

PHYSICO-CHEMICAL PROCESSES
IN ICE AND FROZEN GROUND

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WATER CRYSTALLIZATION UPON FREEZING OF SOILS

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Changes in the amount of unfrozen water remaining in frozen porous wet soils are estimated theoretically for two possible cases of ice nucleation: within bulk pore water and on the surface of mineral particles. The process in the latter case is considered with regard to the composition, physical properties, and surface roughness of soil particles.

Soils, mineral particles, surface roughness, water supercooling

INTRODUCTION

Water undergoes heterogeneous crystallization at temperatures below 273 K on the Earth's surface and in the atmosphere. This is a large-scale process including nucleation of ice crystals on aerosol particles (with subsequent formation of solid precipitation), on particles suspended in water, and on objects near the sea or lake shores and river sides, as well as freezing of lakes and rivers [Golubev, 2000, 2014, 2015; Semenova et al., 2010]. In mid- and high-latitude areas subject to regular air temperature variations, ice crystals can nucleate in pores of wet soils where water is dispersed very unevenly.

The phase transition of H₂O during freezing of porous fine-grained soils is asynchronous even at closely spaced sites of pores [Deryagin, 1956; Anderson, 1967a,b; Lange and McKim, 1967; Ananyan, 1973; Golubev, 1986; Wexl et al., 2013; Are, 2014; Zielke et al., 2016]. Thus, ice can coexist with unfrozen water in any volume of frozen and freezing soils at temperatures $T < 273$ K, i.e., soils always contain some amount of liquid supercooled water [Deryagin, 1956; Grigorieva, 1957; Anderson, 1967a; Ananyan, 1973; Novikov et al., 2016]. Unfrozen water may exist in both natural and manmade materials. Features and physics of this phenomenon are of theoretical and practical interest. The theoretical aspect is a subject of discussions and a key problem in geocryology; in terms of practice, natural and manmade porous fine-grained materials at negative temperatures are used for engineering and economic purposes in industry and construction [Deryagin, 1956; Nersisova and Tsytoovich, 1963; Ananyan, 1973; Ershov, 1995, 1996; Grigoriev, 2013; Are, 2014; Novikov et al., 2016].

CRYSTALLIZATION AND DISTRIBUTION
OF WATER IN THE PORE SPACE OF SOILS

Porous soils, a common porous media in the uppermost lithosphere, consist of solid particles that vary largely in size, morphology, and surface roughness (Fig. 1), as well as in chemistry, mineralogy, and physical properties. Correspondingly, they interact with water in different ways, e.g., differ in wettability and related water phase change patterns [Anderson, 1967a,b; Golubev, 1981, 2000, 2015; Wexl et al., 2013; Zielke et al., 2016].

Crystallized pore water in wet porous soils at $T \leq 273$ K (Fig. 1) can fill the entire pore space and form its own matrix (complete saturation, a regular process) or can cling to contacts and surface defects of soil particles (incomplete saturation, a regular but probabilistic process). Both processes are associated with heterogeneous crystallization of water as a widespread natural melt.

Ice nucleation is possible either within bulk pore water or on rough surfaces of mineral particles [State Standard, 1975], depending on the type of their contacts and interactions with water and ice [Golubev, 1981, 1986, 1997, 2000; Vlahova, 2013].

Case I. *Ice nucleation within bulk pore water, independent of the properties and microstructure of soil particles, at any distance from their surfaces.*

According to the theoretical postulates of homogeneous water crystallization (in a volume of water, without foreign nuclei), the smallest possible equilibrium ice crystal consisting of 470 H₂O molecules, 15.32 nm³ or a sphere of 3.08 nm in diameter, can form only when water supercooling reaches -38 °C [Golubev, 1999, 2015]. These postulates are supported by evidence that small water drops in the atmo-

