

1 Evidence for biological shaping of hair ice

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7

8 Abstract

9 An unusual ice type, called hair ice, grows on the surface of dead wood of broad-leaf trees at
10 temperatures slightly below 0°C. We describe this phenomenon and present physical,
11 chemical, and biological investigations to gain insight in the properties and processes related
12 to hair ice. Tests revealed that the biological activity of a winter-active fungus is required in
13 the wood for enabling the growth of hair ice. We confirmed the fungus hypothesis originally
14 suggested by Wegener (1918) by reproducing hair ice on wood samples. Treatment by heat
15 and fungicide, respectively, suppresses the formation of hair ice. Fruiting bodies of Asco- and
16 Basidiomycota are identified on hair-ice carrying wood. One species, *Exidiopsis effusa* (Ee),
17 has been present on all investigated samples.

18 Both hair-ice producing wood samples and those with killed fungus show essentially the same
19 temperature variation, indicating that the heat produced by fungal metabolism is very small,
20 that the freezing rate is not influenced by the fungus activity and that ice segregation is the
21 common mechanism of ice growth at the wood surface. The fungus plays the role of shaping
22 the ice hairs and to prevent them from recrystallisation. Melted hair ice indicates the presence
23 of organic matter. Chemical analyses show a complex mixture of several thousand
24 CHO(N,S)-compounds similar to fulvic acids in dissolved organic matter (DOM). The
25 evaluation reveals decomposed lignin as the main constituent. Further work is needed to
26 clarify its role in hair-ice growth and to identify the recrystallisation inhibitor.

27

1 1 Introduction

2 1.1 Characteristics of hair ice

3 One of the most exciting types of ice has the shape of fine hairs (diameter near 0.02 mm,
4 length up to 20 cm). It can be observed in forests, on dead wood, usually on the ground, and
5 sometimes on still standing trees (Fig. 1).



6
7 Fig. 1. Hair ice on a stem of dead beech wood (26 Dec 2009, Moosseedorf), hair length up to
8 10 cm.

9
10 This so-called *hair ice* or *ice wool* grows at the surface of the unfrozen wood body of certain
11 moist and rotten branches of broad-leaf trees. The hairs are smooth, often with a silky shine.
12 They are found in bunches of beautiful structures such as curls and waves, sometimes with
13 clear parting or zoning, but without ramification. Although individual hairs are mostly
14 separate they follow a macroscopic order often with surprising regularity. The hair base is
15 rooted at bark-free positions or where the bark is loose, but never on the bark. The outer end
16 is either free or in contact with an ice crust or with surrounding material, such as bark or
17 leaves. Sometimes hairs loop back to the branch. Bands of parallel hairs can sinter along
18 contacting lines without losing the original shape until melt onset. In cold, dry air, however,
19 hair ice sublimates within short time. Therefore it can be observed under calm, humid
20 conditions, only, at air temperatures slightly below 0°C. We observed branches that produced
21 hair ice repeatedly over more than two years. During this time the dry density decreased to
22 about 0.3 g/cm³ while the wood was brightening as a consequence of white rot.

1 Movies of hair-ice growth support visual observations in that the growth is controlled and
2 synchronised over macroscopic parts of the wood. The hair curvature results from lateral
3 gradients in the growth velocity. The primary direction is radial, the hairs being in the
4 prolongation of wood rays (Fig. 2).



5
6 Fig. 2. Cross section of hair-ice producing beech branch (\varnothing 22 mm) with radial wood rays.

7
8 Indeed, our observations indicate that the hairs are rooted at the mouths of these rays (Wagner
9 and Mätzler 2009). Furthermore, the hair-ice thickness (Fig. 3) corresponds to the diameter of
10 the cells (Fig. 8 & 9 in Sect. 2) forming the channels in the wood rays (Schweingruber, 1990).



11
12 Fig. 3. Enlargement of hair ice on beech wood, image width 3.2 mm

13
14 The fine hairs can keep their shape over long time, many hours, even days. This is surprising
15 because recrystallisation of small ice crystals to larger ones is fast, especially at temperatures

1 close to the melting point. The observed stability is an indication that hair ice is doped with a
2 recrystallisation inhibitor. Examples are Anti-Freeze Proteins (AFP), also called Ice-Binding
3 Proteins (IBP), see Griffith and Yaish (2004).

4 When the air temperature exceeds 0°C, hair ice starts to melt. Hairs fixed at both ends are
5 transformed to a type of micro strings covered by small water droplets (Fig. 4) before they
6 decay. Hairs with free ends have been observed to collapse in length. The melted liquid is
7 clear water with a slightly brownish colour indicating the content of organic material.



8
9 Fig. 4. Melting hair ice, showing tiny droplets on hardly visible strings.

10

11 We received many reports on the observation of hair ice mainly at latitudes between 45° and
12 55° N from Canada, France, Germany, India, Ireland, Netherlands, Russia, Scotland,
13 Slovenia, Sweden, Switzerland, U.S.A. and Wales.

14 **1.2 References to earlier work and the fungus hypothesis**

15 Although the literature on hair ice is not abundant it reaches back by about one century.
16 Alfred Wegener (1918), the founder of the theory on continental drifts, published the most
17 relevant paper of the earlier work. He observed hair ice in Winter 1916/1917 in the Vosges
18 Mountains, and in February 1918 in Northern Germany at Rheinsberg in der Mark. He was
19 able to grow hair ice again on the branches that he found. Wegener assumed a relationship
20 between the formation of hair ice and the mycelium visible on the branch surface. His
21 consultant, Arthur Meyer, confirmed that these branches contained fungus mycelia. He
22 assumed a type of Ascomycota, however, he was unable to determine the species. Mühleisen
23 and Lämmle (1975) described the reproduction of hair ice on rotten wood of broad-leaf trees
24 in a climate chamber. They assumed that some type of osmotic pressure is acting.

1 Lenggenhager (1986) observed hair ice in the neighbourhood of Bern, Switzerland from 1979
2 to 1985. Being aware of these observations, Wagner (2005) supposed the involvement of a
3 fungus activity without the knowledge of Wegener's work. Wagner found that the presence of
4 fungus mycelia in the wood body of hair-ice producing branches is manifested in the
5 microscopic and macroscopic view. Fruiting bodies of fungi were observed as shown by
6 Wagner and Mätzler (2009). They developed a method to repeatedly grow hair-ice on a
7 covered balcony during nights with freezing conditions. Their more specific hypothesis, that
8 the metabolism of these fungi is a prerequisite for the formation of hair ice, was supported by
9 their tests. A further hypothesis was the assumption that gas pressure, caused by fungal
10 metabolism, ejects water through wood rays to the wood surface. Furthermore they concluded
11 that hair ice is formed from water stored in the wood. Dash et al. (2006) considered hair ice as
12 a frost-heave phenomenon associated with ice segregation. In the present work we recognised
13 signatures of this effect during hair-ice growth.

