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Atmospheric Chemistry and Physics

25 August 2020

RE: revised manuscript acp-2020-537


Dear Daniel,

Attached please find the revised version of the manuscript titled: “Review of experimental studies of secondary ice production” by Alexei Korolev and Thomas Leisner along with the point-by-point replies to the reviewers’ comments.

We are looking forward to seeing your decision.

Sincerely,

Alexei Korolev,
Research Scientist
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Replies to the reviewer's comments (Andrew Heymsfield) on "Review of experimental studies on secondary ice production" by A. Korolev and T. Leisner

From Authors: The authors appreciate the reviewer's time spent to read the paper and provide a diligent review. We found the comments very helpful in improving the manuscript. Below are point-by-point replies to the comments.

This is an excellent review article of a process that is very important for precipitation development, Secondary Ice Production (SIP). Based on observations I've made and those reported on by others, the process is particularly important when 1) cloud top temperatures are relatively warm, 2) there are relative few but some ice nuclei active at the cloud temperatures, 3) the cloud droplet sizes are relatively large, and the updraft velocities, although present, and not too strong, one to a few meters per second. SIP is therefore likely to be most active and important over relatively warm oceanic areas. Although several SIP mechanisms have been proposed, it is unclear when specific ones are active and under what conditions they occur.

This article discusses the pluses and minuses of the following SIP that have been proposed: (1) shattering during droplet freezing; (2) the rime splintering (Hallett-Mossop) process; (3) fragmentation due to ice-ice collision; (4) ice particle fragmentation due to thermal shock; (5) fragmentation of sublimating ice; and (6) activation of ice nucleating particles in transient supersaturation around freezing drops. The article focuses on laboratory studies, although some field observations are presented. Obviously, laboratory studies benefit from the ability to repeat experiments and narrow down possible processes by modifying the experiments appropriately.

I have relatively few comments because the article is very well written and extremely thorough.

Line 34: Schaefer

Reply: Corrected.

Line 59: "shattering" to "fragmentation"

Reply: Corrected.

Section 2.2, Eqs. (1) and (2), Freezing Fraction. Shouldn't ventilation enter into this discussion? It is factored into Eq. (3).

Reply: The ventilation factor in Eq.1 is included in the term ΔQ which describes the heat loss due to thermal exchange with the environment. Due to a very short duration of the recalescence stage ($10^{-5}\text{s} < t_1 < 10^{-1}\text{s}$ depending on D and ΔT) the thermal exchange between the surrounding environment and droplet is much smaller compared to the energy of the latent heat released during freezing. Accurate assessment of ΔQ suggests that it is much smaller other terms in Eq.1 and it is usually neglected. Eq.3 employs $u(T)$ obtained from experimental measurements. As before the due to a very short time of the recalescence stage the effect of ventilation in calculation of t_1 is neglected.

Section 2.7, Fragmentation during freezing. A table summarizing your discussion of shattering during drop/droplet freezing would be very helpful.

Reply: Table 1 summarizing shattering during drop/droplet freezing was added in the text following the reviewer's comment. In addition, we also added Table 2 summarizing laboratory results of the studies of the HM-process.

Table 1. Summary of experimental studies of droplet fragmentation during freezing by different research groups. The table covers only works that quantified the parameters included in the table.

Reference	Diameter (mm)	Temperature (°C)	Droplet suspension	Method of nucleation	Maximum SIP frequency (%)	max number fragments per drop	Temperature of maximum SIP rate
Mason and Maybank, 1960	30-1000	-2 to -25 ¹	stagnant (fiber)	various ²	47	200	-10C
Adkins, 1960	4-13	n/a ³	free fall	natural ⁴	0	0	n/a
Hobbs and Alkezweeny, 1968	20-150	-8 to -32	free fall	various ⁵	>5	n/a	no temperature dependence
Brownscombe and Thorndike, 1968	50-90	-5, -10, -15	free fall	tiny ice crystals	14	12	-15°C
Dye and Hobbs, 1968	1000	-3 to -15	stagnant (fiber)	tiny ice crystals	0	1	no temperature dependence
Johnson and Hallett, 1968	1000	-5 to -20	stagnant (fiber) +ventilation	tiny ice crystals	>1	n/a	no temperature dependence
Takahashi and Yamashita, 1969	600-800	-18 to -25	free fall	immersion ⁶	11	n/a	-15°C
Takahashi and Yamashita, 1970	75-350	0 to -30	free fall	tiny ice crystals	37	n/a	-15°C
Takahashi, 1975	45-765	-4 to -24	free fall	tiny ice crystals	35	n/a	-16°C
Pruppacher and Schlamp, 1975	410	-7 to -23	airflow	contact ⁷	15	>3	-11°C to -15°C
Bader et al., 1974	30, 42, 84 ⁸	-10 to -30	free fall	immersion ⁹	?	10	n/a
Kolomeychuk et al., 1975	1600	-12 to -25	airflow ¹⁰	natural ⁴	35	142	-15°C to -18°C
Lauber et al., 2018	300 -320	-5 to -30	stagnant (EDB)	tiny ice crystals	35	12	-7C to -13C
Keinert et al., 2020	300- 320	-1 to-30	stagnant (EDB), airflow	tiny ice crystals	1	3	-10C to -15C

1. ice nucleation temperature 0°C to -15°C
2. natural nucleation, silver iodide, contact tiny small ice crystals
3. not available
4. no special efforts were made to nucleate droplets
5. natural or immersed silver iodide
6. kaolinite or silver iodide
7. kaolinite or montmorillonite
8. mean volume diameter
9. silver iodide
10. flow of humidified nitrogen

Line 445: During the freezing process, the surface of the droplet is sublimating, perhaps affecting the fragmentation process.

5 **Reply:** The referee is right, roughly 1 % of the droplet mass evaporate per 1K of initial supercooling. This is a small amount and most of this evaporation occurs during the early stages of the second freezing process (Keinert et al. 2020), while the SIP processes occur during the later stages of the second freezing process. It seems, that it is unlikely that evaporation will affect SIP much, and therefore, we do not discuss it in the manuscript.

10 Line 649: undersaturated>subsaturated.
Reply: Corrected.

15 Line 732 "bigger" to "larger".
Reply: Corrected.

Line 783: the existence of shattering.
Reply: Corrected.

20 Line 824: concentration.
Reply: Corrected.

25 Line 825: You could mention the airborne studies of Mossop and Bigg and the use of balloon borne replicators, etc that can shed light on the problem. Many other airborne studies (Heymsfield and Willis, Lawson et al., Lasher-Trapp etc are directed towards the SIP problem. At the beginning of this section, re-emphasize that this review article is mostly directed towards laboratory and theoretical studies.

Reply: Several early Mossop's airborne studies (1970, 1972, 1985) were referenced in the introduction. The references on the studies of Heymsfield and Willis, Lawson et al., Lasher-Trapp et al. were provided in the concluding section to address the reviewer's comment.

30 The Bigg (1996) studied IFNs in Arctic clouds. There is a brief mentioning of SIP among other possible reasons to explain one of the observations of discrepancy between ice particle and IFN concentrations. This does not provide strong evidences of SIP compared to the early studies, such as that by Koenig, Hobbs, Mossop, and others mentioned in the introduction. The authors consider that referencing of the Bigg (1996) study would be destructive as not directly relevant to this study.

35 At the beginning of the section 9 the following text was added to address the reviewer's comment regarding laboratory studies:

"In this section we discuss results of experimental studies of artificial fragmentation of ice particles during in-situ sampling."

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Replies to the reviewer's comments (Raymond Shaw) on "Review of experimental studies on secondary ice production" by A. Korolev and T. Leisner

55 **From Authors:** The authors appreciate the reviewer's time spent to read the paper and provide a diligent review. We found the comments very helpful in improving the manuscript. Below are point-by-point replies to the comments.

60 This review article fills an important void in the atmospheric chemistry and physics literature by aggregating and synthesizing the broad range of literature relevant to secondary ice production in clouds. The article is thorough in its review of the literature and is helpful in going beyond merely reporting prior results, but placing them within the context of the full body of work and the current understanding. I had two personal impressions while reading the review. First, we as a community have strayed too far from our roots, and while there is some excellent laboratory work still taking place, it is disproportionately small compared to the vast efforts currently focused on field and computational work. I agree with the authors' perhaps provocative statement that laboratory work cannot be replaced by field work if we hope to achieve physically-based understanding and parameterization of SIP processes. Rather, these efforts need to take place hand in hand. Second, there is clear value in bringing all of the relevant experimental results together for a cohesive review, with the result being much more impactful than simply the sum of individual studies. Meaningful theoretical progress rests on the observations from these collective experiments. To put it another way, taking

65 electromagnetism as an example, there would have been no Maxwell without a Faraday. I hope these impressions come through clearly to other readers of this review. I would go so far as to say that the authors should take the liberty of editorializing somewhat more along these lines in the Concluding Remarks section; that is their prerogative, though, and I only share it as my opinion. In any case, I consider this to be a well written and important contribution that will help in providing a deeper understanding of what we know about SIP, and motivation for further work on this topic. Figure 16 is a distillation of the key findings and illustrates the mechanisms in a clear, graphical way that should help the main results be accessible to a broad range of readers, including those from other communities who may have overlapping interests with the subject (e.g., materials science, turbulence, etc.). Variations of this figure will likely appear in future cloud physics textbooks.

80

The following suggestions should be considered in revising the review. I have listed them roughly in order of priority.

85 1. In the "Way Forward" section it would be very helpful to summarize some of the key points that came up throughout the paper, regarding what aspects need to be carefully considered in future laboratory experiments. I came up with the following list, but may have missed some points. Laboratory experiments on SIP mechanisms likely need to consider the following variables, in order to ensure that the results are of atmospheric relevance:

- 90 - Particle fall speed and its influence on enhancement of diffusive fluxes, mixing in turbulent wake (ventilation effects).
- Relative velocity and impact parameter for mechanisms involving particle-particle interactions.
- Ambient atmospheric pressure, temperature and gas properties.
- Thermal equilibration of particles with the surrounding atmosphere (or realistic values of thermal lag for typical atmospheric temperature profiles and turbulence properties).
- 95 - Presence of dissolved gases and other impurities; in particular, unrealistically high concentrations of gases such as CO₂ should be avoided.

Reply: Because of pronounced differences between the parameters controlling production of secondary ice for each of the six mechanisms, the authors consider that summarizing all parameters in one list or table would be

100 not an easy task or even confusing. For example, concentration of CO₂ dissolved in water plays an important
role for droplets fragmentation during freezing. However, it hardly has any effect on fragmentation during ice-
ice collision or ice sublimation. In order to address the reviewer's comment, it was decided to summarize the
list of parameters, which may affect secondary ice production, at the end of the sections related to each specific
SIP mechanism.

105

2. One possibility not considered in defining primary vs secondary ice production: Could there be "primary"
mechanisms that do not involve INP, or that strongly enhance properties of otherwise ineffective INP? Might
these be relevant since they could lead to apparent discrepancy between expected and observed number of
ice crystals, even without the operation of secondary ice processes? I have in mind pressure perturbations
and electrical effects, as examples (citing work with which I am familiar... I am sure there is much more to
consider Yang et al. 2015, Applied Physics Letters "Ice nucleation at the contact line triggered by transient
electrowetting fields" and Yang et al. 2018, Phys Rev E "Nonthermal ice nucleation observed at distorted
contact lines of supercooled water drops").

110
115 **Reply:** According to our definition, electrowetting induced freezing (Yang et al. 2015, 2018) would be
classified as primary ice production as it does not require pre-existing ice particles. We rather want to stick to
our narrow definition of secondary ice production here. There are border line cases however and the following
paragraph was added in section 9.2 to address the reviewer's comment:

120 "Another unexplored possibility is related to enhancing the activation properties of typically ineffective
primary INPs due to changing the local properties of the cloud environment. In section 7, such activation of
ineffective primary INPs occurred in the cloud environment modified by freezing drops (or hail and rimed ice
particles) due to local increase of supersaturation."

3. It also would seem relevant to discuss laboratory or cloud chamber experiments in which no secondary ice
production was observed. Knowing the conditions under which SIP is not required is valuable for determining
what part of parameter space should be searched. Again, drawing from familiar work, and acknowledging
that there must be more, I have in mind the cloud chamber study of Desai et al. 2019, GRL "Aerosol Mediated
Glaciation of Mixed Phase Clouds: Steady State Laboratory Measurements", in which agreement was
observed between injected INP and observed ice crystal concentration, to within experimental uncertainties.
Interestingly, although it was not emphasized in the paper, multiple images of "pac-man" shaped ice crystals
were observed in that study (see their Figure 1), and one can speculate that they are fragmented frozen
cloud droplets. And yet they do not seem to have contributed significantly to ice budgets under the existing
experimental conditions (limited to relatively small particle sizes with only 1 meter of vertical distance for
fallout and thereby limited particle lifetimes).

130
135 **Reply:** The following paragraph was added in section 9.2 to address the reviewer's comment:

140 "When discussing the feasibility of SIP mechanisms, it is important to keep in mind well documented
observations of supercooled persistent mixed-phase clouds with temporally stable low ice concentration (<1-
5L⁻¹) (e.g. Korolev et al. 2017; McFarquhar et al. 2011; Shupe et al., 2006). In these clouds, seemingly
satisfying some conditions required for SIP, no explosive enhancement of ice concentration was observed.
Similar mixed-phase cloud environments with no SIP were also reproduced in laboratory experiments (Desai
et al. 2006). These in-situ and laboratory observations accentuate the importance of identifying the necessary
and sufficient conditions required for the initiation of each of the SIP mechanisms."

4. My first impression was that there is a lack of balance between the ice shattering mechanism covered in
section 2 compared to the other sections. Upon reflection, though, I realize that it is a result of more
literature being available in that area. A word on this at the beginning of section 2 would help orient the
reader, allowing to understand that the fundamentals of ice growth in supercooled liquid, etc., have been
thoroughly studied and are of relevance to the drop shattering problem covered later in the section.

145 **Reply:** The following text was added at the end of Introduction (section 1) to address the reviewer's comment:

150 “The authors would like to acknowledge the length disproportions between the aforementioned sections. Section 2 has the biggest volume, which is a reflection of the large amount on knowledge accumulated on different aspects of water freezing and is directly linked to the secondary ice formation during droplet freezing. The rest of the sections have smaller sizes due to fewer laboratory experiments related to them. These disproportions will be discussed in more detail in section 9.1.”

155 5. The discussion on page 4 (especially near lines 391-392) raises the question of gas equilibration time. For natural cloud droplets grown by condensation the gas content may be substantially different than for droplets generated in a laboratory from atomizing a bulk liquid that is presumably in equilibrium with ambient gases. Could this be a relevant factor to consider?

160 **Reply:** Neglecting chemical reactions inside the droplet, the timescale for gas equilibration for a cloud droplet of 100µm dia. is on the order of magnitude of 10s. This is assumed to be faster than the time required for the droplet to grow to that size, in particular as the trace gases are taken up concurrently with the water vapor during droplet growth and part of the growth process might be the aggregation of smaller saturated droplets. We therefore assume that cloud droplets – like laboratory droplets – are well equilibrated. We do mention dissolved gases as one of the possible “hidden parameters” in lab experiments in the summary of section 2.

165 6. Clarify on lines 58-61 that you are referring to artificial ice shattering that results from sampling/measurement (as opposed to ice shattering from natural processes, which are also considered in this review).

170 **Reply:** The mentioned statement was modified to address the reviewer’s comment: “For the sake of thoroughness, experimental studies of the effects of artificial ice particle fragmentation during in-situ sampling were included in this review as well.”

175 7. Clarify that equation 4 is for the assumption of a spherical droplet in air. Also, for people in other fields who might be accessing this review, provide a reference for the ventilation coefficient and specify that it is a function of terminal speed and therefore of diameter.

Reply: We have modified the respective paragraph to read:

“According to Pruppacher and Klett (1998), the duration of the second stage of the droplet freezing inward can be estimated for a spherically symmetric droplet falling in air as:

$$t_2 = \frac{\rho_w L_m D^2 \left(1 - \frac{\Delta T_c w}{L_m}\right)}{12 f \Delta T \left(k_a + L_s D_v \left(\frac{d\rho_v}{dT}\right)_{sat,i}\right)} \quad (4)$$

180 where ρ_w liquid water density; f ventilation coefficient; D_v is the water vapor diffusion coefficient; k_a is the thermal conductivity of the air; L_s latent heat of ice sublimation; $\left(\frac{d\rho_v}{dT}\right)_{sat,i}$ is the mean slope of the ice saturation vapor density curve over the interval from T_0 to T_m . The ventilation coefficient f describes the acceleration of droplet freezing from forced (due to the velocity between droplet and gas) and free (due to the temperature difference between droplet and gas) convection as compared to stagnant air ($f=1$). For drizzle sized droplets falling freely in air, f will typically assume values between 2 and 4.”

185 8. Clarify on lines 176-178 what is meant by the “spatial scale of the ice crystals”.

Reply: The statement about spatial scale was modified as follows:

190 “One of the important findings of studies on water freezing is that the density of the ice mesh increases with the decrease of temperature, whereas the typical size of the ice crystals perpendicular to a -axis becomes smaller.”