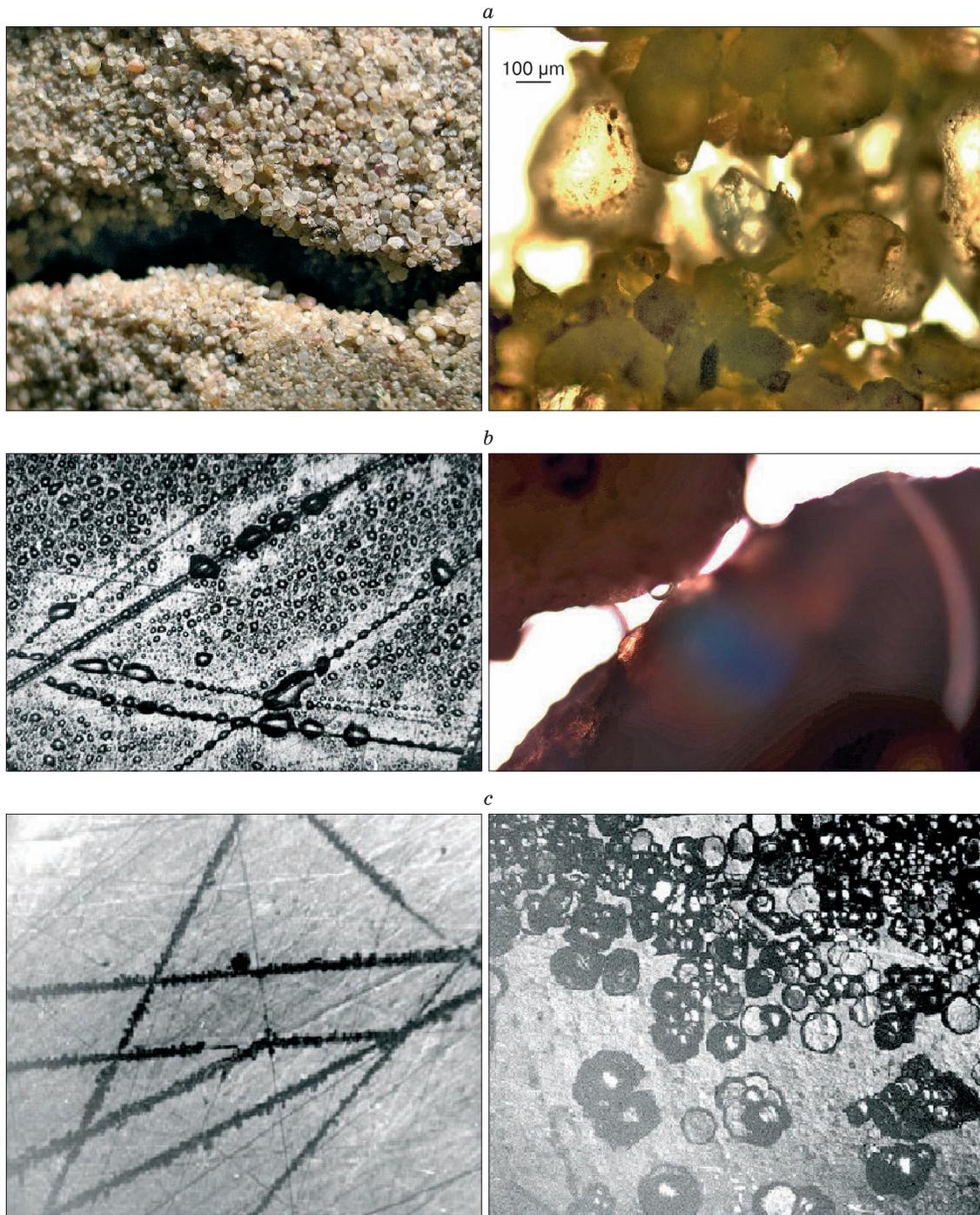


Fig. 1. Typical packing of particles (quartz and feldspar) in wet porous soil and heterogeneities on their surfaces (a), water between contacting soil particles (b), distribution of condensed water drops and ice crystals on substrate at surface heterogeneities (c) (magn. $\times 20$ to $\times 1200$).

sphere freeze up at temperatures below $-39\text{ }^{\circ}\text{C}$ [Fletcher, 1970; Welti et al., 2014]. Thus, the homogeneous crystallization requires deep supercooling of water [Golubev, 1981], and this mechanism of ice nucleation appears hardly possible in bulk pore water of soils.

If it were possible, the nucleated crystals would grow in all directions, including toward mineral particles, and stop growing immediately at or at some distance off their surfaces. In this case, we assume that heterogeneities on the surfaces of mineral parti-

cles, irrespective of their size and morphology, are originally filled with water (Fig. 2, *a*).

The heterogeneities may have various shapes (step, trihedral angle or crack) controlled by the substrate symmetry, while the substrate can trigger water phase change, depending on the area of the substrate-water interface [Golubev, 1981, 1986, 1999]. Further cooling causes complete or partial freezing of water at surface heterogeneities (Fig. 2, *b*).

