

## GASES AND GAS HYDRATES IN EARTH'S CRYOSPHERE

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EFFECT OF GAS COMPOSITION AND PRESSURE  
ON PORE WATER FREEZING POINT IN GAS-SATURATED SEDIMENTS:  
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Confined freezing of pore water in gas-saturated sediments under gas pressure associated with cryogenic gas concentration is studied experimentally. The behavior of pore water freezing temperature in pressurized sediments is modeled for different saturating gases: nitrogen, methane, carbon dioxide, and a CH<sub>4</sub> + CO<sub>2</sub> (1:1) mixture. Natural sand and silt samples from permafrost are frozen in laboratory in a specially designed system which can record temperature change in heated and frozen gas-saturated soil samples under gas pressure specified to be below the level of gas hydrate stability. The freezing point of pore water shows dependence on the gas pressure and composition. The changes of the freezing temperature are notable if the saturating gases are highly soluble (carbon dioxide), but the presence of salt ions reduces the effect. Poorly soluble gases, such as nitrogen and methane, can provide no more than 0.1 °C/MPa reduction of the freezing point unless carbon dioxide is present in the pores, which increases the coefficient to 1.36 °C/MPa. The experimentally estimated effect of gas pressure on the freezing temperature of pore water agrees with the results of thermodynamic calculations based on pore water activity.

*Gas-saturated sediment, freezing under pressure, experimental modeling, freezing temperature, methane, carbon dioxide, nitrogen*

## INTRODUCTION

Permafrost can store large amounts of natural gas, especially, methane and its equivalents, as well as CO<sub>2</sub> and N<sub>2</sub>. It may be gas produced by microbial metabolism in unfrozen zones (taliks) [Glotov and Glotova, 2015] or gas migrating through permeable zones [Are, 1998; Kuzin, 1999] from deep or shallow gas reservoirs, including coalbed methane penetrating into permafrost [Cherskiy et al., 1983; Romanovskiy, 1993; Yakushev, 2015]. Gas often accumulates in local zones of freezing gas-bearing sediments as a result of cryogenic concentration caused by expulsion of gas by the freezing front and related pressure increase. Gas pressure can increase during confined freezing of taliks beneath degrading thermokarst lakes, which leads to deformation, heaving, and even fracture of overlying permafrost, including events of cryovolcanism [Yakushev, 1989; Bogoyavlenskiy, 2014; Kizyakov et al., 2015; Buldovicz et al., 2018].

The specific conditions of pore water crystallization in sediments exposed to gas pressure in confined taliks remains insufficiently studied. The available publications report theoretical and experimental data

on phase transitions of pore water without regard to the pressure and composition of pore gases [Andrianov, 1936; Bozhenova, 1953, 1954; Tsytoich, 1973; Yershov et al., 1979; Grechishchev et al., 1980, 2004; Yershov, 1986; Brovka, 1991; Komarov, 2003; Cheverev, 2004; Kozłowski, 2009; Hui and Ma, 2011; Konovalov, 2014; Wu et al., 2015; Xusheng et al., 2015; Motenko and Grechishcheva, 2016]. The freezing temperature of pore water has been quite well studied in terms of effects from the organic-mineral soil skeleton, as well as salinity, water content, and overload pressure, but few experimental results are available on its response to variations in pore gas pressure [Chuvilin et al., 2000, 2003a,b]. The pressure-dependent behavior of saline pore fluids in freezing gas-saturated sediments has been predicted only lately by thermodynamic calculations [Istomin et al., 2018a,b].

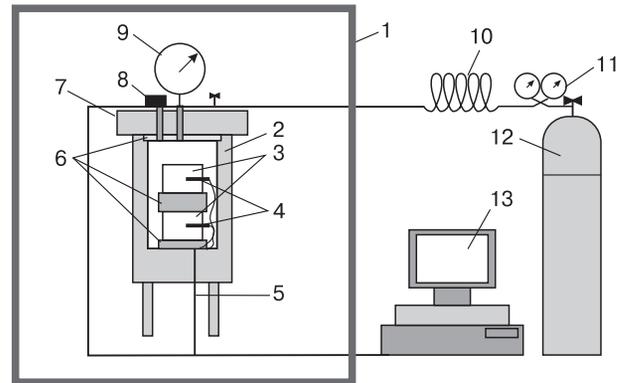
In this respect, physical modeling of this behavior for different gases is especially demanded given the imperfectness of the existing thermodynamic freezing models and the lack of experimental evidence of pore water crystallization in pressurized conditions.