195 9. The meaning of Figure 5 and “the diameter of the monocrystalline frozen drops decreases with the increase of supercooling” is not clear to me. How do I interpret a data point at a specific radius and supercooling? Does it mean that at lower supercoolings the frozen drops are single crystals and at higher

supercoolings the drops are polycrystals? I would have assumed that there is a probability of single versus multiple crystals. Is the data point the probability of 0.5? More explanation is needed here.

Reply: In order to clarify the diagram in Fig.5 the following modification of the related text was introduced:
“The average critical radius of a droplet frozen as monocrystalline decreases with the increase of
200 supercooling ΔT (Fig.5), ...”

The caption to Fig.5 was also modified as:

“Dependence of the polycrystallinity of frozen droplets on the average droplet size and freezing temperature of droplets.”

205 10. In a few places there should be more acknowledgement of uncertainty, such as line 275 where it is probably more reasonable to say “Such a high rate of splinter production may be an important factor in the INP economy”... since it surely depends on many other factors as well. On the other hand, I see at least one place where the view of the field may be overly pessimistic: line 432 “remains poorly understood or unknown” would seem more reasonable to be “remains only partially understood.”

210 **Reply:** Both statements were modified as per reviewer’s suggestion.

Diligent

11. In the caption of Figure 10 you refer multiple times to INP, but in this case you are referring to an ice particle colliding with a supercooled droplet. Strictly speaking, yes, the ice particle could be considered an INP, but to me it seems misleading. If we consider INP as usually defined, then this refers more to
215 heterogeneous (primary) ice nucleation. Indeed, the question of surface versus volume crystallization is intriguing, but it is more closely related to primary ice formation.

Reply: In the caption of Figure 10 the terms “INP” were replaced by “INP or ice crystal” to eliminate potential confusion and address the reviewer’s comment.

220 12. In the paragraph discussing the paper of Baker (1991), near line 750, it should be made clearer that Baker considered static drops during the transient freezing process, whereas others such as Prabhakaran et al. account for continuous production of supersaturation in the wake of a falling particle that is riming (wet growth) or melting. In the next paragraph I would also suggest that it would be helpful to have a better understanding of how INP behave at very high liquid-water supersaturations, since this is a regime not
225 typically achieved with current instruments (Fukuta had a wedge method that produced very high supersaturations and indeed observed higher INP efficiency in that regime).

Reply: Baker (1991) makes order of magnitude estimates of how high supersaturation with respect to ice could get around freezing droplets (up to 25 at -15°C) and then argues that even if that high a supersaturation would pertain throughout the cloud at any time and everywhere this could not explain the factor 10^4 to 10^5 of ice
230 number/INP number found in some clouds. His argument relies on a power law for the number of INP as a function of supersaturation, which might be questioned, but has some support. We agree that this is an important area of future research and have modified the respective paragraph:

235 “However, Baker (1991) argued that even if T_a is as low as -15°C , the total volume with high supersaturation around all freezing drops remains too small to enhance the number concentration of active INP by several orders of magnitude. Therefore, INP activation in transient supersaturation around freezing drops should have a low significance for SIP. This result seems to be conflicting with the conclusion obtained in Rosinski et al. (1975) and Prabhakaran et al. (2020). It should be noted that Baker (1991) assessment of the SIP efficiency was obtained for the static field of supersaturation around droplet and under the assumption,
240 that the number concentration of active INP follows a power law in supersaturation that could be extrapolated to a very high supersaturation.” ...

We also modified a statement at the end of section 7:

“Future laboratory studies should be focused on the behavior of INP at very high ice supersaturation (>10) for a better the quantification of the effect of $T_s - T_a$ of a free-falling hydrometeor on the INP activation.”

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13. My initial reaction was that Section 8 does not really fit with the main theme of the review. It is relevant in the sense that spurious ice crystals may have contributed to the apparent conflict between measured INP and measured ice crystal concentrations. But then it begs the question why other field measurements are not reviewed as well. One aspect that could be emphasized to strengthen the connection to the laboratory focus of the paper is that the high speed videos in the Korolev et al. papers were obtained in a wind tunnel setting (at least that is my recollection). Perhaps this is a good place to emphasize that lab “experiments” have contributed not only to understanding of fundamental mechanisms, but also to the evaluation of measurement techniques applied in the field. Those videos captured in a controlled lab environment settled the question of shattered ice crystals in the minds of many in the community. I would also point out that this section misses an important reference to Jackson et al. 2014, JAOTech, who made a full assessment of measurement-induced ice shattering based on intercomparison of multiple instruments.

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Reply: The relevant text in section 8 was modified as suggested by the reviewer:

“Direct experimental support for the shattering hypothesis has been provided by a series of wind tunnel experiments with controlled environment and reproducible ice spray conditions (Korolev et al. 2011, 2013b). Ice particle impacting with the probe tips at aircraft speed were video-recorded by a high speed camera.” Jackson et al. JAOT, 2015 reference was added in the text.

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265

14. In Section 9.1 it could be useful to elaborate more on “the most striking outcome of this review”, that there is such a wide range of results for each SIP mechanism. In conversation with colleagues I have encountered a sense of exasperation that lab experiments sometimes show bewildering complexity. I even remember a story from an individual involved with experiments in the Hobbs lab in the late ‘60s that suggested that the CO₂ contamination they identified as a cause of drop shattering is one factor that motivated Prof. Hobbs to shift his group’s emphasis to field work. The result of the “striking outcome”, however, should be that we carry out more, not less experimental work, in order to clarify the various unrecognized factors and ultimately to gain a full understanding of the relevant processes.

270

A thorough check for grammatical and typographical errors should be made. Overall the writing is excellent, but there are multiple places where small errors appear. I summarize the ones I found, although I probably did not catch all while reading:

275

Title: It sounds more natural to my ear to say “experimental studies of secondary ice production” rather than “on secondary ice production”. But I’m not a grammar expert, so I would not go so far as to say it is incorrect.

Reply: The authors put their efforts to double check grammar and spelling. The title was modified as suggested by the reviewer.

280

Line 34: Schaefer
Reply: Corrected.

Caption of Figure 4: Delta T = 14.5 C (should not be negative as currently shown).
Reply: Corrected.

285

Line 205 and several other places: A temperature is high or low (not warm or cold, which is only for an object).
Reply: Corrected.

290

Line 208: the Visagie experiments.
Reply: Corrected.

Lines 335-336: experiments that had a droplet suspended (no “is” needed).
Reply: Corrected.

- 295 Caption of Figure 8: I do not find Lauber et al. 2015 in the references. Should it be 2018?
Reply: Corrected.
- Line 425: number of parameters.
Reply: Corrected.
- 300 Line 489: in a cloud chamber.
Reply: Corrected.
- Line 511: studies of Hallett and Mossop.
305 **Reply:** Corrected.
- Line 526: rapid growth of the ice shell.
Reply: Corrected
- 310 Line 581: Phillips (also this sentence might be clearer is written “The studies of Hobbs and Farber, Vardiman, and Phillips et al. were based on the consideration...”).
Reply: Corrected.
- Caption of Figure 14: AgI and Snomax were used as ice nucleating particles.
315 **Reply:** Corrected.
- Lines 722-723: aerosols introduced into the ambient air.
Reply: Corrected.
- 320 Line 737: ice sphere in humid air.
Reply: Corrected.
- Line 738: The word “study” appears twice... should be rephrased.
Reply: Corrected.
- 325 Line 765: Not sure if “feedbacking” is a word.
Reply: Corrected.
- Line 783: the existence of shattering.
330 **Reply:** Corrected.
- Line 843: a complete quantitative theoretical description.
Reply: Corrected.
- 335 Line 848: systematic basis in weather prediction models.
Reply: Corrected.

Review of experimental studies ~~on~~of secondary ice production

Alexei Korolev¹ and Thomas Leisner²

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Abstract

10 Secondary ice production (SIP) plays a key role in the formation of ice particles in tropospheric clouds. Future improvement of the accuracy of ~~the~~ weather ~~predictions~~prediction and climate models relies on a proper description of SIP in numerical simulations. For now, laboratory studies remain a primary tool for developing physically based parameterizations for cloud modeling. Over the past seven decades, six different SIP-identifying mechanisms have emerged: (1) shattering during droplet freezing; (2) the rime splintering (Hallett-
15 Mossop) process; (3) ~~fragmentation due to ice-ice collision~~; (4) ~~ice particle fragmentation due to thermal shock~~; (5) ~~fragmentation of sublimating ice~~; (6) ~~activation of ice nucleating particles in transient supersaturation around freezing drops~~. This work presents a critical review of the laboratory studies related to secondary ice production. While some of the six mechanisms have received little research attention, ~~for~~ others ~~consist of~~ contradictory results ~~have been~~ obtained by different research groups. Unfortunately, despite
20 ~~past~~vast investigative efforts, the lack of consistency and the gaps in the accumulated knowledge hinder the development of quantitative descriptions of any of the six SIP mechanisms. The present work ~~is aimed at identifying~~aims to identify gaps in our knowledge ~~on~~of SIP ~~and on stimulating~~as well as to stimulate further laboratory studies ~~is~~focused on obtaining a quantitative description of efficiencies for each ~~of~~ SIP mechanism.

25 1. Introduction

Secondary ice production (SIP) is defined ~~here~~ as the formation of atmospheric ice as a result of processes involving pre-existing ice particles, in contrast to primary ice production, which commences by the nucleation of ice either homogeneously in strongly supercooled ~~-~~droplets or heterogeneously on the surface of ice nucleating particles (INP) (e.g. Kanji et al, 2017). SIP is one of the fundamental cloud microphysical
30 processes, recognized as a major contributor to the observed concentration of ice particles at temperatures warmer than the homogeneous freezing temperature.

Even though SIP was observed in early laboratory experiments (e.g. Dudetski and Sidorov, 1911, Findeisen, 1940; Findeisen and Findeisen, 1943; Brewer and Palmer, 1949; Malkina and Zak, 1952; Puzanov and Accuratov, 1952; ~~Schaefer~~Schaefer, 1952; Bigg, 1957), the geophysical significance of SIP was
35 recognized only after the beginning of regular airborne studies of cloud microstructure in different geographical regions (e.g. Koenig 1963, 1965; Hobbs, 1969; Mossop, 1970, ~~1985~~1985a; Mossop et al. 1964, 1972; Ono, 1972; Hallett et al. 1978; Hobbs and Rangno 1985, ~~1990~~1989; Beard 1992; and many others). A

systematically observed enhancement of the number concentration of cloud ice particles over the concentration of INP in the same air mass; urged for the provision of an explanation of the physical processes underlying this discrepancy. ~~One of the explanations linked the enhancement of the concentration of ice particles to a mechanism unrelated to heterogeneous ice nucleation.~~

From the late 1950s to early 1970s, six possible mechanisms were proposed explaining the secondary production of ice crystals. However, since then, limited progress has been made in understanding of how each of those mechanisms contribute to the ice particle concentrations and what the necessary and sufficient conditions are for initiating each of these mechanisms. This situation is complicated by the fact that numerical cloud models tend to focus on only one of the six possible mechanisms, namely the rime-splintering (Hallett-Mossop) process, whereas other mechanisms have been disregarded.

Beyond recent reviews on in-situ studies of ice multiplication (e.g. Cantrell and Heymsfield, 2005; Field et al., 2017), little attention has been devoted to exploring the details of laboratory studies on SIP mechanisms. To bridge this gap, this paper provides an extended review of experimental works on SIP. Laboratory studies with reproducible and controlled environments are the basic means of examining physical processes underlying each SIP mechanism, as well as quantifying the rates of secondary ice production, and identifying necessary and sufficient conditions required for initiation of these mechanisms. Without this knowledge, a development of the physically based parameterisations of SIP in weather prediction and climate simulations is not feasible. Due to their coarse spatial and temporal resolution, in-situ airborne (by nature Eulerian) observations should be used for validation and feedback of laboratory and theoretical SIP studies, rather than serve as a primary tool for developing parameterizations for numerical simulations.

This work is an overview of the current knowledge on SIP obtained from laboratory studies. ~~For the sake of thoroughness, experimental studies of the effects of ice particle shattering on SIP observation were included here as well.~~ In-situ observations and theoretical studies of SIP ~~were~~are mentioned here occasionally, though many of them remained outside the frame of this review. ~~For the sake of thoroughness, experimental studies of the effects of artificial ice particle fragmentation during in-situ sampling were included in this review as well.~~

This review aims to provide navigation for future experimental works that seek to enhance our understanding of SIP mechanisms.

The present paper describes laboratory studies of the following SIP mechanisms: the fragmentation of droplets during their freezing (section 2), rime splintering (section 3), fragmentation due to collision of ice particles with each other (section 4), ice particle fragmentation due to thermal shock caused by freezing droplets on their surface (section 5), fragmentation of sublimating ice particles (section 6), activation of ice nucleating particles in transient supersaturation around freezing drops (section 7). Section 8 describes experimental studies that look at spurious enhancement of ice concentration during in-situ measurements, which can be confused with SIP. The concluding remarks are presented in section 9.

The authors would like to acknowledge the length disproportions between the aforementioned sections. Section 2 has the biggest volume, which is a reflection of the large amount on knowledge accumulated on different aspects of water freezing directly linked to the secondary ice formation during droplet freezing. The rest of the sections are smaller in size due to fewer laboratory experiments related to them. These disproportions will be discussed in more detail in section 9.1.

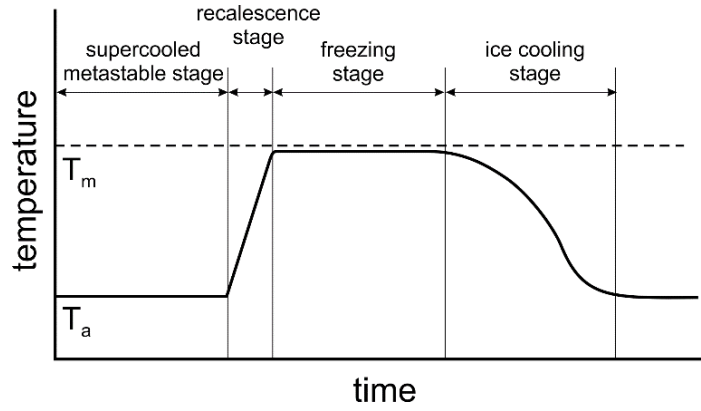
2. Fragmentation of freezing drops

Historically, the first mechanism proposed to explain SIP was the fragmentation of freezing droplets (e.g. Langham and Mason, 1958; Mason and Maybank, 1960; Kachurin and Bekryaev, 1960; Muchnik and Rudko, 1961). During the freezing process of a cloud droplet, liquid water may be trapped inside a growing ice shell formed around the droplet. The expansion of ice during subsequent further freezing results in an increase of pressure inside the ice shell. If the pressure exceeds a critical point, then the ice shell may crack or shatter to relieve the internal pressure. The ice fragments that result from droplet cracking or shattering will serve as secondary ice. In addition, gases dissolved in the droplet might be released during the pressure drop events. Gas bubbles may burst upon freezing at the colder droplet surface, resulting in a second source of fresh small ice fragments.

One of the necessary conditions for SIP during droplet freezing is ~~creating~~ the creation of a closed ice shell and subsequent inward freezing ~~inward~~. Therefore, depending on the way in which the droplet freezes, it may or may not generate secondary ice. Hence, our consideration begins with a review of studies on the process of droplet freezing.

2.1 Freezing stages of a supercooled drop

The process of freezing of a supercooled droplet can be divided into two main stages. The first stage is a process that involves negligible heat exchange with the surrounding air. During ~~that~~ this period, a dendritic ice network (slushy ice) forms through the liquid phase, releasing ~~the~~ latent heat, and heating up the liquid toward the melting point. This stage is usually referred to as the “fast” or “recalescence” stage. The second stage is quasi-isothermal and determined by the freezing of the remaining liquid water. The heat transfer during this stage is directed to the air-droplet interface. The second stage is usually called the “slow” or “freezing” stage. After freezing is complete, the temperature of the frozen droplet gradually decreases towards the ambient temperature to attain a thermal equilibrium.



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Figure 1 A conceptual diagram of temperature changes during the freezing of a supercooled droplet. Here T_m , T_a are the melting and environmental temperatures, respectively.

A conceptual diagram of the temperature changes during the freezing of a supercooled droplet is shown in Fig. 1a. Documented temperature changes during the freezing of supercooled liquid drops can be found in e.g. Mason and Maybank (1960), Muchnik and Rudko (1961), Pena et al. (1969), Bauerecker et al. (2008), Tavakoli et al. (2015).

2.2 Freezing fraction

The amount of frozen liquid water Δm during the recalescence stage can be estimated from a simplified equation of heat balance:

$$\Delta m L_m = \Delta m c_i \Delta T + (m - \Delta m) c_w \Delta T + \Delta Q \quad (1)$$

where m is the droplet mass, $\Delta T = T_m - T_a$ is the droplet supercooling; T_m , T_a are the melting point and initial droplet temperatures, respectively; L_m is the latent heat of freezing, c_i , and c_w are the specific heat of ice and liquid water, ΔQ is the heat loss due to thermal exchange with the environment. After neglecting ΔQ and $(c_i - c_w) \Delta m \Delta T$, Eq. 1 yields an approximation of the fraction of water $\mu = \Delta m / m$ frozen during the recalescence stage as

$$\mu = \frac{c_w \Delta T}{L_m} \quad (2)$$

Down to a temperature of -30°C , Eq. 2 is in a very good agreement with an exact solution of (1) with T-dependent material properties. Using a nuclear magnetic resonance technique, Hindmarsh et al. (2005), measured a fraction of frozen water formed in a supercooled 2mm diameter drop during the recalescence stage of freezing. They found the experimentally measured μ is in good agreement with that predicted by Eq. 2 (Fig. 2).