The thermodynamic potentials of such a system in its initial (G_0) and final (G_1) states are

$$G_0 = S_{is}\gamma_{is} + S_{iw}\gamma_{iw} + kS_{iw}\gamma_{ws} + \mu_w N; \quad (1)$$

$$G_1 = S_{is}\gamma_{is} + kS_{iw}\gamma_{is} + \mu_i N. \quad (2)$$

This potential changes upon transition from state (1) to state (2) as

$$\Delta G = G_1 - G_0 = kS_{iw}(\gamma_{is} - \gamma_{ws}) - S_{iw}\gamma_{iw} + N(\mu_i - \mu_w), \quad (3)$$

where k refers to change in the area of the substrate-water (ice) interface at surface heterogeneities ($3 > k > 1$); μ_w , μ_i are the chemical potentials of H_2O molecules in liquid water and ice, respectively; S_{is} , S_{iw} are the areas of the ice-substrate and ice-water interfaces, respectively; γ_{is} , γ_{iw} , γ_{ws} are the specific free energies of ice-substrate, ice-water, and water-substrate interfaces, respectively; N is the number of water molecules at surface heterogeneities.

Equation (3) can be transformed using either (i) the equation of Frenkel ($\mu_i - \mu_w \approx \lambda\Delta T/T_0$, where λ is the specific energy of the water-ice transition per molecule ($T_0 = 273$ K) and ΔT is the water supercooling, or (ii) the equation of Fletcher ($\gamma_{ws} - \gamma_{is} = m\gamma_{iw}$, where m refers to ice nucleation activity [Frenkel, 1945; Fletcher, 1970].

In Fletcher's equation, γ_{ws} and γ_{is} are most often unknown but γ_{iw} is known to be 0.032 J/m² at T about 273 K. The limits of ice nucleation activity are obviously $-1 < m < 1$: $m = -1$ in the case of ice nucleation within bulk pore water, in the absence of substrate, and $m = 1$ when ice itself is the substrate and its changes are formally similar to changes in the wetting angle, $\cos \alpha$.

Assuming that such a process is possible only at $\Delta G \leq 0$ and substituting $m\gamma_{iw}$ and $\lambda\Delta T/T_0$ for $(\gamma_{ws} - \gamma_{is})$ and $(\mu_i - \mu_w)$, respectively, in (3), we obtain that the amount of water molecules N at surface heterogeneities and the required water supercooling ΔT are related to the ice nucleation activity m and the factor k that refers to increase in the water (ice)-substrate interface area at a heterogeneity as

$$N(\lambda\Delta T/T_0) \leq S_{iw}\gamma_{iw}(1 + km).$$

The cross section of a heterogeneity can be approximated by an equal triangle while the space occupied by water molecules is V_M . Thus, transformations lead to the following equations for quantitative estimation of the specific amount of water molecules

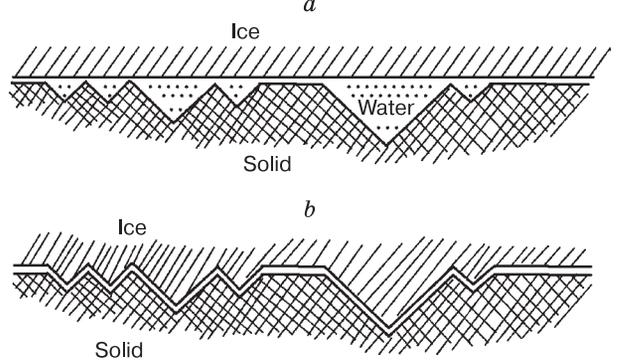


Fig. 2. Possible states of system “foreign solid–ice”.

a: the ice surface remains quasi-flat at 273 K; *b*: ice grows into heterogeneities on particle surfaces at lower temperatures.

N^* at a typical heterogeneity corresponding to the state shown in Fig. 1, *a*:

$$N^* = S_{iw}h^*/(2V_M) \quad (4)$$

and the depth of such heterogeneity is

$$h^* \leq \gamma_{iw}(1 + km)2V_M T_0/(\lambda\Delta T). \quad (5)$$

II. *Ice nucleation on the surfaces of soil particles, with its thermal conditions and location controlled by the composition, properties, and surface microstructure.*

In this case, water freezes up at a temperature above homogeneous water crystallization (-38 °C) as the substrate surface activates water freezing and ice nucleation, i.e. the process of heterogeneous ice nucleation. According to Fletcher ($m = (\gamma_{ws} - \gamma_{is})/\gamma_{iw}$), the effect of the substrate can be formally characterized by the factor of ice nucleation activity which varies in the range $-1 \leq m \leq 1$ depending on similarity in lattice spacing and in shear moduli between the substrate and the ice; on the presence of OH^- groups in the substrate; and on distribution of charges on its surface [Fletcher, 1970].