14 **1.3 Hair ice and ice segregation**

15 Hair ice is growing on a porous substrate containing liquid water. We call this ice type a
16 *basicryogen* in order to distinguish it from ice that grows from atmospheric water. Different
17 basicryogenes grow on different substrates and different ingredients. In common is the co-
18 existence of liquid water, ice and the porous substrate at the ice front. This general
19 phenomenon is called *ice segregation*. The thermodynamic phenomenon of frost heave
20 (Vignes and Dijkema, 1974; Dash, 1989; Ozawa, 1997; Dash et al. 2006) is a common driver
21 for these ice types.

22 Hair ice is growing at the wood surface while a connected network of water inside the wood
23 remains in the liquid state. Due to molecular interactions at the large specific interface area
24 between the wood cells and the water, the melting temperature inside the wood is reduced as
25 compared to bulk water, known as *premelting* (Rempel et al., 2004; Dash et al. 2006). The
26 reduction increases with increasing specific surface, i.e. with decreasing size of capillaries and
27 pores of the wood. The depression can keep the water unfrozen inside the pores while ice is
28 growing outside. The freezing front remains at the wood surface during ice growth. In this
29 way, the ice is segregated from the reservoir of liquid water.

30 How can we understand this process? The large dipole moment of the water molecule causes
31 charges at the surface of liquid water and ice. Energy is needed to set up the associated

1 electric field. Surface energy can be reduced if a liquid-water film remains between the wood
2 and the ice surface due to the flexibility of the liquid to neutralise the local charges. Under
3 freezing conditions suction forces are set up, caused by the interface energy of the wood-
4 water-ice sandwich, to attract liquid water from the pores of the wood toward the freezing
5 front. In this way the liquid-water film is maintained. Frost-heave processes in fine-grained
6 soil also act in this way (Ozawa, 1997; Dash et al. 1995, 2006). Although the theory of ice
7 segregation is still incomplete (Dash et al. 2006), empirical insight in the behaviour was found
8 by experimental studies. Osawa and Kinoshita (1989) investigated ice growing on the surface
9 of a microporous filter. The thin liquid film, separating the ice from the filter material, was
10 confirmed. The authors observed that the growth rate of ice increases proportionally with the
11 depression $\Delta T_f = T_0 - T_f$ of the temperature T_f at the freezing front, where $T_0 = 0^\circ\text{C}$, is the
12 melting temperature of bulk ice (ΔT_f values ranging from 0.0 to 0.3°C). The observations are
13 in agreement with the experiment of Vignes and Dijkema (1974) growing ice at the mouth of
14 a capillary channel that was in contact with a reservoir of supercooled water (ΔT_f values
15 ranging from 0.3 to 0.77°C). With respect to growth rate and temperature range these
16 experiments agree with our observations of hair-ice growth as will be shown.

17 **1.4 Outline**

18 Advancing the understanding of the hair-ice phenomenon has been the objective of this work.
19 In Sect. 2, we will confirm that a winter-active fungus is needed for hair-ice formation. We
20 will identify the acting fungus. In the physical analysis of Sect. 3 we will study the
21 temperature variation of wood during ice formation. Wood samples with and without the
22 acting fungus will be studied. The results point us to the search for a recrystallisation inhibitor
23 produced by the fungus and thus to the chemical analysis of Sect. 4. Final discussions and
24 conclusions will be given in Sect. 5.

25

1 2 Observations and experiments related to the fungus hypothesis

2 2.1 Suppression of hair-ice growth by killing the fungus

3 2.1.1 Experiments with fungicide

4 In Winter 2010/2011 Gerhart Wagner refined the hair-ice experiments of Wagner and Mätzler
5 (2009). A hair-ice active branch was cut into 5 pieces (length 35 cm, diameter 2 cm) and
6 exposed to a commercial fungicide ('Schimmelentferner' MIOCOLOR, Natriumhypochlorit,
7 conc. 4.4%): Piece No 0 remained untreated, No 1 was exposed for 15 minutes, No 2 for 30
8 min, No 3 for 60 min, and No 4 for 120 min. On the first evening (Dec 18, 2010) the air
9 temperature was close to -10°C . Consequently the growth of hair ice was fast, but ended after
10 one hour at a hair length of 1 cm. The result at 21:30 (LT) is shown in Fig. 5. Hair ice was
11 reduced on pieces with fungicide treatment, but complete suppression was observed for the
12 longest treatment, only.



13
14 Fig. 5: Reduction and suppression of hair-ice growth after fungicide treatment, durations from
15 0 to 120 min indicated.

16
17 The following morning all pieces melted at room temperature before they were exposed to the
18 cold again. The air temperature rose from -5°C to 0°C . Two hours later a very similar result
19 was obtained. In the afternoon the experiment was repeated again after wetting the branches
20 in distilled water for a short time. The results showed the expected gradation even more
21 clearly. All results demonstrate that the 15 min treatment causes a significant reduction of
22 hair-ice production, and a treatment for 120 min stopped the production completely. During
23 the following weeks the same branches were repeatedly exposed to the cold. Slow recovery
24 occurred for the fungicide pieces in that they gradually started to grow hair ice again. The
25 pieces with different treatment duration became more and more similar.

1 2.1.2 Experiments with heat

2 A hair-ice branch of about 20 cm in length and 2 cm in diameter was cut into four similar
3 pieces on 3 Jan 2011. Three of them were exposed to hot (90 to 95°C) water for 1 min, 2 min
4 and 4 min, respectively. After the following frost night the reference was covered with dense
5 hair ice, however, the heated pieces did not show any. The repetition with a thin branch (1
6 cm) produced the same result. Some days later the heated pieces started to produce traces of
7 hair ice again.

8 2.1.3 Other treatments

9 Treating the branches with alcohol (70%) or with the weak fungicide, IMAVEROL, an
10 imidazole, also called Enilconazolium (C₁₄H₁₄Cl₂N₂O), often used in veterinary medicine, did
11 not affect hair-ice growth.

12 2.1.4 Results

13 Heat treatment showed the most radical hindrance of hair-ice growth. One minute in hot water
14 was sufficient for a complete suppression. For fungicide the type and duration of the
15 treatment played a role. Whereas our weak fungicide did not have any effect, complete
16 suppression was achieved with the stronger one after treatment for two hours. The results are
17 plausible in view of the fungus hypothesis. At a temperature of at least 90°C the active cells
18 of the fungus are killed rapidly. Fungicides act much more slowly. Several days or weeks
19 after the treatments, hair-ice growth starts again either due to the recovery of the mycelium or
20 due to the survival of spores.