## EXPERIMENTAL METHODS

The freezing point of pore water in gas-saturated porous sediments was estimated using a specially designed experimental system (Fig. 1) consisting of a 0.5 m<sup>3</sup> climate chamber for maintaining the design temperature; a pressure cell equipped with systems for gas input and temperature and pressure monitoring; and an ADC connected to a PC to save the readings. Two wet soil samples in cylindrical metal containers (4 cm high and 4.9 cm in diameter) were placed in the pressure cell (~0.7 L in volume, 10 cm high, and 9.1 cm in diameter). The temperature in the samples was measured by *Honeywell-701 Series* Platinum RTD temperature sensors (1.7 long × 1.2 wide × 0.9 mm high), to an accuracy of ±0.05 °C, and calibrated in a range of 0 to -10 °C on a Thermo HAAKE *Phoenix II P1-C40P* Refrigerated Bath, to 0.02 °C.

The pressure cell with the samples saturated with water to a specified content was vacuumed, filled with gas to a pressure below the level of its hydrate stability, and placed in the climate chamber with the required temperature conditions. To achieve the design water content, air-dry sand mixture was soaked in distilled water for 30 min at room temperature, and the wet sand was compacted layer by layer in a container [Chuvilin and Gurieva, 2009]. The experiments were run with different gases: N<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> and a 1:1 CH<sub>4</sub> + CO<sub>2</sub> mixture. The gas pressure was from 0.1 to 4 MPa for nitrogen, 0.1 to 2 MPa for methane, 0.1 to 0.8 MPa for CO<sub>2</sub> and 0.1 to 1.5 MPa for the CH<sub>4</sub> + CO<sub>2</sub> mixture.

The temperature conditions were changed periodically: after being frozen to -5 °C and filled with cold gas (-5 °C) to the maximum pressure, the pressure cell was heated to +10 °C and then exposed to cooling and heating in +10 to -5 and -5 to +10 °C cycles. Then, the gas pressure was decreased stepwise



**Fig. 1. Experimental setup for estimating freezing point of gas-saturated soil samples.**

1 = climate chamber; 2 = pressure cell; 3 = container with samples; 4 = thermocouples; 5 = thermistor input sleeve; 6 = teflon gasket; 7 = steel lid; 8 = electronic pressure sensor; 9 = digital pressure gauge; 10 = gas tube; 11 = pressure regulator; 12 = gas bomb; 13 = PC with ADC.

at +10 °C, and the samples were cooled down and heated at each step.

The freezing point in the time-dependent curve recording the freezing-heating cycles was defined as the highest and most stable value (a ramp on the curve) that followed a temperature jump corresponding to supercooling of the pore water [Yershov, 2004].

The samples used in the experiments were deformed natural sand and silt sediments (Table 1). Their mineralogy was identified by X-ray diffractometry, the grain sizes (Table 2) were classified according to the State Standard [2014], and the salinity was estimated by chemical analysis of supernatants (Table 3). The physical parameters of the samples were determined with reference to the State Standard

Table 1. **Genesis, age, mineralogy and salinity of soil samples**

Sample	Deposition environment, age	Sampling site	Mineralogy, %		Salinity, %
Sand 1	mQ <sub>III</sub>	South Tambei GCF	Quartz	80	0.19
			XRA	9	
			Microcline	5	
			Oligoclase	4	
Sand 2	gmQ <sub>II</sub> <sup>2-4</sup>	Kharasavei OGCF	Quartz	93.7	0.07
			Kaolinite+chlorite	3.5	
			Microcline	2.3	
Silt	gmQ <sub>II</sub> <sup>2-4</sup>	Vorkuta	Microcline+albite	45	0.08
			Quartz	38	
			Illite	9	
			Kaolinite + chlorite	5	
			Montmorillonite	3	

Note: GCF = gas-condensate field; OGCF = oil-gas-condensate field. Mineral phases exceed 1 vol.%; gm and m stand for glacial-marine and marine deposition environments, respectively. XRA = X-ray amorphous compound.