Equation 2 yields that only a relatively small fraction of water freezes during the first stage. Thus, at -4°C and -20°C , the frozen fraction of water will be approximately 5% and 23%, respectively.

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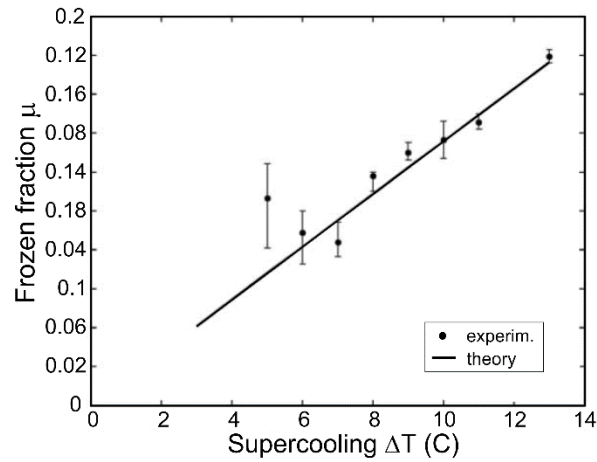


Figure 2. A frozen fraction of water μ formed in a 2mm diameter drops during the recalescence stage versus temperature. The experimentally measured μ is in good agreement with that theoretically predicted by Eq.2 (adapted from Hindmarsh et al. 2005)

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2.3 Droplet freezing time

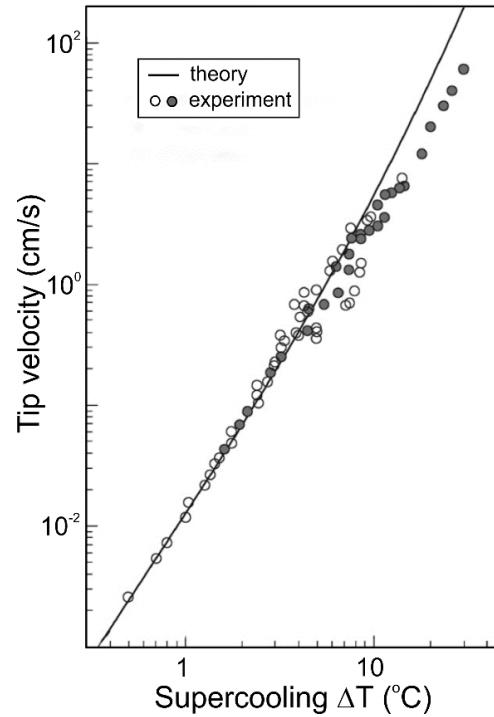
The time scale of the recalescence stage can be assessed as (Macklin and Payne, 1967,1968)

$$\tau_{\text{I}} t_1 = D / u_{\text{I}}(\Delta T) \quad (3)$$

where D is the droplet diameter, and $u_{\text{I}}(\Delta T)$ is the velocity rate of the ice crystal tip growth at water supercooling ΔT . The growth rate $u_{\text{I}}(\Delta T)$ was studied by many research groups (e.g. Lindenmeyer et al. 1959; Hallett, 1964; Pruppacher, 1967,1967a; Feuillebois, et al. 1995; Lindenmeyer et al. 1959; Shibkov et al. 2003, 2005 and others). It was found that the velocity of ice growth along the c -axis u_c is considerably smaller than that along the a -axis u_a (e.g. Macklin and Ryan, 1968). The velocity of freely growing ice is determined as $u = (u_a^2 + u_c^2)^{1/2}$. The summary of studies of the velocity of freely growing ice as a function of ΔT is shown in Fig.3.

145

Following Fig.3 and Eq.3 at $T_0 = -4^\circ\text{C}$ and -20°C the recalescence time t_1 for droplets with $D = 20\mu\text{m}$ will be approximately 5ms, and $5\mu\text{s}$, respectively; and for droplets with $D=2\text{mm}$, 0.5s and 5ms, respectively.



150 **Figure 3.** The measured velocity of freely growing ice as a function of supercooling measured by Lindenmeyer et al. (1959), Hallett (1964), Pruppacher (1967, 1967a), Kullinghall and Barduhn (1977), Furukawa and Shimada (1993), Feuillebois, et al. (1995); Ohsaka and Trinh (1998), Lindenmeyer et al. (1959) (open circles), Shibkov et al. (2003) (solid circles). The theoretical curve is based on Langer Müller and Müller-Krumbhaar (1978) results. Adapted from Shibkov et al. (2003)

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During the freezing stage droplets are cooling due to the thermal exchange with the ambient environment, and thus, the remaining liquid water gradually freezes. The second stage is quasi-isothermal and it is approximately 100-1000 times slower than the first stage. According to Pruppacher and Klett (1998, 1997), the time of the second stage of the droplet freezing inward can be estimated as:

$$160 \quad t_2 = \frac{\rho_w L_m D^2 \left(1 - \frac{\Delta T c_w}{L_m}\right)}{12 f \Delta T \left(k_a + L_s D_v \left(\frac{d\rho_v}{dT}\right)_{sat,i}\right)} \quad (4)$$

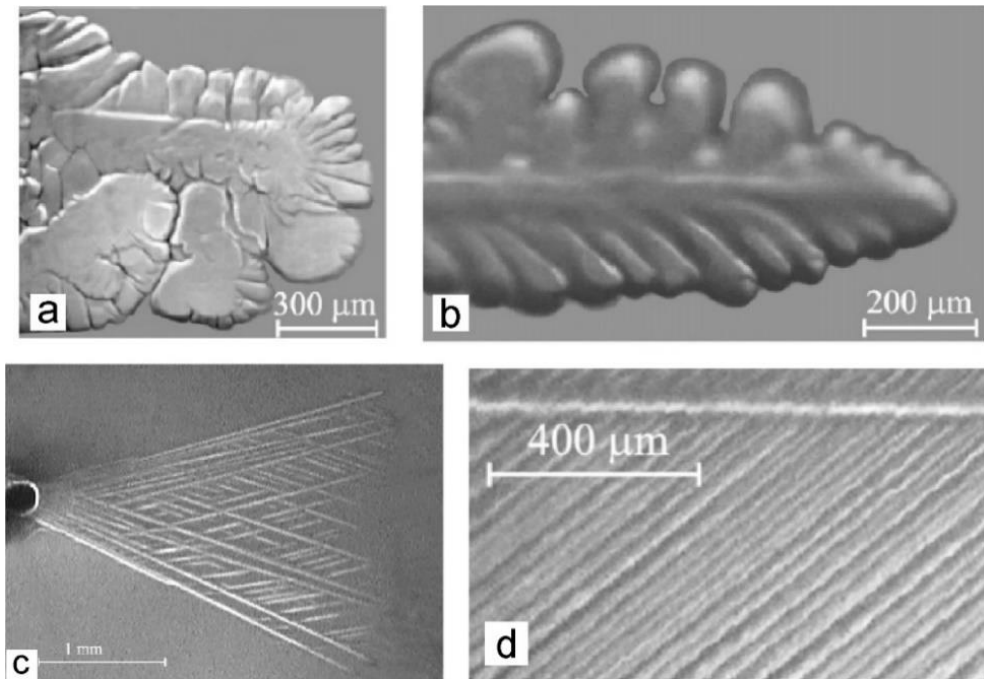
where ρ_w liquid water density; f ventilation coefficient; D_v is the water vapor diffusion coefficient; k_a is the thermal conductivity of the air; L_s latent heat of ice sublimation; $\left(\frac{d\rho_v}{dT}\right)_{sat,i}$ is the mean slope of the ice saturation vapor density curve over the interval from T_0 to T_m . The ventilation coefficient f describes the acceleration of droplet freezing from forced (due to the velocity between droplet and gas) and free (due to the temperature difference between droplet and gas) convection as compared to stagnant air ($f=1$). For drizzle sized droplets falling freely in the air, f will typically assume values between 2 and 4.

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Following Eq.4 at $T_0 = -4^\circ\text{C}$ and -20°C , the freezing time t_2 for droplets with $D = 20\mu\text{m}$ will be approximately 70ms, and 11ms, and for droplets with $D=2\text{mm}$, 80s and 13s, respectively.

Since $t_2 \gg t_1$ the droplet freezing time is determined by the freezing during the second stage.
170 Experimentally, the freezing time was studied by Muchnik and Rudko (1962), Murray and List (1972),
Hindmarsh et al. (2003).

It should be noted that there is a good wealth of theoretical studies on the freezing time t_2 (e.g. Macklin and
Payne, 1967; King, 1975; Gupta and Arora, 1992; Feuillebois et al., 1995; Tabakova et al., 2010). However,
Eq.4 (Pruppacher and Klett, 1998) provides a reasonably accurate assessment of t_2 , which is in good
175 agreement with experimental measurements.



180 **Figure 4.** The morphology of ice crystal habits freely growing in pure water, supercooling at (a) $\Delta T = 0.3^\circ\text{C}$ dense
branching structure; (b) $\Delta T = 1.5^\circ\text{C}$, developed dendrite; (c) $\Delta T = 4.1^\circ\text{C}$, needle-like crystals; (d) $\Delta T = 14.5^\circ\text{C}$ compact
needle mesh. (adapted from Shibkov et al. 2003)

2.4 Crystalline structure of ice

The way in which ice crystals grow through the freezing droplet during the recalescence stage is of great
185 importance for SIP for two reasons. First it affects the formation of the ice shell and it also impacts the way in
which the liquid water freezes inside the droplet. The morphology of ice formation during water freezing was
explored by Kumai and Itagaki, (1953), Hallett (1960, 1964), Macklin and Ryan (1965, 1966), Pruppacher
(1967a,b), Furukawa and Shimada (1993), Ohsaka and Trinh (1998), Shibkov et al. (2003, 2005). It was found
that the shape of the ice crystals depends on the water supercooling ΔT . At low supercooling ($1^\circ\text{C} <$
190 $\Delta T < 3^\circ\text{C}$), ice crystals appear as stellar dendrites or dendritic sheets growing parallel to the basal plane. With
the increase of supercooling, ice crystals start splitting, causing a formation of three-dimensional complex
structures (e.g. Pruppacher 1966, 1967a; 1998; Shibkov et al, 2003). Splitting leads to so-called “non-rational”

195 growth, i.e. growth that cannot be explained by rational crystallographic indices. Hallett (1964) and Macklin and Ryan (1965, 1966) suggested that this non-rational growth is explained by the hopper structure of ice crystal growth. One of the important findings of studies on water freezing is that the density of the ice mesh increases with the decrease of temperature, whereas the ~~spatial-scale~~ typical size of the ice crystals ~~parallel~~ perpendicular to the ~~basal-plane~~ ~~a-axis~~ becomes smaller. These ~~feature~~ transformations of ice crystals with temperature can be clearly seen in Fig.4. The shape of the ice crystals and the density of their network has direct impact on the size and the number of isolated water pockets formed during freezing as well as the tensile stress that is required to rupture the droplet.

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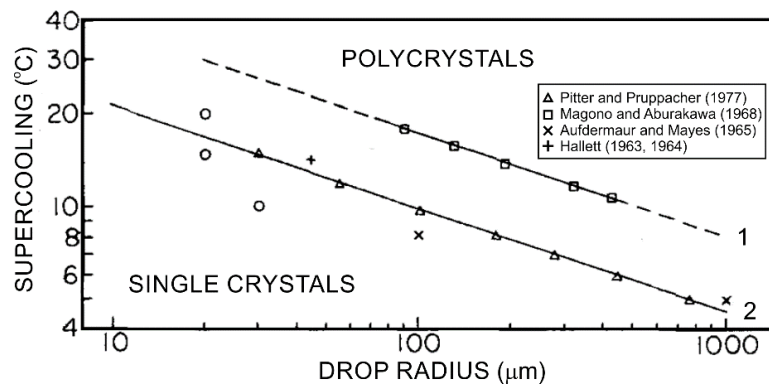


Figure 5. Dependence of the polycrystallinity of frozen droplets on the average droplet size and freezing temperature of droplets. (1) Droplets freely suspended in vertical airflow and nucleated by contact with clay particles. (2) Droplets frozen on the surface of large single crystals. Adapted from Pitter and Pruppacher (1973)

205

Regardless of the visual randomness of crystals growing through supercooled water, the non-rational structures may compose single crystals after the droplet freezing is completed (Macklin and Ryan 1965, 1966). Hallett (1963, 1964), Magono and Aburakawa (1968) ~~Hallett (1963, 1964) 1969~~, Aufdermaur and Mays (1965), Pitter and Pruppacher (1977) 1973) studied the formation of monocrystalline and polycrystalline droplets during droplet freezing. They all found that droplet freezing as a single-crystal critically depends on the diameter-droplet size, supercooling of the ~~monocrystalline frozen drops decreases~~ ~~with~~ droplet before freezing as well as the ~~increase~~ thermal conductivity of ~~supercooling ΔT~~ (Fig.5) the medium, into which the latent heat of freezing is dissipated. As it will be discussed below, ~~shattering~~ droplet fragmentation during freezing and secondary ice production depend on whether droplets freeze as ~~monosingle-crystals or polycrystal~~ polycrystals.

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The average critical radius ~~Figure 5. Dependence~~ of a droplet frozen as monocrystalline decreases with the ~~polycrystallinity on~~ increase of supercooling ΔT (Fig.5), and it can be parameterized as (Pitter and Pruppacher 1973):

$$220 \quad r_c = \left(\frac{aK^b}{\Delta T} \right)^c \quad (5)$$

where K is the ~~diameter~~ thermal conductivity of the ~~frozen~~ medium surrounding the droplet; $a=23$; $b=1/8$; $c=3$. Eq.5 suggests that the lower the heat conductivity of the medium surrounding a given sized drop ~~and~~, the larger the supercooling can be reached when droplet freeze as monocrystal. Another important outcome from Eq.5 is that for the same ΔT , due to higher value of K for the air compared to ice, droplets nucleated by INPs
225 or miniscule ice crystals will have a larger monocrystal freezing temperature. ~~(1) drops freeze size than cases where droplets freeze on the surface of a large single crystals; (2) drops freely suspended in vertical airflow and nucleated by contact with clay particles. Adapted from Pitter and Pruppacher (1977) ice particle.~~

2.5 Pressure inside freezing droplets

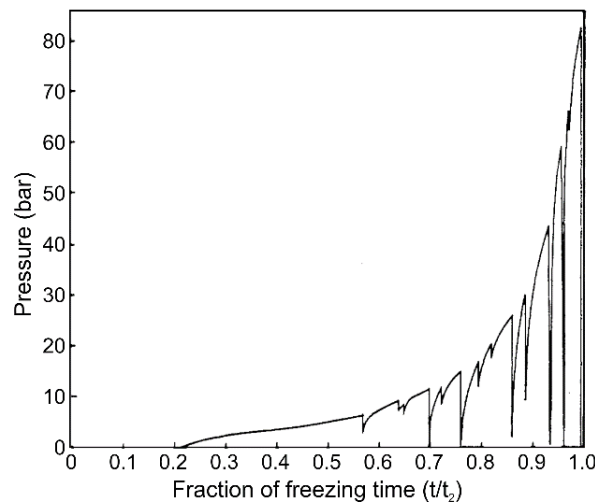
230 The pressure inside freezing drops was measured by Visagie (1969) and King and Fletcher (1973). Water drops with immersed pressure sensors were suspended in between paraffin oil and a carbon tetrachloride bath inside a temperature-controlled chamber. The size of the drops varied from 7mm to 12mm. It was found that, during freezing, the pressure inside a drop gradually built up as the shell became thicker. The pressure increase was repeatedly interrupted due to the complete or partial pressure relief brought on by cracking (Fig.6). In this
235 period, water extruded through a crack and froze on the surface of the drop. After the crack was sealed by frozen water, the pressure would climb back to the previous value and continue to grow. Both studies showed that the pressure increased until reaching its maximum value P_{max} near the point of complete freezing. The highest pressure, $P_{max}=89$ bar in an 11mm diameter drop at -5°C , was observed by King and Fletcher (1973) and 79 bar in 7mm drop at -12.8°C by Visagie (1969). However, no appreciable pressure growth was observed
240 inside drops freezing at temperatures ~~warm~~ higher than -3°C . King and Fletcher (1973) noted that about 20% of droplets contained a residual pressure of 10-20 bar at the completion of freezing.

The formation of cracks during droplet freezing was accompanied by an audible noise detected by microphone in the Visagie (1969) experiments. Loud sounds during droplet freezing and fragmentation were also reported by Dudetski and Sidorov (1911).

245 Visagie (1969) pointed out that besides the shell wall thickness, the cracking pressure is also a function of the temperature gradient across the ice shell (see Fig.6 in Visagie 1969).

King and Fletcher (1973) concluded that large droplet freezing at ~~warm~~ high temperatures will exhibit substantial viscous flow, and the smaller droplets freezing at ~~colder~~ lower temperatures will exhibit more elastic behaviour and crack more often. Between these two extremes, there is probably a size-temperature
250 domain, in which sufficient elastic energy is stored in the shell to shatter it violently.