21 **2.2 Identification of the fungus and microscopic studies on hair-ice producing** 22 **wood**

23 2.2.1 Methods

24 From January to March 2012, from December 2012 to April 2013 and November 2013 to
25 March 2014 a total of 78 hair-ice bearing twigs and branches were collected in the forests
26 near Brachbach/Sieg in Germany (northern slope of “Windhahn”). Some of them were kept
27 on a moss-covered shadowy area in the garden of one of the authors (G.P.) to simulate forest-
28 floor conditions or temporarily on a wet towel in a closed plastic box. Additionally 41 hair-ice
29 bearing trees, boles and branches were observed at their natural location in the forest. Mostly

1 the species, or at least the genus of the dead branches, was identified by species-specific
 2 characteristics visible in the microscopic wood anatomy (Schoch et al. 2004, and Richter and
 3 Dallwitz 2000). Fungi growing on the examined branches and logs were identified if
 4 necessary by microscopic characteristics with the help of Gminder (2008), Haller and Probst
 5 (1983), Jülich (1984), Krieglsteiner (2000), Laux (2010), Moser (1963), and Rothmaler
 6 (1994). Samples of the fruiting bodies were prepared as squash mounts and sometimes
 7 coloured by Phloxin B to stain the basidia. Hand-cut sections of hair-ice bearing wood
 8 samples were prepared as wet mounts and afterwards coloured by "cotton blue" following the
 9 instructions of Bavendamm (1936) according to the description of Riggenbach (1959). This is
 10 an approved method to make fungal hyphae visible within wood cells.

11 2.2.2 Observations and results

12 The type of examined hair-ice wood varied from fallen twigs, attached and fallen branches to
 13 dead standing trees and fallen or felled boles except for one case: a still living hazel tree was
 14 bearing hair ice on a dead part of the wood several times.

15 In the majority of cases the consistency of the dead wood was "rather hard" – indicating an
 16 initial stage of decay – but four samples had a "distinctly softened" texture adopting the terms
 17 of Heilmann-Clausen and Christensen (2003). The integrity of the bark differed from almost
 18 intact to completely lost. If it still existed the bark peeled off from the hair-ice producing
 19 wood surface and often got lost during the observation period.

20 Hair ice was observed on ten different broadleaf tree species belonging to five different plant
 21 families (Table 1).

22 Table 1. Hair-ice bearing wood species, range of diameters and identified fungal species

23 D = *Dacrymyces spec.*, Dd = *Diatrype disciforme*, Dst = *Diatrype stigma*, E = *Exidia spec.*, Ee = *Exidiopsis*
 24 *effusa*, Ff = *Fomes fomentaria*, Hf = *Hypoxylon fragiforme*, Hm = *Hypoxyon multiforme*, Sch = *Schizopora*
 25 *paradoxa*, Pc = *Pycnoporus cinnabaria*, Tm = *Tremella mesenterica*.

26
 27

| Fam. | Species (in brackets, number of finds) | Diameter (cm) | Fungi |
|-----------|--|---------------|-----------|
| Aceraceae | <i>Acer pseudoplatanus</i> (4) | 1.3 – 4.8 | <u>Ee</u> |

| | | | |
|------------|--|------------|------------------------------------|
| Adoxaceae | <i>Sambucus nigra</i> (3) | 1.5 – 2.5 | <u>Ee</u> |
| Betulaceae | <i>Betula pendula</i> (3) <i>Carpinus betulus</i> (15) <i>Corylus avellana</i> (16) <i>Alnus glutinosa</i> (14) | 0.5 – 13.0 | D, Dd, Dst, E, <u>Ee</u> , Hm, Sch |
| Fagaceae | <i>Fagus sylvatica</i> (32) <i>Quercus spec.</i> (12, <i>robur/petraea/bastards</i>) | 0.5 – 18.0 | Dd, <u>Ee</u> , Ff, Hf, Sch |
| Rosaceae | <i>Prunus avium</i> (2) <i>Sorbus aucuparia</i> (18) | 0.6 – 6.0 | Dd, E, <u>Ee</u> , Pc, Tm |

1

2 Eleven different fungal fruiting bodies were identified on the wood samples – in some cases
3 up to three species on the same piece of wood. The list is certainly not complete. One of these
4 fungi, *Exidiopsis effusa* (Ee), deserves closer attention, as it colonised all our hair-ice
5 producing wood samples. In more than half it was the only detectable fungus, but in most
6 cases it was not yet visible macroscopically, when hair ice occurred for the first time in late
7 autumn. Its unspectacular fruiting body appeared some weeks later as a thin whitish coating
8 (Fig. 6) exactly on those areas of the wood surface, where hair ice had grown before (Fig. 6b,
9 d, f) or next to the hair-ice area (Fig. 6d). In the first observation period (winter 2011/2012)
10 the coating was present on every observed sample from February on, in the second and third
11 winter the first fruiting bodies were visible in January. The colour was sometimes slightly
12 bluish, greyish or light pink tinted, depending on the humidity and colour of the wood.

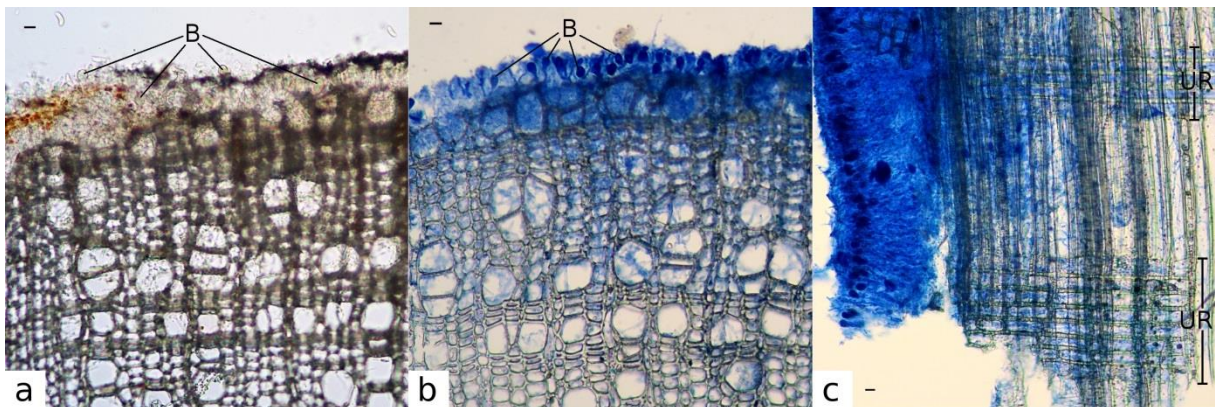


13

1 Fig. 6. Three wood samples, first with hair ice, later with fruiting body of *Exidiopsis effusa*
2 (Ee): *Corylus avellana* (Ø 3.8 cm) on 29 Jan 2012 (a) and 15 Mar 2012 (b), *Carpinus betulus*
3 (Ø 3.2 cm) on 25 Jan 2012 (c) and 7 Mar 2012 (d), *Fagus sylvatica* (Ø 4.9 cm) on 3 Dec 2013
4 (e) and 11 Jan 2014 (f, branch rotated by about 180°).