Theoretical curves of m -depending crystallization temperature (Fig. 3) on the surface of a smooth body and at step-, trihedral angle-, and crack-shaped heterogeneities [Golubev, 1981, 1986, 1997, 1999] show that the ice nucleation temperatures are as warm as 0 °C at $m = 1$, as cold as -39 °C at $m = -1$, and approach -24 °C and -18 °C for trihedral angle and step heterogeneities, respectively, at $m = 0$. The required water supercooling is the lowest (4 and 4a in Fig. 3) if ice crystals nucleate in a smooth pore or a crack which is narrow enough for a crystal to fit between two pore walls [Golubev, 1981, 1986, 1999].

The ranges of limit supercooling values of water drops on the surfaces of different materials (Table 1) correspond to an m range from 0 to 0.9 [Golubev, 1981, 1997, 1999]. After ice proper, m is the second highest in wood and then in mica minerals, but it is

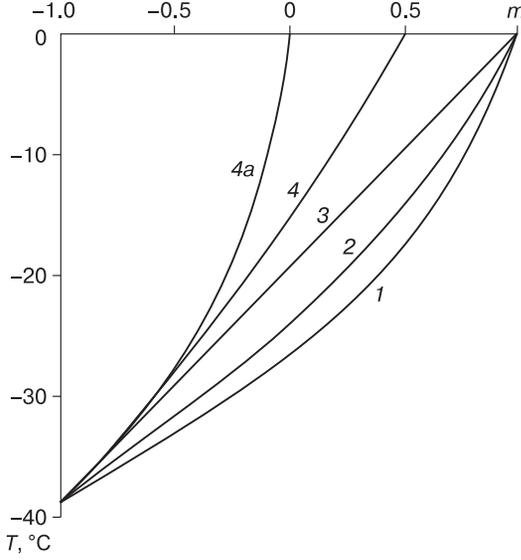


Fig. 3. Theoretical relationship: temperature of heterogeneous water crystallization (crystallization rate $J = 1 \text{ cm}^{-3}\cdot\text{s}^{-1}$) as a function of ice nucleation activity of the substrate (m).

Curves are labeled as: 1 is for perfectly smooth surface; 2, 3, 4 and 4a are for step-, trihedral angle-, and crack-shaped heterogeneities, respectively.

quite low in most of minerals and metals (Table 1). This m distribution is consistent with the principal postulates of the theory of epitaxy [Fletcher, 1970; Golubev, 1997, 1999, 2015]. Specifically, high m (0.8–0.9) in wood is due to the presence of OH^- groups, isoelectric behavior of surfaces, and low elasticity. High density of crack-like heterogeneities on the wood surface may be an additional cause of relatively small water supercooling required for ice nucleation.

The size distribution of heterogeneities on naturally weathered or mechanically deformed solid surfaces fits the lognormal equation [Mossop, 1956; Fletcher, 1970] which can be modified [Golubev, 1981, 1997, 1999, 2015] for the case of porous materials and the presence of heterogeneities of various shapes on the solid surface:

$$n_i = A\psi r^2 \exp[-ba^2 (\ln Z)^2], \quad (6)$$

where A is the number of smallest heterogeneities, with their sizes corresponding to the average lattice spacing of the substrate $R_0 \approx 0.5 \text{ nm}$; ψ , r are the shape and size factors of soil particles, respectively; b refers to the geometry of heterogeneity; a refers to surface roughness ($a \approx 0.2\text{--}0.8$ for mineral particles); $Z = R/R_0$ is the normalized size of a heterogeneity (R is the heterogeneity size in nm). According to (6), 1 cm^2 of a mirror-polished surface ($a = 1.15$) may contain up to 10^7 step-like heterogeneities and fewer heterogeneities of trihedral angle (10^5) and crack (10^3) shapes, from

Table 1. Supercooling of water drops on substrate surfaces

Material	Freezing point	Activity factor (m)
Biotite	−1.5 to −16.9	0.45 to 0.50
Gypsum (selenite)	−8.8 to −26.7	0.05 to 0.10
Granite	−6.7 to −19.5	0.30 to 0.40
Calcite	−6.9 to −29.4	0.00 to 0.05
Quartz	−7.8 to −25.6	0.10 to 0.15
Microcline	−9.0 to −24.8	0.15 to 0.20
Marble	−5.0 to −24.4	0.15 to 0.20
Muscovite	−1.0 to −14.8	0.50 to 0.55
Hornblende	−11.2 to −19.3	0.25 to 0.30
Wood (pine)	−0.3 to −0.9	0.80 to 0.90
Steel	−2.5 to −19.5	0.30 to 0.35

0.125 to 10^3 nm^3 in size. Heterogeneities become more numerous at lower a , especially those of the type of crack and trihedral angle.