Both studies found that the cracking pressure increases with the increase of the thickness of the ice shell during the droplet freezing. However, the dependence of the cracking pressure versus droplet size and temperature remains unknown.



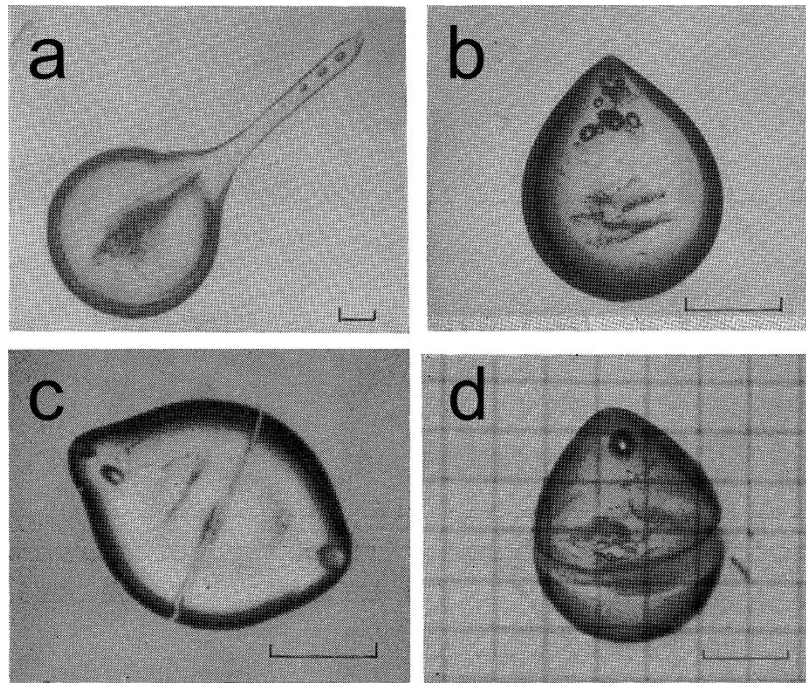
255 **Figure 6.** A time series of pressure changes inside an 11mm diameter drop freezing in a bath at -5C (adapted from King and Fletcher, 1973).

260 Visagie (1969) and King and Fletcher (1973) conducted their experiments with overly large drops (7mm to 11mm) placed in a paraffin oil and carbon tetrachloride bath. This experimental setup affects the temperature gradients in the ice shell around the freezing drops and the rate of heat exchange between the inner part of the drops and their surrounding environment. These are the critical components for the cracking behavior and the inner pressure changes. This brings up the issue of whether the obtained results are applicable to drops of smaller sizes, which typically form in natural clouds.

2.6 Metamorphosis of droplet shape during freezing

265 Visagie (1969) and King and Fletcher (1973) also documented that in addition to cracking, the release of internal pressure inside freezing drops also occurred through deformation of the shape of the ice shell. Deformation of freezing drops was reported in early observations of freezing rain and ice pellets (e.g. Bentley, 1907). However, the physical explanations of freezing drop deformation were provided almost half a century later by Dorsey, (1948) and Blanchard (1951). Deformation of freezing droplets was observed by many authors in their laboratory studies (e.g. Mason and Maybank, 1960; Jonson and Hallett, 1968; Takahashi and Yamashita, 1969; Pitter and Pruppacher, 1973; Takahashi, 1975, 1976; Iwabuchi and Magono, 1975; Pruppacher and Schlamp, 1975; Uyeda and Kikuchi, 1978; Lauber *et al.*, 2018 and many others). Furthermore, Takahashi (1975) identified four main categories of drop deformation: (a) spike (Figs.7a and 8); (b) bulge (Fig.7bc); (c) split (Figs.7c), (d) crack (Figs.7d and 8). During freezing, droplets may simultaneously develop a combination different types of deformations depending on the droplet diameter and temperature, e.g. spikes and cracks (Fig.8). Sketches of a variety of different forms of bulges, cracks and spikes are available from Takahashi (1975).

275



280 **Figure 7.** The main types of droplet deformations during freezing. (a) spike, long thin protrusion usually longer than one-fourth of the drop diameter; (b) bulge, protrusion shorter than one-fourth of the droplet diameter; (c) crack; (d) split. Scales are 100 μ m. Adapted from Takahashi (1975).

Takahashi (1976) found that deformation and shattering are closely related to crystalline structure formed during freezing. Thus, 90-100% of spikes are formed if droplets are polycrystalline. The spikes usually
 285 protrude from the crystal boundary whose mechanical connection is weaker compared to monocrystalline locations. Spikes are also formed if, at the moment of nucleation, the droplet temperature is higher than the ambient temperature. However, spikes scarcely formed when the droplet was in thermal equilibrium with the environment. Takahashi (1975) found that the probability of spike formation increases with the increase of
 290 droplet size. This can be explained by the increase of the occurrence of polycrystalline frozen drops with the increase of their sizes as in Fig. 5. Takahashi (1976) and Uyeda and Kikuchi (1978) studies also showed *c*-axis of a frozen monocrystalline droplet coincide with the *c*-axis of the seed crystal and that bulges are usually aligned with the *c*-axis.

Most experiments on observation of droplet deformation were performed with relatively large drops
 295 $D > 50\mu\text{m}$ and at temperatures $T > -25^\circ\text{C}$. However, López and Ávila (2012) observed the formation of spikes and bulges on small droplets with $8\mu\text{m} < D_{eff} < 30\mu\text{m}$ freezing at temperatures -40°C . Microphotographs of small frozen drops obtained in their experiments did not reveal cracks and splitting. The authors also did not find any evidence of shattering. However, no deformation of small droplets was observed by López and Ávila at $T = -30^\circ\text{C}$. It is worth noting that the interpretation of López and Ávila is hindered by an absence of
 300 information about the nucleating temperature of droplets. Since the droplets were introduced in the cloud chamber at positive temperatures, there is good reason to consider that they froze at temperatures higher than

that of the environment. This kind of condition is favorable for spike formation (Takahashi, 1975). Deformed small droplets frozen at $T_a < -40^\circ\text{C}$ were also observed by Schaefer (1962).

305 **2.7 Fragmentation during freezing**

The following discussion will consider works focused on laboratory studies looking at the processes behind splintering and fragmentation of freezing droplets.

Mason and Maybank (1960) studied the fragmentation of freezing droplets $30\mu\text{m} < D < 1\text{mm}$ in the temperature range of $-15^\circ\text{C} < T < -10^\circ\text{C}$. Droplets were suspended on a fiber in a small ($\sim 40\text{cm}^3$) cloud
310 chamber. It turned out that, on average, the occurrence of droplet shattering decreased with the decrease of air temperature and droplet size. The occurrence of shattering for a 1mm diameter drop reached up to 47% with a maximum number of 200 splinters per drop. Such a high rate of splinter production ~~is~~ may be an important factor in the INP economy during precipitation formation.

However, Pruppacher (~~1967~~1967a) pointed out that when Mason and Maybank (1960) performed their
315 experiments, droplets did not reach thermal equilibrium at the moment of nucleation, and their temperature was warmerhigher than that of the air by 1°C to 12°C . He argued that these conditions are favorable for the formation of an ice shell and for droplets freezing inward, which are critical for droplet shattering. Pruppacher questioned the relevance of the conditions used in the Mason and Maybank experiment to those in natural clouds.

Dye and Hobbs (1968) and Johnson and Hallett (1968) attempted to reproduce the Mason and Maybank
320 (1960) experiments. They found that a 1mm diameter water drop suspended on a fiber did not shatter when nucleated after attaining thermal equilibrium. Dye and Hobbs (1968) also demonstrated that enhanced concentration of dissolved CO_2 resulted in increasing the occurrence of droplet shattering. They argued that the Mason and Maybank (1960) experiments were affected by increased concentrations of CO_2 , which was used as
325 a coolant. Johnson and Hallett (1968, Fig.2) also demonstrated that for the drops where the nucleating temperature was higher than that of the air ($T_n > T_a$), the ice shell forms around a pure liquid core and ice mesh does not penetrate their centre. Such drops may create a stronger ice shell with a higher internal pressure, and therefore, be more susceptible to shattering.

~~Later,~~ Hobbs and Alkezweeny (1968), Takahashi and Yamashita (~~1968~~1969, 1970), Bader et al. (1974),
330 Pruppacher and Schlamp (1975) found that during freefall, droplets shatter after reaching a temperature quasi-equilibrium with the environment. It is important to note, that these results are in disagreement with those obtained by Dye and Hobbs (1968) and Johnson and Hallett (1968).

Despite the differences in experimental setups, most laboratory studies showed a general trend that large droplets are more susceptible to shattering during freezing than small ones (summarized in Lauber et al. 2018).
335 However, Takahashi (1975) found that the relationship between the occurrence of shattering, droplet diameter and air temperature is more complex. He showed that in the air temperature range $-20^\circ\text{C} < T_a < -7^\circ\text{C}$, free falling

drops have the highest occurrence of shattering in the size range $75\mu\text{m} < D < 135\mu\text{m}$. Whereas at $T_a = -25^\circ\text{C}$, the probability of droplet shattering nearly monotonically increases from $50\mu\text{m}$ to $500\mu\text{m}$. Takahashi (1975) also found that at $T_a = -4^\circ\text{C}$, droplets with $50\mu\text{m} < D < 200\mu\text{m}$ do not shatter. In this regard, it is worth mentioning that
340 Brownscombe and Thorndike (1968) observed a 9% occurrence of shattering in droplets with $50\mu\text{m} < D < 90\mu\text{m}$ at -5°C , which is in agreement with Keinert et al. (2020) reporting a 15% occurrence of droplet breakup at -5°C , which occurred only under free fall ventilation but not in stagnant air.

Laboratory studies also did not show a consistency for the lower threshold diameter for droplet fragmentation. Adkins (1960) found no splintering for droplets $D < 10\mu\text{m}$. Hobbs and Alkezweeney (1968)
345 observed no fragmentation of droplets $20\mu\text{m} < D < 50\mu\text{m}$. Johnson and Hallett (1968) reported no shattering observed for droplets $5\mu\text{m} < D < 38\mu\text{m}$. However, Mason and Maybank (1960, Table 1) observed droplet shattering in the size range of $30\mu\text{m} < D < 80\mu\text{m}$ when the droplets were at thermal equilibrium. The inconsistency of the latter result may be related to the enhanced concentration of CO_2 in the laboratory setup. It is worth noting, that based on the theoretical analysis of the energy balance, Wildeman et al. (2017) concluded
350 that symmetrically freezing droplets smaller than $50\mu\text{m}$ in diameter cannot shatter.

Ambient air temperature has a significant effect on the occurrence of freezing drop shattering. Both Takahashi and Yamashita (1970) and Lauber et al. (2018) found that the maximum rate of shattering is observed between -10°C and -20°C for droplets ranging in size $85\mu\text{m} < D < 350\mu\text{m}$. This is generally consistent with the results found by Brownscombe and Thorndike (1968) for droplets with $80\mu\text{m} < D < 120\mu\text{m}$, although
355 their temperature range was limited by $-15^\circ\text{C} < T_a < -5^\circ\text{C}$. However, for large drops with $D > 500\mu\text{m}$ the maximum occurrence of shattering was observed at $T_a < -25^\circ\text{C}$ (Takahashi, 1975). Hobbs and Alkezweeney (1968) found that the rate of shattering of droplets $50\mu\text{m} < D < 150\mu\text{m}$ does not depend on the temperature over the range $-32^\circ\text{C} < T_a < -20^\circ\text{C}$. Whereas, in his experiments, Takahashi (1975, Fig.7) found a strong temperature dependence of droplets shattering in this size range.

A review of the laboratory studies showed that the reported rate of shattering during droplet freezing varied significantly. For example, Takahashi (1976) found that the maximum rate of shattering for free fall droplets ($200\mu\text{m} < D < 350\mu\text{m}$) at $-20^\circ\text{C} < T < -10^\circ\text{C}$ was close to 40%. However, Lauber et al. (2018) showed that, for droplets suspended in electro-dynamic balance, the maximum shattering rate for the same temperature size range is close to 12%. This, however, increased notably to about 25% when the experiments were conducted
365 under terminal velocity ventilation (Keinert et al., 2020). Brownscombe and Thorndike (1968) observed a 14% rate of shattering for free fall droplets with $80\mu\text{m} < D < 120\mu\text{m}$ freezing at -15°C .

A significant inconsistency of the efficiencies of ice splintering and their dependency on temperature and droplet size obtained by different research groups is quite evident. This poses a key question about the differences in experimental setups and the potential effects of other parameters. Already, Johnson and Hallett
370 (1968) have pointed out the importance of the effect of ventilation on droplet shattering. When a droplet with

$D=500\mu\text{m}$ was suspended on a thread and ventilated at an equivalent to the free fall speed, no shattering was observed. However, when the droplet was rotated around an axis perpendicular to the airflow, shattering and cracking invariably occurred. This finding raised questions about the realism of the experiments that had a droplet ~~is~~-suspended with a fixed orientation on a fiber or other mount. Under these conditions, the thermal exchange between the droplet and the ambient air is different compared to the free fall condition.

Pitter and Pruppacher (1973) demonstrated that a droplet suspended in the airflow begins to tumble and spin immediately after nucleation, thus providing a radially more symmetric heat loss. Drop spinning after nucleation was also reported by Dye and Hobbs (1968), Kolomeychuk et al. (1975) and Keinert et al., (2020). Initiation of tumbling and spinning after droplet nucleation can likely be explained by the asymmetrical shape and heterogeneous surface roughness that builds up quickly after freezing, thereby leading to a fluctuating torque being exerted by the terminal airflow.

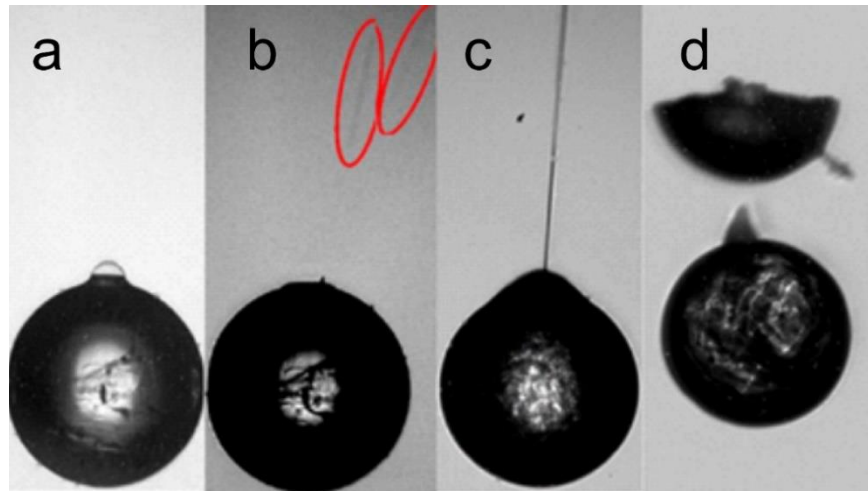
Takahashi (1976) also revealed the importance of the crystalline nature of ice that forms inside freezing drops to their subsequent shattering. He found that 90-100% of shattering occurs when drops freeze as single crystals. Takahashi also showed that splitting occurs perpendicular to the c -axis dividing the drop in two equal parts (e.g. Fig. 9e7c,d). The equatorial cracking and splitting of freezing drops was also reported by Wildeman et al. (2017, Fig. 3a,b) and Lauber et al. (2018, Figs. 5,6). Takahashi (1976) systematized how drops may shatter with respect to their crystalline boundaries. In most cases of polycrystalline drops, their fragmentation occurs along the crystal boundaries, where mechanical connectivity is weaker.

One of the first classifications of ‘types of fragmentation’ during drop freezing goes back to the work of Stott and Hutchinson (1965). They nucleated 0.9mm to 1.9mm diameter drops that were suspended on a fiber at -1°C and then froze them at the air temperature of -15°C . Even though this particular arrangement is not fully relevant to conditions in natural clouds, it helped identify the most common patterns of the drop fragmentation. The droplet fragmentation was classified as follows: (a) violent shattering with multiple pieces; (b) central breaks or splitting; (c) spicule breaks with liquid; (d) spicule breaks after solidification; (e) spicule bubble breaks; (f) cracks.

Wildeman et al. (2017) conducted experiments with millimeter sized drops freezing on a super-hydrophobic substrate. The high-speed videos documented explosive shattering of freezing drops, which generated a cascade of ice fragment sizes. One of the videos (V2) documented secondary shattering of one of the fragments formed after primary shattering. This suggests that during droplet freezing, liquid water may form several pockets across the droplet volume, rather than one big unfrozen volume in the central part. As discussed above, the connectivity of unfrozen pockets of water inside the ice shell is likely to be controlled by the type of the ice network formed inside the droplet and temperature exchange between the droplet and environment.

One of the caveats of the Wildemann et al. laboratory setup is that the experiments were performed at very low pressure ($3.4 \cdot 10^{-3}\text{atm}$), and the droplets cooled much faster than they would cool in the atmosphere.

Johnson and Hallett (1968) showed that below 0.13atm, every drop in their experiments shattered violently. In this way, the results are not directly applicable to environmental conditions.



