising from:
  - re-arrangement of the site
  - destruction by freezing
  - dissolution
  - adherence of other materials

Modeling options:

For a closed system (drops with suspended INPs):

- With gradually lowering temperatures, the use of the singular model is a good approximation. Use of R(T), k(T) and K(T) provide adequate prediction of freezing.
- For little more precision or if periods with constant temperature intervals are invoved, the TDFR model (Vali and Snider, 2015) is a good start.

For atmospheric clouds (open systems), the description of INP content is an aerosol-cloud interaction problem, with source, abundance and transfer issues, all bound up with cloud dynamics. Beyond that, the tools for closed systems work.