The surface heterogeneities of characteristic sizes (depths) $h \geq h^*$ become filled with ice, while the presence of liquid water is thermodynamically reasonable at $h < h^*$. The value h^* can be estimated by substituting the values $m = 0.3\text{--}0.5$ common to most of natural minerals (Table 1) into (5) and assuming the change of water (ice)–substrate interface at surface heterogeneities to be $k = 2$:

$$h^* \approx (10^{-5}/\Delta T) \text{ cm.}$$

Thus, supercooled water is expected to exist at all heterogeneities with $h^* < 10^{-5} \text{ cm}$ at a temperature of -1°C , in an amount found proceeding from the total number of heterogeneities of the respective size.

For step-like heterogeneities with lognormal size distribution,

$$n_h = A \exp[-3a^2(\ln(h/h_0))^2],$$

where n_h is the number of heterogeneities of a given size; $A = 10^{12} \text{ cm}^{-2}$ is the number of heterogeneities

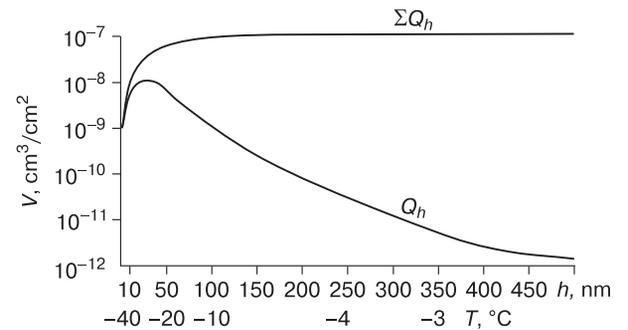


Fig. 4. Amount of unfrozen water Q_h at surface heterogeneities with the size h_i and total amount of unfrozen water at all heterogeneities from h_0 to h_i ($\sum_{h_0}^{h_i} Q_h$).

Nonlinear scale below x axis is water freezing point ($^\circ\text{C}$) at heterogeneities of the size h_i , according to (7).

per unit surface area with a size corresponding to the substrate lattice spacing ($h_0 \approx 0.5$ nm); a is the roughness, $a \approx 0.6$ for naturally weathered minerals; h is the size of heterogeneities. The volume of water stored at a step-like heterogeneity, with the depth h and the length about $10h$, is $V_h = 10h^3$, while the total amount of water Q_h at heterogeneities of this size is

$$Q_h = V_h n_h = 10^{13} h^3 \exp[-3a^2 (\ln(h/h_0))^2]. \quad (7)$$

Figure 4 shows theoretical relationship between the amount of water stored at heterogeneities of a given size per unit surface area of a discrete mineral particle and the heterogeneity size (7), as well as critical temperatures below which the heterogeneities become filled with ice.

The total amount of liquid supercooled water per 1 cm² of the substrate surface stored at heterogeneities of different sizes is

$$Q = \sum_{h_0}^h V_h n_h = \sum_{h_0}^h Q_h.$$

The total number of heterogeneities ($\sum_{h_0}^h n_h$) changes quite little as the h range changes, and is assumed to be 10^{12} cm⁻² in the first approximation. Therefore, the change in the amount of unfrozen water on the surface of a solid (Q_h) upon the system temperature change will depend primarily on the size of heterogeneities that store unfrozen water at the given temperature. Figure 4 also shows the total water amount stored at heterogeneities obtained by summation of Q_h for heterogeneity sizes from h_0 to h . The resulting theoretical estimates agree well with reported measured amounts of unfrozen water on the surface of different materials [Deryagin, 1956; Grigorieva, 1957; Anderson, 1967a,b; Lange and McKim, 1967; Ananyan, 1973; Ershov, 1995, 1996; Golubev, 1999, 2000, 2015; Grigoriev, 2013; Are, 2014].

CONCLUSIONS

1. Wet porous materials contain meniscus water clinging to the contact point of soil particles or liquid water at heterogeneities on rough particle surfaces (macroscopic and microscopic water drops, respectively). Thus, it is possible to hypothesize the presence of numerous water drops that do not contact with one another without postulating the formation of a bound water film over the surface of porous materials.

2. Difference in volumes within separate macroscopic and microscopic water drops, as well as difference in interactions of soil particles with water controlled by their composition and properties, leads to asynchronicity in ice nucleation. Therefore, the rate of water-to-ice transition is generally inversely proportional to the magnitude of water supercooling, which agrees with published experimental evidence on the amount of supercooled unfrozen water in porous fine-grained materials at negative temperatures.

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