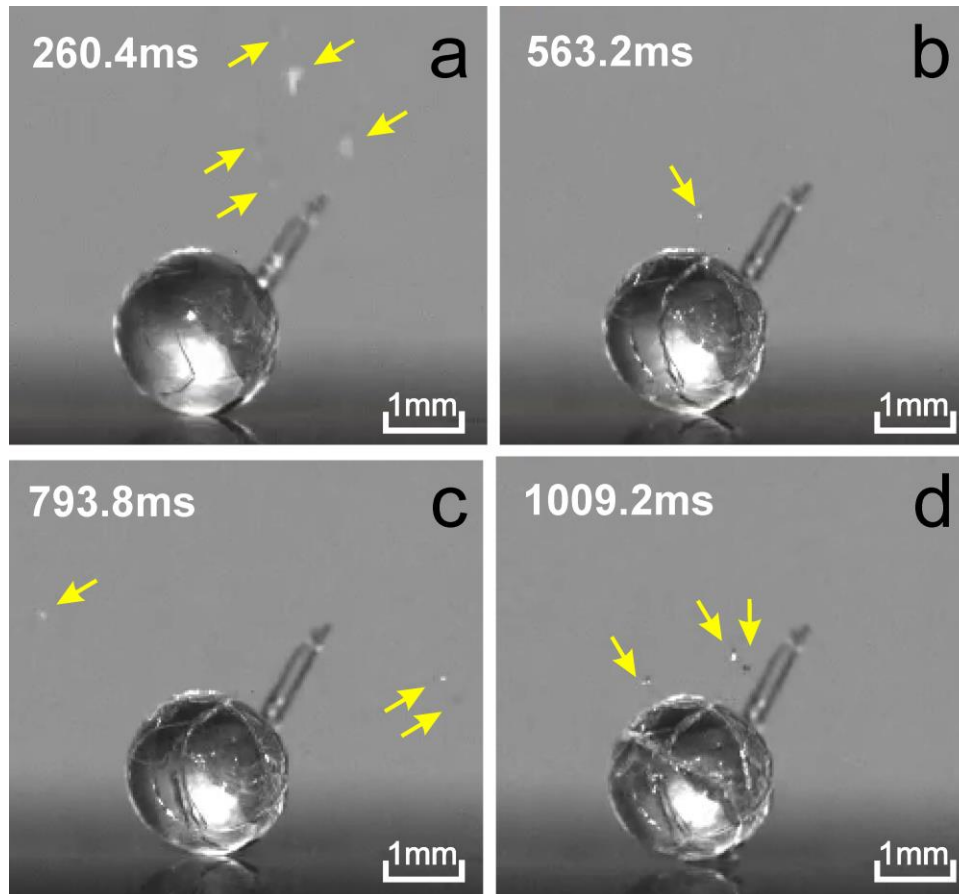
410 **Figure 8:** Secondary ice processes, as observed by high speed microscopy (a) a bubble has formed on the surface of a
freezing droplet. Cracks are visible in the surface. (b) the droplet from (a) but 12 ms later: the bubble has burst, two
415 fragments are highlighted by red ellipses. (c) jetting: a jet of liquid water is expelled violently through a hole in the ice
shell. (d) breakup: a freezing droplet splits in two halves, a few small fragments are sometimes observed (adapted from
Lauber et al. 2015, 2018).

415

In a series of experiments conducted with electrically charged droplets levitated in an electrodynamic
balance, Kiselev and colleagues observed droplet freezing with a high speed video microscope and categorized
secondary ice processes as breakup, cracking, bubble bursting and jetting, cf. Fig. 8. Opposite to previous
studies, they did not observe violent shattering of freezing droplets into many fragments. The relative and
420 absolute frequency of the secondary processes did not only depend on droplet size and temperature, but also on
droplet ventilation and the presence of solid inclusions or dissolved salts. The effect of solid inclusions
(polystyrene latex particles) was twofold. While they suppressed droplet shattering upon freezing of large
($d=300\mu\text{m}$) drizzle droplets (Lauber et al. 2018), they strongly enhanced droplet shattering in small ($d=80\mu\text{m}$)
drizzle droplets (Pander et al. 2015). Large droplets were found to shatter at ~~warm~~ higher temperatures and
425 much more frequently when suspended at terminal air velocity compared to being suspended in stagnant air
under otherwise identical conditions (Keinert et al. 2020). Dissolved sea salt hindered droplet shattering at all
sizes at concentrations above about 100 mg/L. It is reasoned that dissolved substances and solid inclusions are
expelled from the growing ice phase and concentrate in the liquid phase during freezing. Here, they hinder the
formation of a monocrystalline ice shell. So, on one hand, this reduces the pressure needed for breakup, but on
430 the other hand may open pathways for pressure release prior to breakup. Pressure release events such as jetting
or spiking have been found to occur. Once high concentrations of dissolved gases build up in the liquid phase
of the droplet interior, pressure release induces gas bubble formation in the droplet interior. These bubbles may
escape through spikes or cracks in the ice shell giving rise to bubbles. Upon freezing of the bubble skin, the

430

435 skin breaks and may form a source of additional tiny ice particles. Even though bubble bursting has been found
to be a frequent secondary ice process (Pander et al. 2015; Lauber et al. 2018), the number of emitted ice
particles has not been quantified up to date. Droplet ventilation had a major influence on secondary ice process
frequency and type (Keinert et al 2020). Droplets moving at terminal velocity with respect to the surrounding
air generally showed more frequent secondary ice processes when compared to droplets levitated in stagnant
440 air. The dominant process observed shifted from cracking at stagnant conditions to breakup under free fall
conditions. The latter could be observed even at temperatures warmer than -5°C .



445 **Figure 9.** High-speed video snapshots of a 2mm drop at different stages of freezing. The pictures show progressive
increase of the number of cracks covering the drop during its freezing. The yellow arrows indicate the locations of ice
splinters ejected during cracking. The ambient temperature $T=-7^{\circ}\text{C}$. The numbers in the top left corners indicate time
since nucleation. Adapted from video V2 from the supplementary material to Wildeman et al. (2017).

450 **King and Fletcher (1973)** hypothesized that the numerous discontinuities in the pressure changes inside the
freezing drops are indicative of the large-scale movements of the ice shell, and therefore, it may be a source of
particles, even if the droplet does not shatter. This hypothesis was confirmed in experimental studies of droplet
freezing by Wildeman et al. (2017). The production of ice splinters during cracking of 2mm freezing drop was
documented in the supplementary high-speed video V2. Visual analysis of this video allowed for the
identification of several ice splintering events during cracking prior to final droplet shattering. Four of those

455 events are shown in Fig. 89. In general, the number of secondary ice particles due to droplet cracking during freezing could be formulated as the product of the number of cracking events per freezing event and the average number of secondary particles per cracking event. However, the actual number of splintering during cracking events may be higher in comparison to those observed visually. This is because microphotography allows for the detection of only those splinters that occurred within the depth-of-field of the microscope or whose sizes were larger than the detecting threshold of the optical system, and because not all cracking events
460 are detectable by optical microscopy.

Splintering during cracking is an important finding, since it shows that freezing droplets may be a source of secondary ice even though they do not shatter by the end of freezing.

2.8 -Summary

465 The review of the laboratory studies showed that the fragmentation of freezing drops is sensitive to a large number parameters such as: (a) droplet size D , (b) environmental temperature T_a , (c) droplet nucleating temperature T_n , (d) air pressure P , (e) type of ice mesh formed during the recalescence stage (dependant on T_n), (f) crystalline nature of freezing droplet (i.e. monocrystalline or polycrystalline), (g) thermal conductivity of surrounding medium K ; (h) size of nucleating particle (small INP vs large ice particle, affects polycrystallinity); (i) ventilation $f(D, T_a, P)$ (e.g. static air, ~~free fall~~, drop rotation during freezing), ~~(h, free fall)~~, (j) fall velocity ~~(dependant on $u_z(D \text{ and } T_a, P)$)~~, ~~(i)~~; (k) dissolved gases (specifically CO_2 , ~~dependant~~ dependent on T_a and P). Several types of ice fragmentation during droplet freezing were documented: (a1) splitting with few fragments, (b2) explosive shattering with multiple fragments, (e3) cracking-splintering, (d4) bubble bursting, (e5) jetting. Unfortunately, the dependency of ice fragmentation
475 during droplet freezing on the above parameters remains ~~poorly~~ only partially understood ~~or unknown~~.

A review of the laboratory studies on droplet freezing showed a large diversity of obtained results. The summary of the laboratory studies on droplet fragmentation during freezing is shown in Table 1. Thus, for a single experimental setup under the same conditions, the number of fragments formed for the same size drop during its freezing varied from zero to a few hundred. Similarly, under the same laboratory conditions, studies
480 observed that only a fraction of the droplets shattered, whereas the other fraction did not produce any fragments. This suggests that the laboratory experiments might contain hidden non-controlled parameters, which hindered obtaining reproducible results for each freezing droplet.

One of these parameters may be the orientation of the crystallographic axis of the INP with respect to the droplet surface at the moment of nucleation (Fig. 10a,b,c). Since the growth rate of ice along the a - and c -axes is different (e.g. Macklin and Payne, 1968), the process of the droplet filling with the ice network during the recalescence stage may create a different types of non-uniform temperature distribution of temperature inside the droplet, and ultimately affect the symmetry of the ice shell. In the case of a polycrystal INP it is expected

that during the recalescence stage a droplet will be filled by the ice network more uniformly (Fig. 9e10c) as compared to a monocrystalline INP (Fig. 10ab).

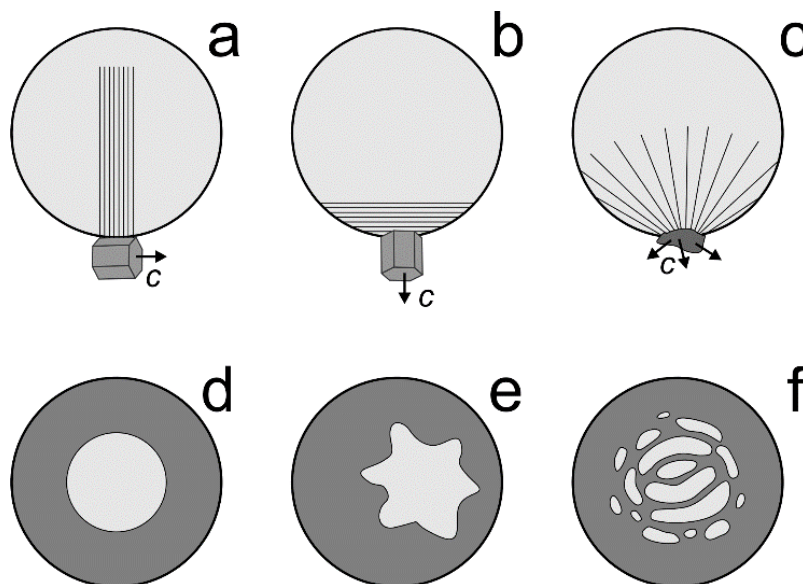
490 Humidity of the surrounding environment may be another hidden aspect affecting SIP- (Keinert et al 2020). Depending on the humidity level, the droplet may either grow or evaporate prior to nucleation. This may create additional temperature gradients at the droplet surface depending on its diameter. The near-surface temperature gradients may either hinder or facilitate the formation of the ice shell.

495 The topology of liquid volumes inside the freezing drop may also be an important factor for SIP. Thus, the cracking rate may be affected by the symmetry of the ice shell as well as the displacement of the liquid core with respect to the droplet center (Fig. 10d,e). The tensile stress formed in the ice shell is also expected to depend on how liquid water volumes are distributed across the freezing droplets: inside one big (Fig. 10d,e) or multiple small volumes (Fig. 10f). Unfortunately, no attention was given to this effect in previous laboratory studies.

500 There are a number of other parameters which received little attention in laboratory experiments that include: (a) size distribution of ice fragments, (b) minimum size of splinters, which may form during fragmentation, (c) minimal size for droplets to shatter, (d) effect of the angle between the *c*-axis and the droplet surface on ice shell formation, (e) humidity of the air.

505 Growing evidence from in-situ observations (e.g. Korolev et al. 2004, 2020; Rangno, 2008; Lawson et al. 2017) suggests that fragmentation during droplet freezing is an important SIP contributor to the concentration of cloud ice particles. Unfortunately, the diversity of laboratory results related to fragmentation during drop freezing hinders the development of a quantitative description and refined theory of this mechanism in order to use in cloud simulations. A variety of parameters and fragmentation types makes the experimental studies and quantification of this mechanism a challenging and intricate problem.

510



515 **Figure 10.** A conceptual diagram showing different possibilities of freezing of a supercooled droplet after nucleation by (a) monocrystalline INP or ice crystal with c-axis parallel to the droplet surface; (b) monocrystalline INP or ice crystal with c-axis perpendicular to the droplet surface; (c) polycrystalline INP- or ice crystal. The visuals in (d, e, f) show various possible topologies of liquid zones formed during freezing: (d) idealized spherical liquid volume symmetrically centered with the ice shell (frequently used in numerical simulations of droplet freezing); (e) non-symmetrical liquid volume displaced towards the ice shell wall; (f) multiple disconnected liquid volumes.

520

Table 1. Summary of experimental studies of droplet fragmentation during freezing by different research groups. The table covers only works that quantified the parameters included in the table.

Reference	Diameter (µm)	Temperature (°C)	Droplet suspension	Method of nucleation	Maximum SIP frequency (%)	max number fragments per drop	Temperature of maximum SIP rate
Mason and Maybank, 1960	30-1000	-2 to -25 ¹	stagnant (fiber)	various ²	47	200	-10°C
Adkins, 1960	4-13	n/a ³	free fall	natural ⁴	0	0	n/a
Hobbs and Alkezweeny, 1968	20-150	-8 to -32	free fall	various ⁵	>5	n/a	no temperature dependence
Brownscombe and Thorndike, 1968	50-90	-5, -10, -15	free fall	tiny ice crystals	14	12	-15°C
Dye and Hobbs, 1968	1000	-3 to -15	stagnant (fiber)	tiny ice crystals	0	1	no temperature dependence
Johnson and Hallett, 1968	1000	-5 to -20	stagnant (fiber) +ventilation	tiny ice crystals	>1	n/a	no temperature dependence
Takahashi and Yamashita, 1969	600-800	-18 to -25	free fall	immersion ⁶	11	n/a	-15°C
Takahashi and Yamashita, 1970	75-350	0 to -30	free fall	tiny ice crystals	37	n/a	-15°C
Takahashi, 1975	45-765	-4 to -24	free fall	tiny ice crystals	35	n/a	-16°C
Pruppacher and Schlamp, 1975	410	-7 to -23	airflow	contact ⁷	15	>3	-11°C to -15°C
Bader et al., 1974	30, 42, 84 ⁸	-10 to -30	free fall	immersion ⁹	?	10	n/a
Kolomeychuk et al., 1975	1600	-12 to -25	airflow ¹⁰	natural ⁴	35	142	-15°C to -18°C
Lauber et al., 2018	300 -320	-5 to -30	stagnant (EDB)	tiny ice crystals	35	12	-7°C to -13°C
Keinert et al., 2020	300- 320	-1 to -30	stagnant (EDB), airflow	tiny ice crystals	1	3	-10°C to -15°C

1. ice nucleation temperature 0°C to -15°C
2. natural nucleation, silver iodide, contact tiny small ice crystals
3. not available
4. no special efforts were made to nucleate droplets
5. natural or immersed silver iodide
6. kaolinite or silver iodide
7. kaolinite or montmorillonite
8. mean volume diameter
9. silver iodide
10. flow of humidified nitrogen

525

530

3. Splintering during riming

3.1 Efficiency of rime splintering

535 Splintering during ice particle riming is another mechanism that can explain SIP. Macklin (1960) observed splinter production in a small wind tunnel during the collection of droplets on an icing rod with 0.6cm diameter at temperatures $-5^{\circ}\text{C} < T_a < -20^{\circ}\text{C}$. The droplet diameters in their size distribution varied from several to $140\mu\text{m}$ ($\text{MVD} \sim 67\mu\text{m}$) and their speed changed from 2m/s to 12m/s. A microscopic examination revealed long spicules and a few micrometer-sized ice features formed on the surface of the rod. The small fragile formations were hypothesized to be a source of the splinters. The ice crystal concentration during experiments 540 was frequently observed to increase by a few orders of magnitude, reaching values of the order of 10^{-1}cm^{-3} at temperatures as high as -5°C .

Latham and Mason (1961) observed riming of freezing droplets on the hailstone simulator, accompanied by the ejection of ice splinters. They established that the splinter production varied with the air temperature, drop diameter and impact velocity. A maximum production rate of 14 splinters per droplet, was observed in droplets 545 with diameter $70\mu\text{m}$, impacting at 10 m/s at a temperature of -15°C .