Table 2. Particle size distribution, %

Sample	Particle size, mm								Lithology*
	1.0–0.5	0.5–0.25	0.25–0.1	0.1–0.05	0.05–0.01	0.01–0.005	0.005–0.001	<0.001	
Sand 1	0.1	12.5	62.9	21.9	1.0	0.5	0.8	0.3	Fine sand
Sand 2	1.7	44.5	40.5	5.2	4.1	1.0	1.0	2.0	Fine to medium sand
Silt	0.3	1.0	2.4	38.1	39.3	4.4	10.0	4.5	Heavy fine silt

\*Lithology is according to classifications of E. Sergeev (sand) and V. Okhotin (silt).

Table 3. Major-ion chemistry of supernatants

Sample	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Ca <sup>2+</sup>	Na <sup>+</sup> + K <sup>+</sup>	Mg <sup>2+</sup>	Dry residue, % (total dissolved salts)
	mg-eq/100 g						
Sand 1	0.40	1.04	1.40	0.45	1.99	0.40	0.19
Sand 2	0.09	0.27	0.12	0.09	0.35	0.04	0.07
Silt	0.66	0.04	0.30	0.64	0.20	0.16	0.08

Table 4. Physical properties of samples

Sample	Water content, %	Density, g/cm <sup>3</sup>	Porosity	Water saturation	Pore water activity*	Specific surface area, m <sup>2</sup> /g
			u.f.			
Sand 1	14	1.92	0.37	0.62	0.9950	0.2
Sand 2	14	1.94	0.37	0.65	0.9985	0.3
Silt	17	1.92	0.39	0.72	0.9968	4.9

\*Pore water activity determined at room temperature.

[2015] and Building Norms and Regulations [1990] (Table 4).

The experimentally evaluated freezing temperatures of pressurized gas-saturated rocks were compared with the respective values retrieved from pore water activity by thermodynamic calculations for specified water contents [Istomin *et al.*, 2018b]. The pore water activity was determined with a *WP4-T* instrument by a method described in detail previously [Istomin *et al.*, 2017a,b].

## EXPERIMENTAL RESULTS AND DISCUSSION

The experimentally observed responses of the pore water freezing point in sediments saturated with different gases to pressure changes are summarized in Table 5 and in Fig. 2.

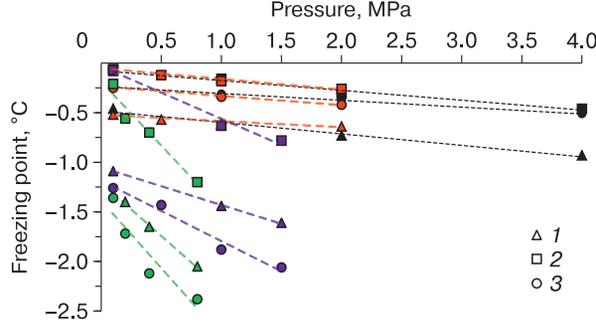
The freezing temperature of pore water in *methane*-saturated sediments decreased as gas pressure

increased (Fig. 2). At atmospheric pressure, it was  $-0.52$  °C for sand 1,  $-0.06$  °C for sand 2, and  $-0.25$  °C for silt. Pore water in sand 1, which was more saline (0.19 %) than sand 2, with high contents of sodium chlorides and sulfates, calcium, and magnesium, froze at a lower temperature. The freezing point of pore water in silt was only slightly lower than that for sand 2 as the two had similar salinities. The pressure-induced reduction of the freezing point was on average 0.06 °C/MPa for sand 1 and 0.10 °C/MPa for sand 2 and silt (Table 6).

In the case of *nitrogen* saturation, the freezing temperature of pore water behaved in a similar way as with the methane saturation (Table 5; Fig. 2). It decreased linearly (for 0.4–0.5 °C in the sand samples and 0.3 °C in silt) as the gas pressure increased to 4 MPa, while the average reduction coefficients were 0.12, 0.10, and 0.07 °C/MPa in sand 1, sand 2, and silt, respectively (Table 6).