5 Under humid conditions (in nature or in a closed plastic box containing a wet towel) and
6 temperatures above the freezing point small water droplets often appeared on the surface of
7 the fruiting body of Ee over night (Fig. 6f). This might be a case of guttation which means the
8 active exsudation of an aqueous solution. The phenomenon is well known from different
9 vascular plants, but also from some fungi (Knoll 1912, Thielke 1983). The observation of
10 Sprecher (1959), who describes a reinforcing effect at temperatures near +4°C on the
11 guttation activity of a fungus, is particularly interesting with regard to the formation of hair
12 ice. Further studies on Ee are necessary to clarify this aspect.

13 Cross sections of the fruiting body were 30 to 100 µm thick with great variability (Fig. 7a, b,
14 c). It mainly consists of ovoid to pyriform basidia in a layer of thin, clamped hyphae.

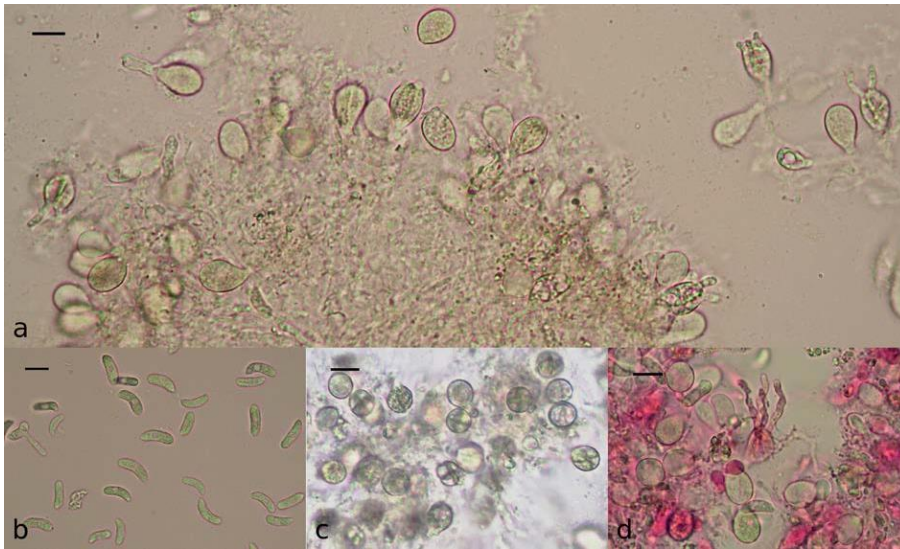


15 a b c
16 Fig. 7. Microscopic views of a hair-ice wood sample (*Alnus glutinosa* twig, Ø 9 mm) with the
17 fruiting body of Ee. In pictures b and c the fungal hyphae and basidia were coloured by
18 "cotton blue" (scale bar 10 µm, B = basidium, UR = uniseriate ray). a and b: Cross sections of
19 an *Alnus glutinosa* twig with a thin fruiting body of Ee. The wood vessels are shown in cross
20 section. c: Radial section of the *Alnus glutinosa* twig with a thick fruiting body of Ee showing
21 two uniseriate rays in longitudinal section. The wood vessels are cut longitudinally, too.

22

23 The basidia, too, are clamped at their base, 4-septate (Fig. 8a, c, d), longitudinally divided
24 (Fig. 8a), about 10 µm in diameter and circa 15 µm long without the sterigmata. The spores

1 (Figure 8b) are weakly allantoidal, 13-15 μm long and 4-5 μm in diameter and often contain
2 one big oil drop in the middle.

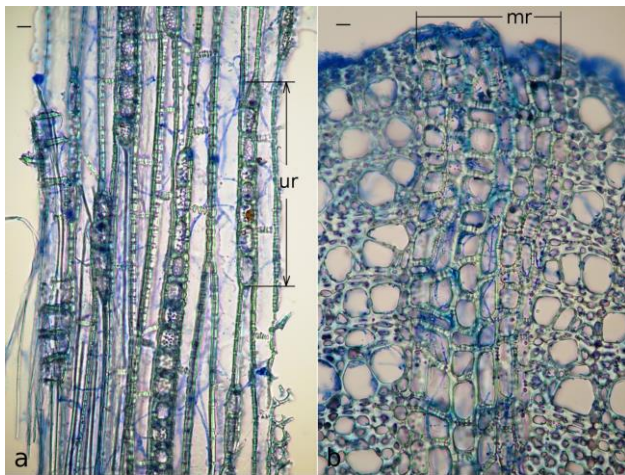


3
4 Fig. 8. Microscopic characteristics of the fruiting body of Ee (scale bar: 10 μm). a: Fruiting
5 body of Ee showing longitudinal-divided basidia with four sterigmata (squash mount); b:
6 Spores of Ee, one is germinating; c: 4-septate basidia in cross-sectional view (squash mount);
7 d: Basidium with four long sterigmata (squash mount, coloured by Phloxin B)

8

9 Based on these characteristics the fungus was identified as *Exidiopsis effusa* (Ee) with the
10 help of the manual of Jülich (1984). The descriptions at www.mycobank.org (Robert et al.
11 2005) and www.mycology.com (Petersen and Læssøe 2003) confirm the result, while
12 Krieglsteiner (2000) classifies the fungus as *Exidiopsis grisea* var. *effusa*.

13 Beneath the fruiting body the superficial wood cells are almost filled by hyphae (Fig. 7a, b).
14 The fungus seems to grow along the wood vessels (Fig. 9a) and to intrude into the deeper
15 wood tissue along the wood rays (Fig. 7c and 9b).



1
 2 Fig. 9. Microscopic view of hair-ice wood showing fungal hyphae coloured by "cotton blue"
 3 within the wood tissue. The varying thickness of the fungus hyphae was caused by the
 4 colouring procedure (scale bar: 10 μ m, UR = uniseriate ray, MR = multiseriate ray). a:
 5 Tangential section (similar to the look on the surface) of an *Alnus glutinosa* twig (\varnothing 8 mm),
 6 that was partly covered by the fruiting body of Ee. Several uniseriate rays are shown in cross
 7 section, the wood vessels are cut longitudinally. b: Cross section of a *Fagus sylvatica* twig
 8 (\varnothing 6 mm) bearing hair ice, that had not yet developed the fungal fruiting body of Ee. The
 9 wood vessels are shown in cross section, one multiseriate ray is cut longitudinally.