Hobbs and Borrows (1966) and Aufremermaur and Jonson (1972) studied charge separation between an ice target and the flow of cloud particles on impact with each other. However, no significant ice splintering was found in both experiments. Hobbs and Borrows (1966) argued that the high rate of splintering observed by Latham and Mason (1961) may be related to carbon dioxide, which might be present in the experimental setup. 550

Bader et al. (1974) observed rime splintering during accretion of monodisperse droplets on a small copper target. The experiments were conducted for the ambient temperature ranging from $-15^{\circ}\text{C} < T < -9^{\circ}\text{C}$. Droplets fell at terminal velocity and deposited on the rimer. The number of accreted droplets per ejected ice splinters decreased from 2000 for droplets of $56\mu\text{m}$ diameter to 200 for droplets of $100\mu\text{m}$ diameter. These numbers correspond to 5 and 10 ice particles per milligram of rime, respectively. Ice particles were only ejected when 555 there was an open chain-like structure on the rimer surface. However, no ice fragments were seen when water accretion was high enough to give a completely glazed deposit. The latter was likely associated with reaching the Ludlam limit (Ludlam, 1951).

Later, Hallett and Mossop (1974) and Mossop and Hallett (1974) observed splinter formation during riming in the cloud chamber with liquid water content $\sim 1\text{g/m}^3$ and droplet concentration 500cm^{-3} . They found that 560 splinter production is active in the temperature range $-8^{\circ}\text{C} < T_a < -3^{\circ}\text{C}$. Furthermore, the rate of splinter production had a pronounced maximum at the air temperature of -5°C and the drop impact velocity 2.5m/s (Fig.11). At these conditions, one splinter was produced per 250 droplets of diameter $D > 24\mu\text{m}$. The phenomenon of splinter production during riming is usually referred to as the Hallett-Mossop (HM) mechanism.

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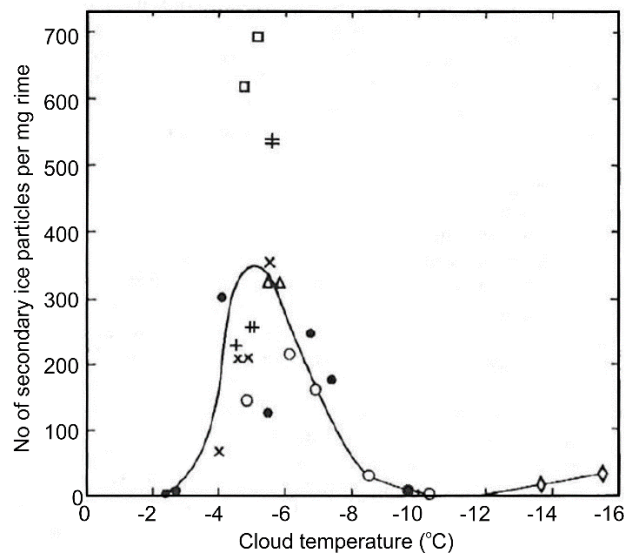


Figure 11. The dependence of the number of splinters per mg of rime on ambient temperature at speed 2.7m/s obtained experimentally by Hallett and Mossop (1974).

570 Mossop (1978, 1985) found that the presence of droplets with $D < 12 \mu\text{m}$ in addition to those $D > 24 \mu\text{m}$ increases the splinter production further. Saunders and Hosseini (2001) studied the splinter production in a wider range of impact velocities of up to 12m/s. They found that the maximum secondary ice ejection occurs at 6m/s with the number of splinters nearly five times lower than it was found in the Hallett and Mossop (1974) and Mossop and Hallett (1974) experiments.

575 The amount of dissolved gases is typically not specified in most laboratory experiments. Even if equilibrium has been reached, in nature this amount might depend on the chemical composition of the droplet, e.g. cloud droplet pH value.

Heymsfield and Mossop (1984) studied the effect of the rimer surface temperature on the production of secondary ice particles. They found that raising the surface temperature of the riming particle by 1°C transposes the splinter production curve virtually unchanged to air temperatures 1°C lower. This led them to conclude that splinter production due to the HM-mechanism may occur at air temperatures lower than -8°C depending on liquid water content (LWC) and the rimer fall velocity, which are the main factors determining the surface temperature of the riming particle. This conclusion is consistent with earlier work by Foster and Hallett (1982).

585 The quantification of the rime splintering production obtained from the experimental studies of Hallett and Mossop created a basis for various formulations of SIP parameterizations (e.g. Cotton et al. 1986; Meyers et al. 1997; Reisner et al, 1998 and others), which are widely used in numerical simulations of clouds.

3.2 Physical mechanism of rime splintering

Several studies are aimed at understanding the physical mechanisms responsible for splinter production. For instance, Macklin (1960) documented that fine ice structures formed during riming could be easily detached from the rimer and form splinters. One of these fine ice features are shown in Fig.12a.

Mossop (1976) proposed four possible mechanisms responsible for the HM-process: (1) formation of ice shell around accreted droplets with its subsequent fragmentation during freezing; (2) detachment of droplets that make glancing contact with rime; (3) growth and subsequent detachment of frail ice needles at
595 temperatures around -5°C ; (4) detachment of rimed ice by evaporation (see section 6).

Choularton et al. (1978, 1980) suggested that, if droplets $D > 25\mu\text{m}$ are accreted to the ice substrate by a thin neck, they will minimize the heat transfer toward the rimer. This arrangement may induce symmetrical heat loss to the air, which then leads to the formation of a complete ice shell around a droplet as it freezes. The freezing of liquid will result in a pressure build up inside the droplet which may cause shell disruptions with
600 subsequent production of fragile protuberances of frozen water (Fig.12b). Mossop (1980) credited this hypothesis by pointing out that the ice shell is weakened by the presence of ammonia and results in a reduced number of protuberances and splinters. He also showed that the increased ammonia concentration in droplets results in a reduction of the rate of splinter production. Griggs and Choularton (1983) suggested that the cut-off at about -8°C is due to ~~the more~~ rapid growth of the ice shell, which is too strong to be disrupted by the
605 internal pressure.

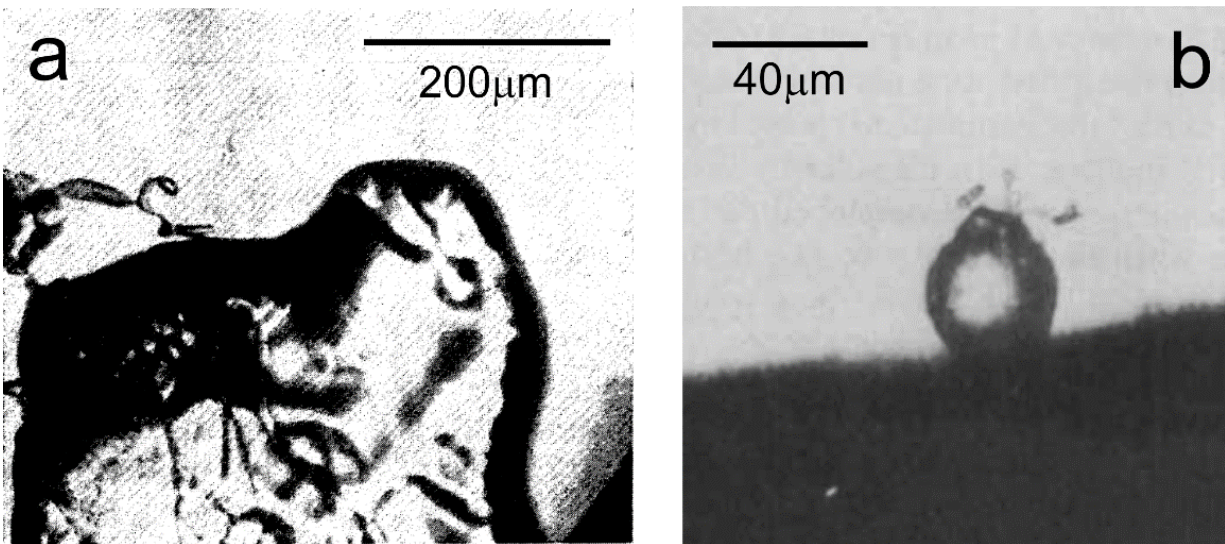


Figure 12. Pictures of the rime fragments: (a) frozen splash observed at $T_a = -6^{\circ}\text{C}$ and speed 6m/s (Macklin, 1960); (b) disruptions of protuberances formed out of a $35\mu\text{m}$ rimed droplet at $T_a = -7^{\circ}\text{C}$ and speed 1.5m/s (Choularton et al. 1980)
610

Dong and Hallett (1989) reported that after impact with ice, droplets tend to spread over the surface of ice at all temperatures above -8°C . They concluded that splinter production by pressure build-up inside individual frozen droplets is unlikely to be responsible for the shattering. They suggested that fragmentation is associated with the stress build up within an accreted droplet. This occurs when the droplet experiences a temperature
615 gradient between the colder substrate and the surface of the droplet, freezing at 0°C . However, the absence of protuberances, when the droplets rime onto an ice surface above -10°C , contrasts with the observation of

Choulaton et al. (1980) who showed photographs of discrete frozen droplets together with protuberances obtained in the temperature range -3°C to -7°C (Fig.12b).

620 Emersic and Connoly (2017) studied microscopic riming events on an ice target using a high-speed video recording. The droplet sizes ranged from 5 to 50 μm . It was found that the droplet behavior on impact depends on the uniformity of the rimer surface. Thus, droplets tend to spread flat on flat ice surfaces at temperatures associated with the HM-process, as was earlier observed by Macklin and Payne (1969) and Dong and Hallett (1989). However, with increasing rime depth, which is more commonly associated with graupel, growing rime spires protrude from the surface into the airflow around the rimer. No protuberances or liquid ejection was
625 observed during the riming process, nor was any mechanical rime splintering event observed in approximately 1300 droplet freezing events. Based on the results of their study, Emersic and Connoly (2017) hypothesized that the rime spikes that develop with continuing droplet accretion could break off during particle tumbling or hinging by small droplets.

3.3 Summary

630 The literature review showed that, apart from some early studies (Hobbs and Borrows, 1966; ~~Aufreimand~~Aufreimaur and Jonson, 1972), most laboratory experiments on the HM-process confirmed splinter production during riming. However, there was no consistency in the rate of the rime splintering observed by different groups. This can be clearly seen from Table 2 summarizing main laboratory results of the HM-process studies. This discrepancy is most likely related to different laboratory setups and techniques
635 used for splinter counting.

The analysis of laboratory studies suggests that the efficiency of secondary ice production during the HM process depends on (a) air temperature T_a (max efficiency at $-8\text{C} < T_a < -3\text{C}$); (b) surface temperature of the rimer T_s (depends on u_z and LWC); (c) size L_{rm} and density ρ_{rm} of the rimer; (d) fall speed of the rimer u_z (determined by the size and density of the rimer and air density $u_z(L_{rm}, \rho_{rm}, \rho_a)$); (e) droplet size distribution
640 $F(D)$. The condition applied to $F(D)$ requires presence of droplets with $D > 24\mu\text{m}$ and $D < 12\mu\text{m}$. Another condition for $F(D)$ limits maximum LWC by the Ludlam limit (Ludlam 1951) when the rimer growth will turn into wet growth. In this case, the rimer's surface will be covered by a layer of liquid water, which will suppress splintering.

To conclude this section, it should be emphasized that after several decades of rime splintering studies, the
645 physical mechanisms behind this phenomenon are still under debate. Without clarifying the nature of this process, a development of a physically based parameterizations for numerical simulations of clouds does not seem to be feasible.

Table 2. Summary of experimental studies of droplet fragmentation during freezing by different research groups. The table covers only works that quantified the parameters included in the table.

Reference	Diameter (μm)	Temperature (°C)	velocity (m/s)	Maximum rate of SIP (#splinters/mg)	Temperature of maximum SIP rate (°C)	Velocity of maximum SIP rate (m/s)
Latham and Mason, 1961	20-120	-2 to -18	0 to 30	~8000 ¹	-8 to -18	5 to 15
Hobbs and Borrows, 1966	30-70	-4, -8	4 to 11	0	n/a ²	n/a
Aufrermaur and Jonson, 1972	20-100	-5 to -15	10	0	n/a	n/a
Bader et al., 1974	56-100	-9 to -15	free fall	10	n/a	n/a
Hallett and Mossop, 1974 Mossop and Hallett, 1974	<35	-2 to -16	0.7 to 3.1	700	-5	1.5
Mossop et al., 1974	15+50	-8, -10	0.8	0.24	-8	n/a
Mossop, 1976	3-45	-5	1.4 to 3	<550 ³	n/a	1.4 to 3
Heymsfield and Mossop, 1984	2-40	-2 to -9	1.8	220	-4 to -6 ⁴	n/a
Mosop, 1985b	5-40	-2 to -8	0.55 to 5	300	-4.3	2 to 4
Saunders and Hosseini, 2001	5-40	-5 ⁵	1.5 to 12	70	n/a	6

1. 14 splinters per droplet 70μm diameter
2. not available
3. 1 splinter per 250 droplets >24μm diameter
4. depending on LWC
5. rimer surface temperature

4. Fragmentation due to ice-ice collision

660 Collision of ice particles may result in their mechanical fragmentation and production of secondary ice (Langmuir, 1948, p.186). This hypothesis was stimulated by observations of ice particle fragments collected during airborne (e.g. Hobbs and Farber, 1972; Takahashi, 1993) or ground-based (Justo and Weickmann, 1973) studies.

665 There were only two known laboratory works on collisional ice fragmentation. Vardiman (1978) explored fragmentation of natural cloud ice particles on impact with a metal mesh. He found that “graupel is surprisingly ineffective in generating fragments”. However, light to moderate rimed spatial crystals are the most efficient source of ice fragments. For planar crystals, the degree of fragmentation increases with the degree of riming.

670 Takahashi et al. (1995) studied the dependence of mechanical fragmentation resulting from collision of 2cm in diameter rimed ice spheres. The ice spheres were attached to the edges of 10cm long spinning metal rods- ~~The ice spheres~~ and were made to collide with each other at a speed of 4m/s. ~~These speeds were~~ This speed was used to simulate a collision of a 4mm diameter lump graupel with a density of 0.3-0.4g/m³. The collisional force changed incrementally from 20dyn to 500dyn. Takahashi et al. found that the number of fragments depends on the degree of riming, temperature, and collision force. The maximum number of fragments per collision (up to 800) was observed at -16C.

675 It is hard to judge the consistency of the results obtained by Vardiman (1978) and Takahashi et al. (1995) because of the differences in the experimental setups and environmental conditions. It is also difficult to identify the degree of applicability of the rate of SIP obtained in these experiments to free falling ice particles grown in natural clouds.

680 Collisional ice fragmentation was also studied theoretically- by Hobbs and Farber (1972), Vardiman (1978), ~~Phillips~~Phillips et al. (2017)). These studies were based on the consideration of collisional kinetic energy and linear momentum. Such considerations would be relevant only for cases of direct central impact. In a general case, angular momentum and rotational energy should be taken into consideration. Since oblique particle collisions are more frequent than central collision, the efficiency of SIP obtained in these works is expected to be overestimated.

685 The theoretical considerations of collisional fragmentation in Yano and Phillips, (2011), Yano et al. (2016) and Phillips et al. (2017) were based on the rate of ice production from Takahashi et al. (1995). A detailed analysis of the Takahashi et al (1995) laboratory setup indicated that the riming of ice spheres occurred in still air, which resulted in more lumpy and fragile rime compared to that formed in free-falling graupel. The collisional kinetic energy and the surface area of collision of the 2cm diameter ice spheres also significantly
690 exceed the kinetic energy and collision area of a few mm sized graupel. Altogether, it may result in overestimation of the rate of SIP, compared to graupel formed in natural clouds.

It should also be mentioned that ice particle fragments observed in-situ (e.g. Hobbs and Farber, 1972) may be a result of particle breakups induced by the sampling instrument- (see section 8). Schwarzenboeck et al. (2009) identified that 18% of observed incomplete dendrites are the result of natural fragmentation. The
695 identification of natural fragments was based on the observation of the ice shapes near the expected break area, which were interpreted as “subsequent growth”. However, it could be argued, that incomplete dendrites may naturally form because of growth suppression of one or more branches due to defects or dislocations on the crystal. Examples of 1-, 2-, 3- and 4-branched stellar and dendritic crystals with underdeveloped defected branches were documented by Bentley and Humphreys (1962, pl.198-204), Auer (1970, Figs.9,28,30), Kikuchi
700 and Uyeda (1978, Fig.2).

The analysis of literature suggests that the efficiency of SIP during ice-ice collision depends on (a) properties of the colliding particles, such as size, mass, density, shape, surface roughness; (b) air temperature T_a (determines physical properties of ice, e.g. crispness), (c) relative fall velocity of colliding particles (depends on the aerodynamic size of particles and air density).

In summary of this section, it can be concluded that the efficiency of SIP during ice-ice collisional
705 fragmentation remains uncertain due to the lack of laboratory studies. No parameterizations of SIP due to ice-ice collisional fragmentation can be developed at that stage based on two laboratory observations, whose results are conflicting with each other. Additional laboratory studies are required to explore ice-ice collisional fragmentation of free-falling ice particles with different habits. Ice fragments observed in-situ should be
710 considered with caution due to potential particle breakups during sampling (see Section 8).

5. Fragmentation due to thermal shock

When a supercooled drop rimes on the surface of an ice crystal, it freezes, and its temperature rises to the melting point (section 2). Some fraction of the latent heat released during freezing will be transferred into the
715 ice crystal. This may cause a thermal shock at the location of the droplet attachments and fragmentation due differential expansion of the ice crystal (Koenig, 1963, p.35).