10

11 Some hair-ice wood samples found in November were examined by microscope, too. At that
 12 time of the year, there was no macroscopic sign of a fungal fruiting body on the wood surface.
 13 But when microscopic mounts were coloured by "Cotton Blue", they showed, that the wood
 14 tissue was pervaded by fungal hyphae running along the wood vessels and rays (Fig. 9b).
 15 Except for the density of the hyphae the findings looked exactly like those from the wood
 16 samples with a fruiting body of Ee.

17 As our main result, we unravelled the mystery about the whitish covering described by
 18 Wegener (1918) and Wagner (2005) by the identification of Ee. The opinion of Wegener's
 19 consultant, A. Meyer, who did not expect the appearance of a fruiting body and thought that
 20 the determination of the species would be impossible, has been disproved. Furthermore the
 21 result specifies the fungus hypothesis of Wagner & Mätzler (2009).

22

1 3 Physics of hair ice

2 3.1 Thermal effects during hair-ice formation

3 Insight in the physics of hair ice is found from thermal signatures of hair-ice wood, i.e. the
4 temperature enhancements caused by heat sources associated with the ongoing processes.
5 These include (1) heat generated by fungal metabolism, (2) latent heat of fusion when water
6 freezes in contact with the wood, and (3) heat used or generated by recrystallisation.

7 Heat generated by these processes diffuses into its environment by radiation, heat conduction,
8 air turbulence, evaporation and sublimation and therefore exact measurements are difficult to
9 achieve. However, by careful design of the experiments, the main heat loss can be reduced to
10 black-body radiation. For heat sources that change rapidly with time the temperature changes
11 are damped according to the heat capacity of the wood. On the other hand, under stationary
12 conditions, the heat power P generated in the wood (at temperature T_1) is equal to the net
13 power that the wood loses to its environment (at temperature T_2). Then the temperature
14 difference can then be expressed by

$$15 \quad \Delta T = T_1 - T_2 = 0.25 P \sigma^{-1} A^{-1} T^{-3} \quad (1)$$

16 where $\sigma=5.673 \cdot 10^{-8} \text{Wm}^{-2}\text{K}^{-4}$ is the Stefan-Boltzmann constant, A the branch surface area, and
17 T the mean absolute temperature of T_1 and T_2 . The proportionality allows us to express the
18 generated power by temperature differences. Two examples are given below.

19 3.1.1 Fungal metabolism

20 For the combustion of nutrients by fungal metabolism we assume a heat of combustion
21 $Q_b=15.6 \text{ kJ g}^{-1}$, representative for glucose. A typical branch used in our experiments has a
22 volume of $V=82 \text{ cm}^3$ and a surface area of $A=150 \text{ cm}^2$ (length $l=26 \text{ cm}$, diameter $d=1.8 \text{ cm}$).
23 Such a branch is able to produce hair ice over about one year. For the active phases of the
24 fungus we assume a duration of 3'000 h. Furthermore, assuming 5 g of nutrients, the rate of
25 combustion is on the order of 1.5 mg h^{-1} . Multiplying this value with Q_b gives $P = 7 \text{ mW}$, and
26 for $T = 273 \text{ K}$ in Eq. (1) we get $\Delta T = 0.1 \text{ K}$, a value that should be measurable under
27 favourable conditions.

1 3.1.2 Heat of fusion

2 Now, assuming for the same branch geometry, that latent heat is generated by freezing 1 g of
3 water per hour, the generated heating power follows from the latent heat of fusion of ice,
4 $L_f=333 \text{ J g}^{-1}$ at $T=273\text{K}$, as $P = 92 \text{ mW}$, and inserting this value in Eq. (1) gives $\Delta T = 1.3 \text{ K}$.
5 This temperature difference should be easy to measure. Note that it is proportional to the
6 freezing rate.

7 3.1.3 Measurement setup

8 Branches of beech wood with hair ice were collected in a forest at Moosseedorf, Switzerland.
9 The samples were thoroughly wetted in rainwater. Then they were arranged on a plastic
10 socket put on wet snow to stabilise temperature and to keep the humidity at saturation to
11 avoid evaporation and sublimation. The entire stack was put in a plastic tub that was covered
12 and further insulated with a towel to reduce vapour fluxes and heat conduction inside the tub.
13 The tub was put in a garden hut from mid January to early March 2011, and again in January
14 2012. Hair ice formed on wood samples during cool nights. From time to time wetting was
15 repeated. With this setup we realised conditions for precise temperature measurements and
16 approaching the assumptions that the net heat flux can be represented by Eq. (1). For
17 temperature measurements we used Pt-100 sensors (length 10 mm, diameter 2.6 mm). After
18 calibration with an ice-water mixture at 0.00°C , the sensors were inserted into the wood with
19 the cylinder axis along the radial wood rays (Fig. 10). Temperatures were registered once per
20 second to monitor changes with sufficient time resolution. The effective temperature of the
21 environment was a mean of $T_0 = 273.15 \text{ K}$ of the underlying wet snow and of the tub walls
22 cooled from outside. To represent this value of T_2 we either used the air temperature inside
23 the tub or the temperature of a dry, passive tracer (hazel wood in 2011) close to the wetted
24 wood samples.



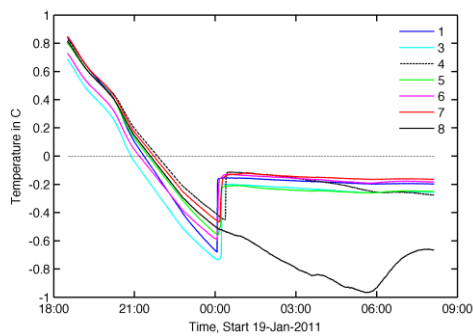
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 2 Fig. 10: Situation in the morning of 15 Jan 2012: heat-treated piece (1, bottom right), piece (2,
 3 top) with abundant hair ice, air temperature sensor (3, bottom left) with red insulation.

4

5 3.1.4 Experiment of 18-20 Jan 2011

6 First measurements occurred in January 2011. During the first night, Jan 18-19, the
 7 temperature stayed above 0°C (Mätzler et al. 2013). The time-averaged temperature of the
 8 hair-ice branches was 1.213°C whereas the value of the passive tracer was 1.203°C. The
 9 difference of 0.010°C is very small, similar to the measurement uncertainty.

10 First hair-ice growth was monitored from 19 to 20 Jan 2011 with temperature variations
 11 shown in Fig. 11.



12
 13 Fig. 11: Temperatures variation during the first experiment: beech-wood samples (1, 3, 4, 5,
 14 6, 7) with growing hair ice, and dry hazel wood (8) as passive tracer of ambient temperature.

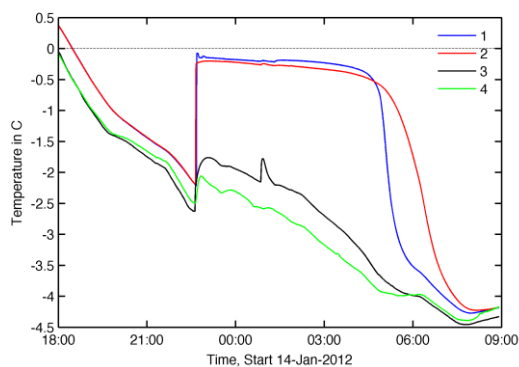
15

16 Before midnight all temperatures decreased linearly with time including the passive tracer. At
 17 midnight, sudden increases occurred for all hair-ice branches, indicating ice nucleation and

1 start of latent-heat release by hair-ice growth. The start is almost simultaneous in all branches,
2 with slightly different nucleation temperature (-0.4 to -0.7°C). Ice was growing until the end
3 of the measurement period in the following morning. During this period the temperature of
4 the hair-ice branches remained nearly constant near -0.2°C. On the other hand, the passive
5 tracer (8), representing T_2 , continued to cool to -1°C until 05:30 (LT) without any jump.
6 Further experiments confirmed these results. The simultaneity of temperature jumps for
7 different hair-ice woods was observed again, but exceptions occurred as well.

8 3.1.5 Experiments of 13-15 Jan 2012

9 In the second year we tried to find out if the fungus activity is a prerequisite of the observed
10 temperature jumps, in other words, if the jumps are signatures for hair-ice formation. We
11 selected a beech-wood sample with abundant hair-ice growth. After wetting and cutting in
12 half, both pieces still showed abundant hair-ice growth during the night from 13 to 14 Jan
13 2012 with jumps similar to Fig. 10. Then one piece (1) was held in hot water for 5 minutes to
14 kill the fungus. Both pieces were exposed to the cold again during the following night. As
15 shown in Fig. 11, the untreated sample (2) produced dense hair-ice again, but no hair ice was
16 found on the heat-treated sample (1); instead, a thin ice crust covered this wood. The
17 temperature variations are presented in Fig. 12. All sensors started slightly above 0°C, and all
18 values were near -4.3°C at 09:00 (LT) on the following morning. Due to colder weather the
19 cooling was faster and reached lower values than in Fig. 11. Both wood samples - with and
20 without hair ice - showed similar and almost simultaneous increases, indicating the onset of
21 freezing at 22:35 (LT). Air temperatures at the centre (3) and edge (4) of the container
22 indicate forced cooling with minor modulations.



23
24 Fig. 12: Temperature variation during the second experiment: heat-treated piece (1), untreated
25 piece (2) with hair ice, air temperature close to wood samples (3), and further away (4).

1

2 **3.2 Discussion**

3 Before the onset of freezing the temperature of hair-ice branches cannot be distinguished from
4 the environmental temperature. The small difference (0.01°C) found during the first night in
5 2011 is representative for the measurement error. This means that heating by fungal
6 metabolism is much smaller than estimated in section 3.1.1. In other words the combustion
7 rate of nutrients in our test sample is clearly less than 1 mg/h.

8 Before freezing begins the wood temperatures in Fig. 11 and 12 decrease to supercooled
9 conditions below 0°C . A sudden increase marks the onset of freezing by the release of latent
10 heat. The onset in one branch triggers the onset in near-by branches usually within short time.
11 Ice nucleation appears as an explosive event distributing microscopic ice particles. The
12 temperature increase is similar for samples with hair-ice formation and for samples with
13 killed fungus.

14 During the phase of ice growth the wood temperature (-0.1°C to -0.4°C) is nearly constant. In
15 addition to the data of Fig. 11 & 12, this range was found in all other measurements that we
16 made (Mätzler et al. 2013). These values are signatures of premelting and thus of ice
17 segregation. The stabilisation is based on the heat of fusion. With falling ambient temperature
18 the freezing rate increases and thus the transfer of latent heat to the wood increases, too. The
19 associated temperature increase compensates for the decrease of the ambient temperature,
20 keeping the branches close to the melting point. The stabilisation acts as long as there is
21 sufficient liquid water in the wood rays. The continued freezing dehydrates the branch. When
22 the liquid supply is exhausted, ice production comes to an end, the heat production stops, and
23 the wood temperature converges to the ambient one. This transition is shown near the end in
24 Fig. 12.

25 The temperature difference between the pieces with and without hair-ice production is small,
26 indicating that the freezing rates are similar. The result means that the fungus activity hardly
27 plays a role for the rate of ice formation. This finding may appear as a surprise when looking
28 at the difference between the branches (1, 2) of Fig. 10. But, note that hair ice is extremely
29 fine, its density being extremely small. On the other hand the ice crust on the heat-treated
30 piece (1) mainly consists of bulk ice. To show that its mass is indeed similar to the hair-ice
31 mass, we compare two situations with the same ice volume, one consisting of N hairs per

1 branch surface area, the other one consisting of an ice crust covering the branch surface with a
2 constant thickness d . If we denote the hair diameter by d_h and the hair length by l_h , it is easy to
3 show that

$$4 \quad d = \frac{\pi}{4} N l_h d_h^2 \quad (2)$$

5 To get an estimate of d we need the parameters on the right-hand side of (2). From Fig. 3 and
6 similar observations we find: $d_h \approx 0.014$ mm, $N \approx 20/\text{mm}^2$, and for the hair length we choose
7 $l_h = 50$ mm to get $d = 0.15\text{mm}$, for the crust thickness. The comparison is consistent with the
8 two branches of Fig. 10.

9 With regard to Fig. 12, minor differences between Curves (1) and (2) can be noted. Firstly,
10 after freeze onset, Curve (1) shows small oscillations possibly due to recrystallisation. On the
11 other hand, the temperature variation of Curve (2) is very smooth. Secondly, towards the end,
12 when the strongest cooling occurs, the temperature decrease is slower for Curve (2) with hair
13 ice than in Curve (1) due to thermal insulation by the *ice wool*.

14 The similarity of the temperature and thus of the rate of ice growth means that ice segregation
15 is the common mechanism for ice production at the wood surface. The role of the fungus is in
16 shaping the ice as hairs and to prevent it from recrystallisation. This is the main result from
17 the physics of hair ice. Furthermore it indicates that temperature and pressure enhancements
18 associated with fungal metabolism in hair-ice wood (Wagner and Mätzler, 2009) do not
19 appear to be noticeable.

20

21 **4 Chemistry of melted hair ice**

22 **4.1 Organic carbon**

23 First investigations of non-filtrated and filtrated melt water samples from hair ice by means of
24 Total Organic Carbon analyser (TOC-VCPH, Shimadzu, Japan) show similar and significant
25 amounts of organic carbon (> 200 mg L⁻¹) beside small amounts of (total) nitrogen (> 10 mg
26 L⁻¹). Ion chromatography revealed that the main part (70%) of nitrogen consists of ammonium
27 ions. We conclude that melting of hair ice provides us with a real organic carbon solution,
28 mostly free of wood and aerosol particles.