Dye and Hobbs (1968) observed during laboratory experiments that, when an ice crystal on some occasions became attached to a freezing drop, it would often break into 5 to 10 pieces as the drop froze. Sometimes, the breakup of the crystal would occur when the drop cracked. On other occasions the crystal would break without
720 any apparent changes to the freezing drop. They concluded that breaking up ice crystals, which collide with and nucleate supercooled drops, may play important role in increasing concentration of ice particles in natural clouds.

Hobbs and Farber (1972) observed in the laboratory shattering of a dendritic crystal into several pieces after bringing it in contact with 2mm diameter supercooled drop. This observation is of considerable interest, for it
725 suggests that the breaking up of ice crystals that collide and nucleate supercooled drops, may play an important role in increasing the concentration of ice particles.

From his lab experiments, Gold (1963) found that the surface temperature shock of 6°C is necessary to produce the stress required for ice cracking.

730 Using thermoelastic theory, King and Fletcher (1976a) calculated thermal stresses in idealised ice shapes on impact with liquid droplets, when a small area was warmed to 0°C. They concluded that a thermal shock mechanism is unlikely to be responsible for SIP at temperatures $T_a > -5^\circ\text{C}$.

King and Fletcher (1976b) conducted a series of experiments to study the effect of thermal shock on cracking of macroscopic polycrystalline spheres ($D \sim 2\text{-}3\text{cm}$) and thick ($\Delta h = 1.7\text{cm}$) and thin ($\Delta h = 1\text{-}2\text{mm}$) cylindrical plates with diameter $b = 5\text{cm}$ at temperatures down to -40°C . The cracking probability of ice plates 735 versus temperature was studied for several ratios $a/b = 0.2, 0.4$ and 0.6 , where a is the diameter of the heated area. In such arrangement the thermal shock is expected to be more severe than that experienced by microscopic ice crystals during riming. Depending on the thickness of the plates and the ratio a/b , the cracking temperature threshold varied from -5°C to -35°C . None of the plates fragmented or separated. King and Fletcher concluded that thermal shock is unlikely to be an important ice multiplication mechanism at 740 -5°C .

Experiments using thermal shock with macroscopic slabs and spheres by King and Fletcher (1976b) are not fully scalable down to microscopic monocrystalline ice particles. Moreover, the conclusions obtained in their studies are not consistent with the laboratory observations of Gold (1963), Dye and Hobbs (1968) and Hobbs and Farber (1972).

745 The review of the studies of SIP due to fragmentation of ice particles due to thermal shock depends on (1) air temperature T_a ; (b) mass and shape of ice particle; (c) droplet diameter; (d) local geometrical configuration of ice particle at the location of the droplet attachment; (e) relative velocity of droplet and ice particle at the moment of impact (determines thermal connection of the droplet and ice particle); (f) ventilation (determines convective heat losses to the air).

750 Despite the seeming feasibility of this SIP process to occur in natural clouds, this phenomenon got little attention from the cloud physics experimental community. Based on the previous experimental and theoretical studies, the efficiency of ice fragmentation due to thermal shock is expected to primarily depend on the air temperature, droplet size, ice crystal size and its habit. Unfortunately, none of these dependencies have been addressed experimentally. Therefore, the effect of thermal shock ice fragmentation on SIP remains 755 inconclusive.

6. Fragmentation of sublimating ice particles

Ice particle fragmentation and formation of secondary ice may occur during sublimation in ~~undersaturated cloud regions~~ subsaturated cloud regions. Mossop et al. (1974, section 4c) observed sublimation of rime under 760 the microscope. They reported detachment of $20\mu\text{m}$ size rime particles from their original locations and identified it as an “unexpected phenomenon”, which may explain SIP.

Oraltay and Hallet (1989) studied evaporation of ice particles suspended on a fiber at a wind speed emulating their fall velocity. They observed the fragmentation of dendritic ice shapes at subfreezing temperatures only when relative humidity over ice was $RH_i < 70\%$ and ventilation velocity was 10 to 20 cm/s. However, no sublimation breakup was observed for columnar and plate-like crystals. Dong et al. (1994) studied fragmentation of rimed ice and needles at $50\% < RH_i < 90\%$, $-18^\circ\text{C} < T_a < -5^\circ\text{C}$ and ventilation speed $\sim 1\text{m/s}$. In their experiments, they found that a few mm long rimed ice particles may generate up to 100 fragments during evaporation at $RH_i < 70\%$ within 1-2 minutes.

Bacon et al. (1998) studied fragmentation of sublimating ice particles suspended in electrodynamic balance inside a thermo-diffusional chamber at $85\% < RH_i < 100\%$ and $-30^\circ\text{C} < T_a < 0^\circ\text{C}$. The observed fragmentation tended to affect prolate ice particles with an aspect ratio higher than 3. An example of images of sublimating ice particle is shown in Fig.13. All three studies concluded that breakup rates depend on temperature and humidity, but largely on the initial shape of the ice particle.

During in-situ observation of metamorphosis of shapes of sublimating ice particles in natural clouds, Korolev and Isaac (2004) came to a conclusion that ice particle fragmentation during sublimation does not play an important role in SIP.

The laboratory experiments suggest that fragmentation of ice particles depends on (a) ice particle shape and size; (b) relative humidity; (c) pressure; (d) air temperature; (e) air temperature T_a ; (f) fall velocity and ventilation coefficient.

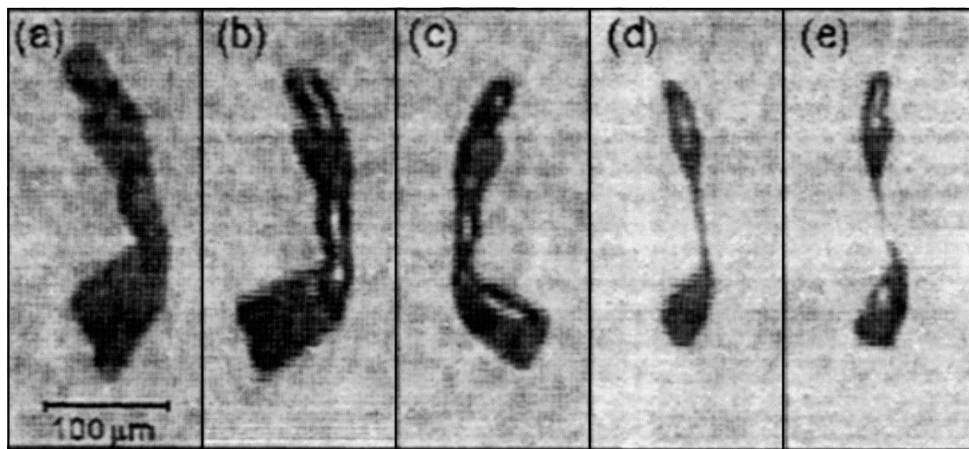


Figure 13. A sequence of images of a sublimating ice particle levitated in an electromagnetic balance. Time before breakup (a) 6 min, (b) 4 min, (c) 2 min, (d) 20 s, and (e) at the moment of breakup (Bacon et al. 1998).

In order for the ice fragments formed during sublimation to result in ice multiplication, they have to re-enter back into a supersaturated cloud region. Since small ice fragments have lower terminal fall velocity, their residence time in the undersaturated environment may be long enough to result in their complete evaporation before they can re-enter a supersaturated environment. This appears to be a significant limitation of the SIP mechanism due to sublimation breakup. This mechanism is also unlikely to explain explosive concentrations

of small ice crystals frequently observed in convective and stratiform frontal clouds (e.g. Lawson et al., 2017;
790 Korolev et al, 2020).

7. Activation of INPs in transient supersaturation around freezing drops

Muchnik and Rudko (1961) and Dye and Hobbs (1968) reported observation of a halo of small droplets
formed around a freezing drop immediately after the moment of its nucleation. Dye and Hobbs (1968)
795 explained the origin of small droplets by the activation of CCNs in the region of high transient¹ supersaturation
formed around freezing droplets. After ice nucleation, the droplet surface temperature T_s rises to 0°C. Under
the condition that the surrounding air has $T_a < 0^\circ\text{C}$, the surface of the freezing drop acts as a source of water
vapor to a colder environment. The resulting water vapor diffuses radially outward. Depending on the air
humidity, it may create at some distance from the droplet a region with supersaturated air. Nix and Fukuta
800 (1974) developed a theoretical framework for the calculation of the supersaturation field around a stationary
freezing drop-, which was determined by molecular diffusion. They showed that maximum supersaturation
increases with the decrease of T_a and the increase of drop size.

Cheng (1970) attempted to explain the origin of small droplets due to their ejection from the freezing drop.
However, this explanation was challenged by Hobbs (1971). Rosinski et al. (1972) also described laboratory
805 results refuting Cheng's interpretation of the halo around freezing drops.

Later, Gagin (1972) proposed a mechanism explaining SIP due to activation of INP in high transient
supersaturation area around freezing drops. He argued that high supersaturation may result in activation of
insoluble INPs, which normally do not activate at typical cloud supersaturation levels ($SS < 1\%$).

Rosinski et al. (1975) studied activation of silver iodide and soil particles placed on a flat plate at different
810 distances from 2mm freezing drops. They found that silver iodide nucleated as water at temperatures $T_a > -9.8^\circ\text{C}$,
and as ice at $T_a < -9.8^\circ\text{C}$. Soil particles with sizes 20 μm and 40 μm nucleated as water at temperatures -20°C and
 -16°C , and as ice at ~~colder~~ lower temperatures, respectively. Rosinski et al. concluded that "production of ice
particles by- condensation-followed-by-freezing in a parcel of a cloud containing large freezing drops is orders
of magnitude higher than by contact nucleation".

815 Gagin and Nozyce (1984) suspended 1mm-2mm diameter drops inside a gradually cooling chamber. The
drops froze at a mean temperature -6.5°C as they contained silver iodide. Complete drop freezing occurred in
5-6 minutes, when the ambient temperature decreased down to -10°C -12°C . From the aerosol in the ambient
air they found that during drop freezing –on average 1.6-2.1 ice crystals were activated around freezing drops.
The nucleation of ice crystals was attributed to supersaturation sensitive INPs.

820 ~~Nix and Fukuta (1974) performed calculations for a quasi-steady state case, where the transient
supersaturation was determined by molecular diffusion.~~ In laboratory experiments of Rosinski et al. (1975) and

¹ Some studies use the term "transitional".

Gagin and Nozyce (1984) the transient supersaturation in addition to the molecular diffusion was also contributed by a mixing with a convective flow, induced by the temperature difference between the drop surface and environment. None of the above studies accounted for a ventilation effect for free falling drops. In this regard, it was not clear whether the obtained results are applicable to natural clouds, since the mixing will occur in the wake of falling drops, and it will be mainly determined by turbulent mixing.

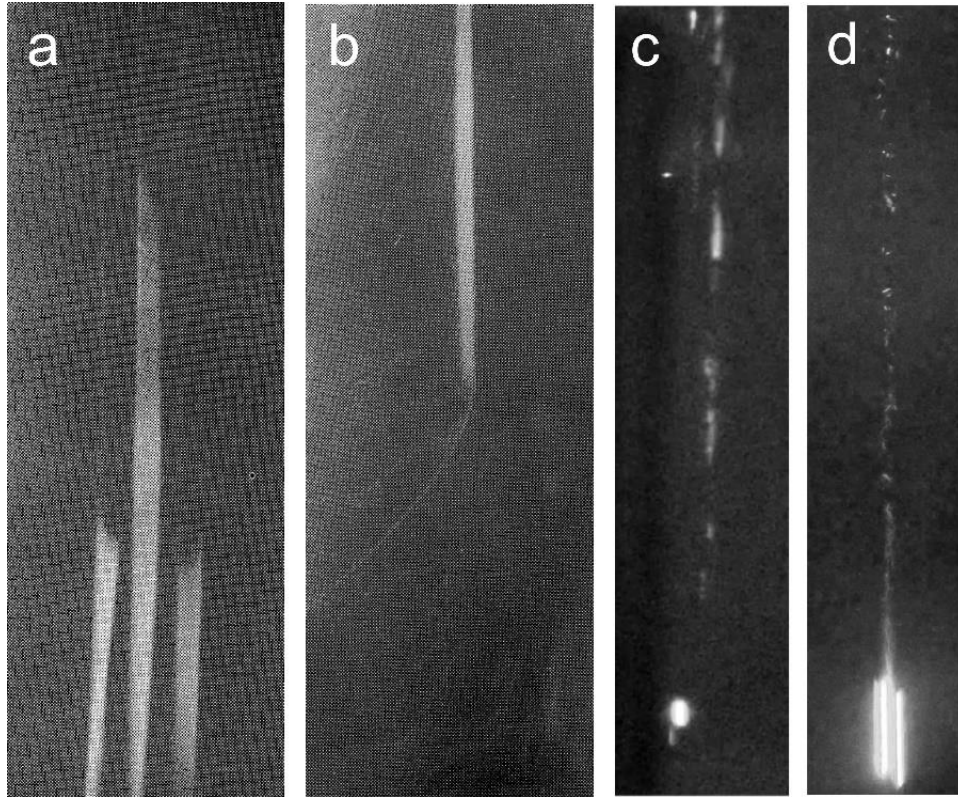


Figure 14. The trajectories of falling drops with $D = 100\mu\text{m}$ visualised by nucleation of CCN and INP in the high supersaturation formed around freezing drops at the moment of (a) initiation of freezing and (b) by the end of freezing at ambient temperature $T_a \approx -65^\circ\text{C}$ (Iwabuchi and Magono, 1975). Nucleation of water droplets and ice particles in the wake of falling with $D \approx 2\text{mm}$ (c) $T_a \approx -20^\circ\text{C}$, $RH \approx 60\%$, $0^\circ\text{C} < T_a < 2^\circ\text{C}$; (d) $T_a = 18^\circ\text{C}$, $RH=60\%$, $T_a=10^\circ\text{C}$ In these experiments AgI and of the Snomax were used as ice nuclei (Prabhakaran et al., 2020).

Iwabuchi and Magono (1975) in their experiments on freezing electrification documented formation of fog along the trajectories of $90\mu\text{m}$ - $160\mu\text{m}$ free falling freezing drops at $T_a=-65^\circ\text{C}$ (Fig.14ab). They used the fog formation to identify the start and end moments of the drop freezing.

Prabhakaran et al. (2020) conducted experiment experiments with a 2mm diameter free falling drops in the environment with $T_a=-18^\circ\text{C}$ and $RH=60\%$ - 80% . The experiments were conducted using Snomax and AgI aerosols induced into the ambient air. The drop temperatures varied in the range $0^\circ\text{C} < T_{dr} < +20^\circ\text{C}$. The high drop temperatures were used to enhance supersaturation and exaggerate ice nucleation in the undersaturated air. The free-falling drops formed fog trails consisting of activated cloud droplets and ice (Fig.14cd).

Nix and Fukuta (1974) also pointed out that hailstones during wet growth have a surface temperature close
845 to 0°C, and therefore they may act as a source of high supersaturation. Under such conditions, hailstones may
activate many more supersaturation sensitive INPs than a freezing droplet, since the affected volume in such a
case will be much larger. Fukuta and Lee (1986) performed calculations of supersaturation around falling
graupel with different sizes (2mm, 4mm, 6mm) at different ambient temperatures (-10°C, -20°C, and -30°C).
They found that ~~bigge~~larger graupel with larger sweeping volume has lower maximum supersaturation. Thus,
850 over 2mm and 6mm falling graupel maximum supersaturation with respect to water at -10°C, -20°C and -30°C
reaches approximately 10%, 40%, 100% and 5.5%, 23%, 35%, respectively. The finding that for falling
freezing drops maximum supersaturation is decreasing with the increase of the drop size is opposite to that for
stationary drops in Nix and Fukuta (1974).

Chouippe et al. (2019) performed direct numerical simulations (DNS) of a free-falling ice sphere in a
855 humid air accounting for heat and mass transfer. This study was focused on ~~the study of exploring~~ accuracy of
numerical simulation. It confirmed the conclusion obtained in previous studies that supersaturation increases
with the increase of the temperature difference $\Delta T = T_s - T_a$. ~~However, the effect of graupel size on~~
~~supersaturation was not discussed there~~Krayer et al. (2020) used the same model. They found that significant
values of supersaturation can be attained in the wake of warm hydrometeors, which persist long enough to be
860 observed at more than 50 particle diameters downstream of the meteor for sufficiently high differences in
temperature. The supersaturated volume of air exceeds the estimations by Fukuta and Lee (1986) by far, which
is attributed to the more accurate representation of the flow in the DNS model.

It is worth noting, that high transient supersaturation may form not only over a particle with a surface
temperature $T_s > T_a$. Similar effect may also occur over a graupel or hailstone, for which the surface
865 temperature did not reach equilibrium, and remains ~~cooler~~lower than the ambient air. Thus, Schaefer and
Cheng (1971, Fig.1a) observed initiation of ice around a simulated graupel with temperature ~~cooler~~lower 5°C
than the ambient air temperature. Unfortunately, no other details of the experimental setup were available from
their work.