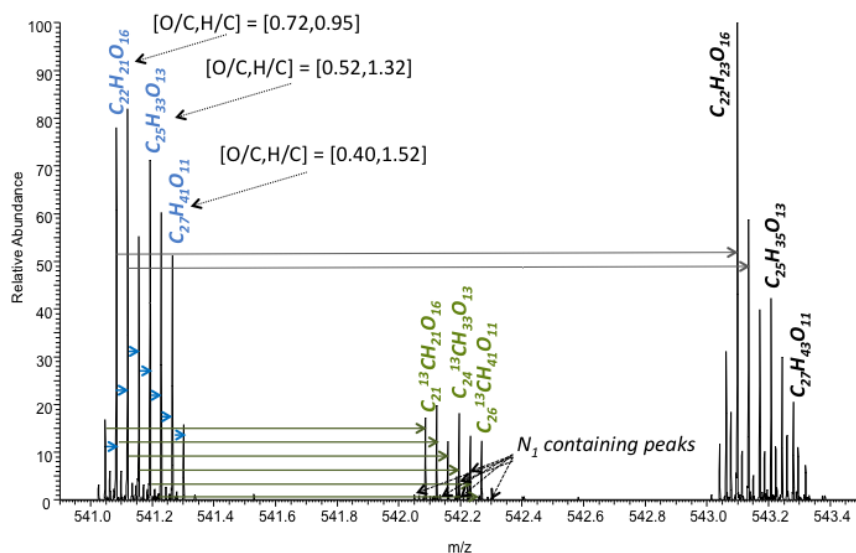
1 4.2 Mass spectrometry

2 For the elucidation of the unknown components we applied mass spectrometry (MS) aiming
3 at a complete spectrum of organics with regard to molecular size and polarity. Representative
4 screening was achieved by various ionisation techniques in combination with appropriate
5 separation techniques. First, we performed gas chromatography, coupled with electron-impact
6 mass spectrometry (GC-EI-MS) of filtrated aqueous solutions according to Turska et al.
7 (1997), followed by the more sensitive Head Space-GC-EI-MS (Seto 1994, Snow and Slack
8 2002). For small carboxylic acids (known e.g. as plant exsudates) and peptides/ proteins
9 (possible degradation products and/or anti-freeze proteins), we used capillary electrophoresis
10 and Electrospray Fourier-Transform Ion-Cyclotron Resonance-Mass Spectrometry (ESI-FT-
11 ICR-MS, Marshall et al. 1998). None of these methods yielded any significant peak.

12 In the second step, we applied our most sensitive mass spectrometer equipped with an
13 electrospray source coupled to Ultra Performance Liquid Chromatography (UPLC-ESI-MS,
14 Swartz, 2005; Guillarme et al. 2010), resulting in first (non-resolved) chromatograms. The
15 full-scan spectra of positive *as well as* negative mode and from different retention times,
16 respectively, are highly complex - ranging over the whole mass range, but similar among
17 themselves. Such spectra - gaussian in shape with emerging odd-numbered peaks - look
18 similar to fulvic/humic acids in dissolved organic matter (DOM) of terrestrial/marine water,
19 soil/sediments, peat bog, kerogen up to crude oil (Kujawinski, 2002; Sleighter and Hatcher,
20 2007; Hertkorn et al. 2008).

21 Therefore, in the third step, we simultaneously desalted and concentrated hair-ice samples by
22 Solid-Phase Extraction (SPE). The methanolic eluates, mixed with 20% water for better
23 ionisation yield, were introduced again as flow injection in the ultrahigh-resolving ESI-FT-
24 ICR-MS. In contrast to our former investigation, we arranged the measuring conditions
25 towards complex samples (averaging of 7 spectra of 50 transients each) to improve the
26 statistics. The high-resolution spectrum in the mass range 200-1000 Da [1 Dalton (Da)
27 = 1.660539×10^{-27} kg, corresponding to $1/12$ of the mass of a C-12 atom] show a bimodal
28 distribution (maxima at 500 and 610 Da, respectively, not shown). The detailed evaluation of
29 these spectra revealed the typical presence of molecular families containing ions that differ
30 from each other in the number of CH₂ groups, degree of saturation (grey arrows in Fig. 13)
31 and functional group substitution (blue arrows in Fig. 13) with a significantly higher intensity
32 of the odd-numbered masses (description of such spectra in Leinweber et al. 2009). The

1 reason for the latter phenomenon is the mass spectrometric nitrogen rule: under electrospray
2 conditions the ionisation is by proton transfer to $[M-H]^-$ or $[M+H]^+$ ions, therefore nitrogen-
3 free organics like CHO and CHOS compounds are odd numbered, while organics with one (or
4 three or five, respectively) nitrogen atom(s) are even numbered.

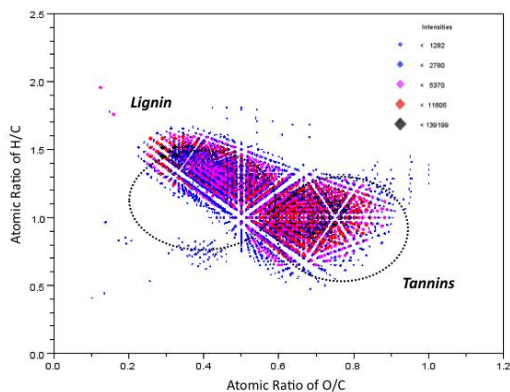


5
6 Fig. 13: Detail of a high-resolution mass spectrum of melted hair ice.

7
8 In Fig. 13, ions with the mass space of 0.0364 Da (blue arrows) were derived from the mass
9 difference between CH₄ and O, representing the most important formal functional group
10 substitution, giving the typical clusters within a nominal mass. Furthermore, expanded
11 sections of successive, randomly selected nominal masses show that every single (intensive)
12 odd-numbered mass peak has a corresponding lower abundant even-numbered mass peak
13 higher in one m/z - the exact mass space of 1.0034 Da is thereby attributed as its ¹³C isotopic
14 peak (olive arrows). Still less intense are the mostly one-nitrogen-containing peaks in hair ice.
15 This result shows the same qualitative tendency like our first organic analyses in terms of
16 organic nitrogen to organic carbon ratio of only approximately 0.014:1 - but under the
17 consideration that complex ESI spectra are never quantitative because of quench effects of
18 easily to poorly ionizing substances.

19 We developed a post processing to formula assignment of all compounds based on Scilab
20 routines. The resulting mass lists are transformed to Excel Tables for sorting and/ or

1 preparation of graphical figures describing the characteristics of DOM. The *van Krevelen*
2 *diagram* - H/C versus O/C for all detected compounds - is mostly used to classify the
3 compounds in terms of polarity and aromaticity. Furthermore, Sleighter and Hatcher (2007)
4 and Hockaday et al (2007) published ranges of biogeochemically important compound classes
5 in such plots. The [O/C, H/C] values found for melted hair ice range between [0.40-0.72,1.52-
6 0.95], correspond to the Sleighter's lignin and tannin ranges, indicated by ellipses in the van
7 Krevelen plot of hair ice and are presented in Fig. 14.



8

9 Fig. 14: Van Krevelen Plot of the CHO compounds of hair ice (for peak intensities > 600
10 counts), underlayed with ellipses, indicating typical ranges selected biopolymer components,
11 adapted from Sleighter and Hatcher (2007)

12

13 4.3 Discussion

14 Mass spectrometry has shown that hair-ice water contains fragments of lignin and tannin.
15 Lignin is a main ingredient (20 to 30 % of dry mass) of wood, stabilising the cells against
16 compression. In contrast to cellulose, it is more difficult to decompose. Lignin is indigestible
17 by animal enzymes; only some fungi (causing white rot) and bacteria are able to secrete
18 lignase and thus to biodegrade the polymer. Lignin is an irregular biopolymer with molecular
19 mass in excess of 10³000 Da, consisting of various types of substructure, that are repeated in a
20 haphazard manner. Similarly irregular are tannins with molecular weights between 500 and
21 3000 Da and up to 20,000 Da (proanthocyanidins). Lignin and tannin consist of hydrophobic
22 skeletal structures with numerous polar functional groups. The hydrophobic lignin/ tannin
23 macromolecules may act as crystallisation nuclei.

1 The lignin and tannin classification was obtained by atomic ratios, shown in Fig. 14. By the
2 application of electrospray, the most gentle mass spectrometric ionisation technique, covalent
3 bonds stay intact whereas the weaker ones (Van der Waals and electrostatic, respectively) are
4 destroyed. Consequently, molecules in the mass range between 200 and 800 Da result like in
5 general for fulvic acids. This means that we are unable to distinguish between the original
6 lignin/ tannin macromolecules and their (partial) degradation products.

7 We also detected sulphur- and nitrogen- containing compounds, but with very small
8 intensities in contrast to the CHO peaks and in accordance with our TOC and TN
9 measurements. We assume that we detected marginal leftovers from the total degradation of
10 more easily degradable (and nutritious) wood compounds, like proteins, on their way to
11 mineralization. This would explain the significant ammonium concentration in melted hair
12 ice.

13

14 **5 Conclusions**

15 Our investigations shed light on the mystery of hair ice that can grow on certain branches of
16 dead wood. The formation is tied to a winter-active fungus. Comparatively dense mycelium
17 was observed in the superficial wood cells of hair-ice bearing sections of the investigated
18 branches. If the fungus activity is stopped, either by a fungicide or by hot water, the
19 production of hair ice ceases as well.

20 Hair-ice shape and direction are influenced by the geometry at the mouth of the wood rays
21 where the hairs are formed when the water is freezing. Most surprising is the extreme ratio of
22 hair diameter to hair length on the order of 1:10'000. In spite of the fact that surface tension
23 tries to reduce this ratio, the shape is maintained over many hours, and sometimes several
24 days at temperatures close to the melting point. A recrystallisation inhibitor must be
25 responsible for stabilising the hairs. It may be contained in the thread-forming fibre that
26 appears when hair ice starts to melt, and it could be related to lignin, the main organic
27 component that we found.

28 With respect to the origin of water, hair ice is a basicryogen, meaning that the ice originates
29 from water in a porous substrate, in our case, the wood. Inside the substrate, the melting point
30 is lowered by intermolecular forces at the interface between ice and the substrate, called
31 premelting. When the external temperature is sufficiently low, water freezes on suitable nuclei

1 at the substrate surface and transfers latent heat of fusion to the substrate. Once ice nuclei
2 have formed, ice segregation starts to extract additional water from the substrate, leading to
3 the growth of ice and to the dehydration of the substrate. We found that this effect occurs
4 under the same conditions with similar freezing rates in wood with and without hair-ice
5 production.

6 The fungus provides decomposed lignin and tannin as organic materials. That they may act as
7 recrystallisation inhibitors is indicated by properties found for ligninsulfonate (waste of
8 cellulose production) in Sandermann and Dehn (1951) to delay the hardening of cement.

9 The fungus activity plays a minor role with regard to the rate and amount of ice formation.
10 Hair-ice branches with active and with killed fungus undergo similar temperature curves,
11 indicating that the freezing rates are very similar and that fungal metabolism is too weak to
12 cause a measurable temperature enhancement. The difference must be in shaping the ice.
13 Whereas the untreated branches produce hair ice, the heat-treated ones produce crusty ice
14 sticking to the wood surface. Although the fungus effect is still a mystery, it must be directly
15 related to the hair-ice shape because the suppression of hair-ice growth acts immediately after
16 the fungus activity is stopped.

17 Our findings not only confirm Wegener's hypothesis that fungal activity plays an important
18 role, but they unravel the mystery about the whitish covering on hair-ice producing wood,
19 described by Wegener (1918) and Wagner (2005). There is clear evidence to suggest a causal
20 relationship between the fungus, *Exidiopsis effusa*, and the growth of hair ice. This fungus is
21 known to cause white rot. Indeed, the brightness of hair-ice wood increases with age, and its
22 dry density decreases more and more, indicating wood decomposition. The chemical analysis
23 confirms and specifies the degradation. Explaining further details of the connection between
24 the fungus and hair ice will be tasks for future research.

25

26 **6 Author contribution**

27 C. M. has been working (in collaboration with G. W.) since several years on hair ice, its
28 observation in nature, reproduction and the test of a fungus hypothesis. In the presented paper
29 he is mainly responsible for the physical measurements and interpretations, described in Sect.
30 3. G. P. investigated the fungi and the wood samples by microscopic techniques, described in
31 Sect. 2.2 leading to the identification of *Ee*. D. H. performed and interpreted the chemical

1 analyses, presented in Sect. 4. The paper is a strong collaboration of scientists different fields
2 to one object with collective discussions.

3

4 **7 Acknowledgments**

5 We thank Gerhart Wagner for contributing Sect. 2.1 including Fig. 5. We regret his wish not
6 to act as a co-author. We thank for support by the Institute of Applied Physics, University of
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8 to us possible relationships between hair-ice and ice-segregation processes. Bernhard Steffen,
9 JSC, Forschungszentrum Jülich, developed the Scilab-based evaluation program.

10

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