The above studies suggest that the activation of INP is expected to grow with the increase of the
870 temperature difference ~~between T_s and T_a~~ $T_s - T_a$. However, Baker (1991) argued that even if T_a is as low ~~enough~~as
-15°C, the total volume with high supersaturation around all freezing ~~droplet~~isdrops remains too small
~~compared to regions with high~~enhance the number concentration of ice-active INP by several orders of
magnitude. Therefore, INP activation in transient supersaturation around freezing drops should have a low
significance for SIP. This, result ~~is~~seems to be conflicting with the conclusion obtained in Rosinski et al.
875 (1975) and Prabhakaran et al. (2020). It should be noted that Baker (1991) assessment of the SIP efficiency
was obtained for the static field of supersaturation around droplet and under the assumption, that the number
concentration of active INP follows a power law in supersaturation that could be extrapolated to a very high
supersaturation.

880 In summary of this section it can be concluded that efficiency of SIP due to INP activation in transient supersaturation depends on (a) droplet diameter D ; (b) air temperature T_a ; (c) droplet surface temperature T_s ; (d) droplet fall speed u_z ; (e) relative humidity RH ; (f) air density ρ_a ; (g) turbulence intensity ε ; (h) droplet freezing time (depends on $D, T_a, \rho_a, u_z, RH, \varepsilon$); (i) concentration and nucleation activity of interstitial INPs.

885 The studies described above provide experimental and theoretical support that activation of supersaturation sensitive INPs in the wake of free-falling freezing drops, wet hailstones or riming graupel is one of possible mechanisms of SIP. Unfortunately, due to limited experimental studies, the effect of INP activation around falling hydrometeors cannot be quantified and employed in cloud simulations. ~~The future~~Future laboratory studies should be focused on the behaviour of INP at very high ice supersaturation (>10) for a better the quantification of the effect of $T_{d\neq s} - T_a$ of a free-falling hydrometeor on the INP activation.

890 **8. Spurious enhancement of ice concentration during sampling**

In this section we discuss results of experimental studies of artificial fragmentation of ice particles during in-situ sampling. Artificial ice particle fragmentation may result in a significant enhancement of the measured ice concentration and be confused with SIP. Airborne in-situ measurements is the main source of information about the concentration of ice particles in natural clouds and the environmental conditions associated with SIP. 895 The accuracy of in-situ measurements of small ice particles is of great importance for the closure of SIP parameterizations and ~~feedbacking laboratory studies. In this section we discuss the issues of in-situ cloud particle sampling, which may result in artificial enhancements of measured ice concentration.~~provides feedback to laboratory studies.

At the initial stage of regular cloud observations with optical particle probes (Knollenberg, 1981) it was 900 found that small ice particles were observed in all ice clouds including precipitating and undersaturated cloud regions where existence of small particles conflicted with their small fall velocity and rapid sublimation, respectively. Such observations required developing additional mechanisms to explain the omnipresence of small ice crystals.

The hypothesis of enhanced ice concentration induced by airborne instruments has been discussed over a 905 long period of time. Larger ice particles may bounce off the forward probe's tips or inlet, and shatter into smaller fragments. After rebounding, the shattered fragments may travel into the probe's sample ~~are a~~volume and cause multiple artificial counts of small ice. Cooper (1977) was the first to recognize a potential significance of **instrumental** particle shattering and suggested filtering the shattered artifacts based on the characteristically short interarrival times between successive particles passing through the probe's sample 910 volume. Several following works based on comparisons between several airborne instruments (Gardiner and Hallett, 1985; Gayet et al., 1996) or analysis of the particles' interarrival time (Field et al., 2003) posed the question of whether the observed high concentration of ice particles is real or an artifact.

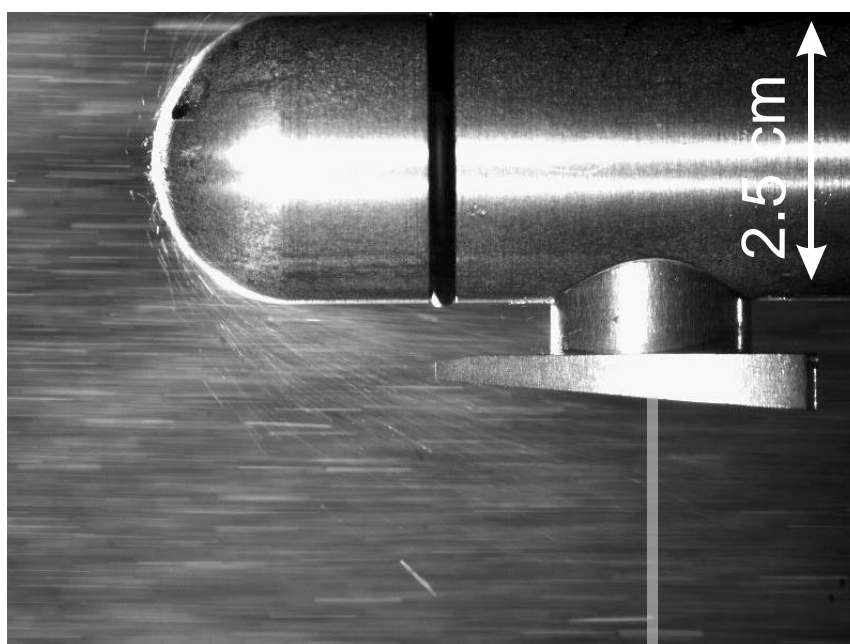
Korolev and Isaac (2005) documented OAP-2DC, OAP-2DP, and HVPS images of fragmented precipitation size ice particles as a direct evidence of the existence of shattering. However, it did not clarify the origin of the enhanced concentration of small ice.

Field et al. (2006) applied an interarrival time algorithm to identify and filter out shattering artifacts in OAP-2DC and CIP measurements. It was found that after filtering artifacts, the OAP-2DC and CIP concentrations were reduced by up to a factor of four, when the mass-weighted mean size exceeded 3mm.

Heymsfield (2007), McFarquhar et al. (2007), Jensen et al. (2009), **Vidaurre and Hallett (2009)** based on the comparisons between different airborne instruments, built up more evidence about the spurious enhancement of concentration of small ice particles.

Despite the growing evidence of the significance of the effect of shattering on ice particle measurements, the shattering hypothesis was not commonly accepted in the cloud physics community for many years. Many researchers argued that shattered particle fragments, after bouncing from the probe's upstream surface, shed along the surface of the arms or inlets, and that they could not travel several centimeters across the airflow at an aircraft speed of 100m/s to reach the probe's sample volume.

Direct A direct experimental support for the shattering hypothesis has been provided by a series of **high-speed videos of the wind tunnel experiments with controlled environment and reproducible ice spray conditions** (Korolev et al. 2011, 2013b). **particles behavior on impact** Ice particle impacting with the probe tips at an aircraft speed (~~Korolev et al. were video-recorded by a high-speed camera. 2011, 2013b~~). These videos documented that after rebounding from the probe's tips, shattered small fragments can travel several centimeters across the airflow and reach the probe's sample volume (Fig.15).



935 **Figure 15.** A snapshot from a high-speed video showing a flow of shattered ice fragments rebounding from the hemispherical tip of the OAP-2DC particle probe. The shattered ice fragments deflected toward the sample area (bright vertical band) are counted by the probe and artificially enhance the measured concentration. The video recording was performed in an ice spray at 80m/s in the Cox and Co. Icing Wind Tunnel Facility (for more details see Korolev et al. 2011, 2013ab).

940

Korolev et al. (2011, 2013a), Lawson (2011), Korolev and Field (2015), Jackson et al. (2015) showed that the effect of shattering can be mitigated by using both antishattering K-tips (Korolev et al. 2013b) and the interarrival time algorithm (Field et al. 2006). It was also demonstrated that the interarrival time algorithm, when used alone, is not capable of identifying all shattering artifacts. Korolev et al. (2013a) showed that measured concentration of ice particles smaller 200 μ m can be enhanced due to the shattering effect by up to two orders of magnitude, whereas the concentration of ice particles larger than 400 μ m remains mainly unaffected.

Another source of artifacts in measurements of high concentration of ice particles by optical array probes (OAP), is related to fragmentation of particle images when particles pass through the sample volume close to the edge of the depth-of-field (DoF) (Korolev 2007, Guélin et al., 2019). A few one-two pixel images resulted from fragmentation of large out-of-focus images have an enhanced artificial contribution into particle concentration due to their very small sample volumes. This is a purely optical phenomenon, and it is relevant only to imaging particle probes. Currently, the problem of fragmented images is recognized by many research groups. One of possible solutions of this problem is the exclusion of the first two or three size bins compromised by the ambiguity of the DoF definition and contamination by image fragments. Due to the extent that particle counts from the first two or three size bins (smaller than 30 - 80 μ m depending on the OAP type) may significantly contribute to the ice concentration, a limitation is imposed on the measurements of total concentration of ice particles in SIP cloud regions.

These findings brought up a question whether early airborne studies of SIP were contaminated by shattering artifacts, which resulted in an artificial enhancement of the measured concentration of small ice. However, numerous recent in-situ measurements, which employed the antishattering techniques and updated processing algorithms, are in general consistent with the early SIP observations, and they also showed that in many clouds, ice particle concentrations are still much higher than the INP concentration (e.g. Crosier et al. 2011, 2014; Crawford et al. 2012; Heymsfield and Willis, 2014; Stith et al. 2014; Lawson et al. 2015; 2017; Lloyd et al. 2015; Lasher-Trapp et al. 2016; Keppas et al. 2017; Ladino et al. 2017; Korolev et al. 2020; and others).

965

9. Concluding remarks

9.1 General comments

Figure 16 shows a summary diagram with conceptual models of six SIP mechanisms discussed above.

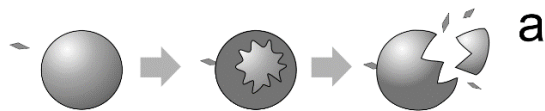
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The analysis provided in this work shows that the experimental studies SIP are distributed quite unevenly between different SIP-mechanisms. Most of the SIP experimental studiesworks are associated with examining

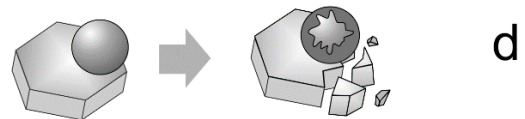
the mechanism of droplet fragmentation during freezing (3233 publications²). A large number of laboratory works are dedicated to studying the rime splintering (HM-process) (22 publications). The other four mechanisms received far too little attention from the lab research community: ice-ice collisional fragmentation (2 publications), thermal shock fragmentation (3 publications), sublimating ice fragmentation (9 publications); INP nucleation in transient supersaturation (45 publications). Even though none of the above mechanisms have a ~~competed~~ quantitative theoretical description, there is a reasonably good understanding of what physical processes are involved in these mechanisms with the exception of the HM-process. The situation regarding the HM process is contradictory: on one hand, the parameterization of the HM-mechanism is widely used in cloud simulations and weather prediction models, on the other hand, there is no clear understanding of the physical processes underlying this mechanism. At the same time, none of the other five mechanisms is employed on a systematic basis in ~~the~~ weather prediction models.

The most striking outcome of this review is the diverse range of results obtained by different research groups for each of the SIP mechanisms. This is one of the major issues hindering the development of physically based parameterizations for numerical simulations. On the other hand the diversity of the results of laboratory studies challenges the existing SIP parameterizations employed in numerical simulations of clouds and weather prediction models.

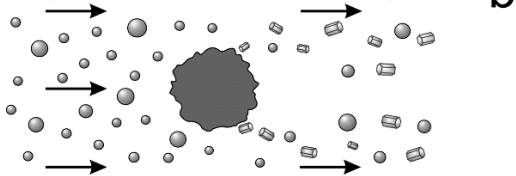
Droplet fragmentation during freezing



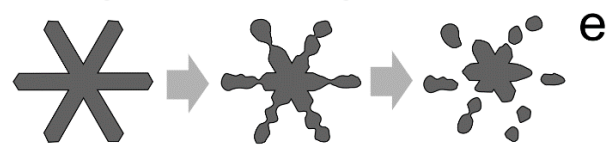
Ice fragmentation during thermal shock



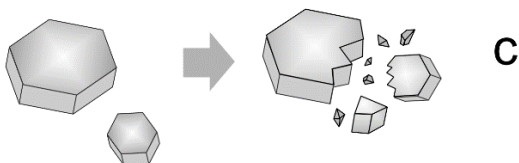
Splintering during riming (Hallett-Mossop process)



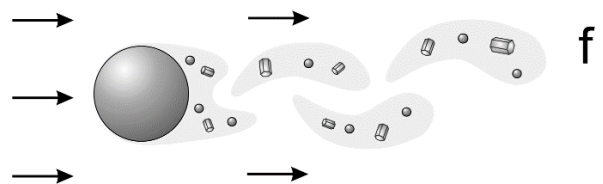
Fragmentation during sublimation



Fragmentation during ice-ice collision



Activation of INP in transient supersaturation



² A publication is considered related to a specific SIP mechanism if it includes *experimental* results related to this specific mechanism. Theoretical and in-situ observational works were not counted. Note, that some publications were not cited in this work.

990 **Figure 16.** A conceptual diagram summarizing six SIP mechanisms (a) fragmentation droplets during freezing; (b) rime splintering (Hallett-Mossop process); (c) fragmentation of ice particles during ice-to-ice collision; (d) fragmentation of ice particles during thermal shock caused by a freezing drop attached to their surfaces; (e) fragmentation of ice particles during their sublimation; (f) activation of supersaturation sensitive INP in the transient supersaturation formed around freezing drops or wet graupel/hailstones.

995 **9.2 Feasibility of SIP mechanisms**

One of the important questions related to ice multiplication is whether all six mechanisms can occur in natural clouds.

1000 The review of the lab experiments suggests that the mechanism of droplet fragmentation during freezing may be active across a wide range of temperatures. There is an increasing amount of evidence indicating universality of this mechanism, which may occur in both convective and stratiform clouds.

The rime splintering (HM) mechanisms require the presence of heavily rimed graupel with high fall velocity. Formation of such graupel is most likely to occur in convective mixed phase cloud regions in a quite narrow temperature range $-8\text{C} < T_a < -3\text{C}$.

1005 Ice-ice collisional fragmentation requires a large separation of vertical velocities of ice particles to enhance kinetic energy of their collision. The most likely candidates for this process are lightly and heavily rimed ice particles. The formation of graupel usually occurs in mixed phase convective regions. Whether diffusionally grown ice particles may get fragmented colliding with each other remains unclear.

1010 The theoretical analysis of the thermal shock fragmentation (King and Fletcher, 1976a) suggests that it requires precipitation size drops and temperatures ~~older~~lower than -10°C . Such conditions would be relevant for mixed phase convective cloud regions where large drops could be transported by a vertical updraft to levels with ~~old~~low temperatures.

1015 **Activation of SIP due to the fragmentation of sublimating ice requires spatial proximity of undersaturated and supersaturated cloud regions. In this case, secondary ice particles formed in the undersaturated cloud regions can be rapidly transported into the supersaturated regions prior their sublimation. Such conditions may occur in cloud regions affected by entrainment and mixing with out-of-cloud dry air.**

INPs activation in transient supersaturation requires precipitation size drops and high supercooling. As indicated above, such conditions are typical for convective cloud regions.

1020 Out of six SIP mechanisms, the droplet fragmentation during freezing and INP activation in transient supersaturation mechanisms appear to be primary candidates for initial production of secondary ice at the early stage of ice formation in convective clouds. The rest of the mechanisms require preexisting aged ice, and they may contribute ~~into~~ the ice concentration at later stages of cloud development.

~~9.31.1~~ **The way forward**

~~The large discrepancies within the experimental results obtained by different research groups necessitates the development of laboratory setups that account for a variety of possible parameters that may be implicated in different SIP processes.~~

It is worth mentioning that the possibility of additional SIP mechanisms beyond the purview of this paper (Fig.16) remains unexplored. In this regard, studying the existence of other SIP mechanisms not described in this study is still on the agenda of SIP investigation (e.g. Knight 2012).

When discussing the feasibility of SIP mechanisms, it is important to keep in mind well documented observations of supercooled persistent mixed-phase clouds with temporally stable low ice concentration ($<0.5 \cdot 5L^{-1}$) (e.g. Korolev et al. 2017; McFarquhar et al. 2011; Shupe et al., 2006). In these clouds, seemingly satisfying some conditions required for SIP, no explosive enhancement of ice concentration was observed. Similar mixed-phase cloud environments with no SIP were also reproduced in laboratory experiments (Desai et al. 2006). These in-situ and laboratory observations accentuate the importance of identifying the necessary and sufficient conditions required for the initiation of each of the SIP mechanisms.

Another unexplored possibility is related to enhancing the activation properties of typically ineffective primary INPs due to changing the local properties of the cloud environment. In section 7, such activation of ineffective primary INPs occurred in the cloud environment modified by freezing drops (or wet hail and rimed ice particles) due to local increase of supersaturation.

9.3 The way forward

~~The large discrepancies within the experimental results obtained by different research groups necessitates the development of laboratory setups that account for a variety of possible parameters that may be implicated in different SIP processes.~~

Because of the complexity involved in researching SIP, obtaining consistent results from independent research groups is an important task for SIP studies. This would require consolidating efforts across the cloud physics community- at the international level (Shaw et al., 2020). Laboratory investigations should go hand in hand with the development of theoretical descriptions of the SIP processes on a microscale level- and in-situ observations. This will create a foundation for physically based parameterizations for weather and climate models, which is the ultimate goal of all these efforts.

Authors' contribution: AK and TL prepared the manuscript.

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