Table 5. Gas composition and pressure

Sample	Gas pressure, MPa															
	4	2	1	0.1	2	1	0.5	0.1	1.5	1	0.5	0.1	0.8	0.4	0.2	0.1
	N <sub>2</sub>				CH <sub>4</sub>				CH <sub>4</sub> + CO <sub>2</sub>				CO <sub>2</sub>			
Sand 1	-0.93	-0.73	-0.63	-0.46	-0.64	-0.61	-0.57	-0.52	-1.61	-1.44	-	-1.09	-2.05	-1.65	-1.40	-
Sand 2	-0.46	-0.31	-0.16	-0.08	-0.26	-0.18	-0.12	-0.06	-0.78	-0.63	-	-0.07	-1.20	-0.70	-0.56	-0.21
Silt	-0.51	-0.38	-0.31	-0.24	-0.42	-0.34	-	-0.25	-2.06	-1.88	-1.43	-1.26	-2.38	-2.12	-1.72	-1.36



**Fig. 2. Freezing point of pore water in gas-saturated sediments as a function of gas pressure, for different gas compositions.**

1 – sand 1; 2 – sand 2; 3 – silt. Color marks different gases: black for N<sub>2</sub>, red for CH<sub>4</sub>, purple for CH<sub>4</sub> + CO<sub>2</sub>, and green for CO<sub>2</sub>.

The pressure of the *methane + carbon dioxide* mixture affected more strongly the freezing temperature of pore water than that of nitrogen and methane (Fig. 2), primarily because CO<sub>2</sub> is highly soluble in water, especially under pressure. As the pressure increased, the freezing point of pore water in the samples saturated with 50 % CH<sub>4</sub> + 50 % CO<sub>2</sub> became lower, with the reduction coefficients 0.37, 0.52, and 0.61 °C/MPa for sand 1, sand 2, and silt, respectively (Table 6). The effect of the gas mixture pressure was especially prominent in sand 2 and in silt. Although the average reduction coefficients did not differ much, the freezing temperature in more saline sand 1 saturated with CH<sub>4</sub> + CO<sub>2</sub> was almost 1 °C lower than in less saline sand 2 at a pressure of 0.1 MPa, whereas the difference did not exceed 0.5 °C in the cases of nitrogen and methane. This behavior of pore water in the saline sample of sand 1 resulted from the presence of salt ions which enhanced the effect of CO<sub>2</sub> on the freezing temperature. At 1.5 MPa, the freezing point of samples saturated with CH<sub>4</sub> + CO<sub>2</sub> reached -1.61 °C in sand 1 and -0.78 °C in sand 2. In silt, the gas pressure effect was generally similar to that for sand 1, but the freezing point decreased more strongly, both at atmospheric pressure (for 0.17 °C) and at 1.5 MPa (for 0.45 °C).

In sand samples saturated with *carbon dioxide*, the pressure-induced freezing point reduction exceeded that for CH<sub>4</sub> + CO<sub>2</sub> (Fig. 2). At 0.8 MPa, the freezing temperature reached -2.38 °C for silt and to -2.05 and -1.2 °C for sand samples 1 and 2, respectively. The low saline sand 2 sample had a lower freezing temperature than silt, possibly, because the latter contained carbonates which transformed into bicarbonates upon CO<sub>2</sub> saturation. The presence of carbonates is indicated by high contents of HCO<sub>3</sub><sup>-</sup> (0.66 mg-eq/100 g) in supernatants from silt (Table 3). The average coefficients of freezing point reduc-

**Table 6. Coefficients of pressure-induced freezing point reduction (°C/MPa) in sand and silt samples**

Sample	N <sub>2</sub>	CH <sub>4</sub>	CH <sub>4</sub> + CO <sub>2</sub>	CO <sub>2</sub>
Sand 1	0.12	0.06	0.37	1.07
Sand 2	0.10	0.10	0.52	1.29
Silt	0.07	0.10	0.61	1.36

tion in CO<sub>2</sub>-saturated samples were 1.07, 1.29 and 1.36 °C/MPa in sand 1, sand 2, and silt, respectively (Table 6), close to the values reported earlier [Melnikov *et al.*, 2014; Istomin *et al.*, 2018b]. In general, the temperature reduction coefficients vary depending on the presence of CO<sub>2</sub> and on contents of dissolved salts in pore water.

### EXPERIMENTAL RESULTS AND CALCULATIONS, COMPARED

The experimentally obtained pressure-dependent freezing temperatures of pore water in samples saturated with different gases were compared with those retrieved by thermodynamic calculations as [Istomin *et al.*, 2018b]:

$$t_{fr} = 103.25 \ln(b) + 5.57(1 - b)^2, \quad (1)$$

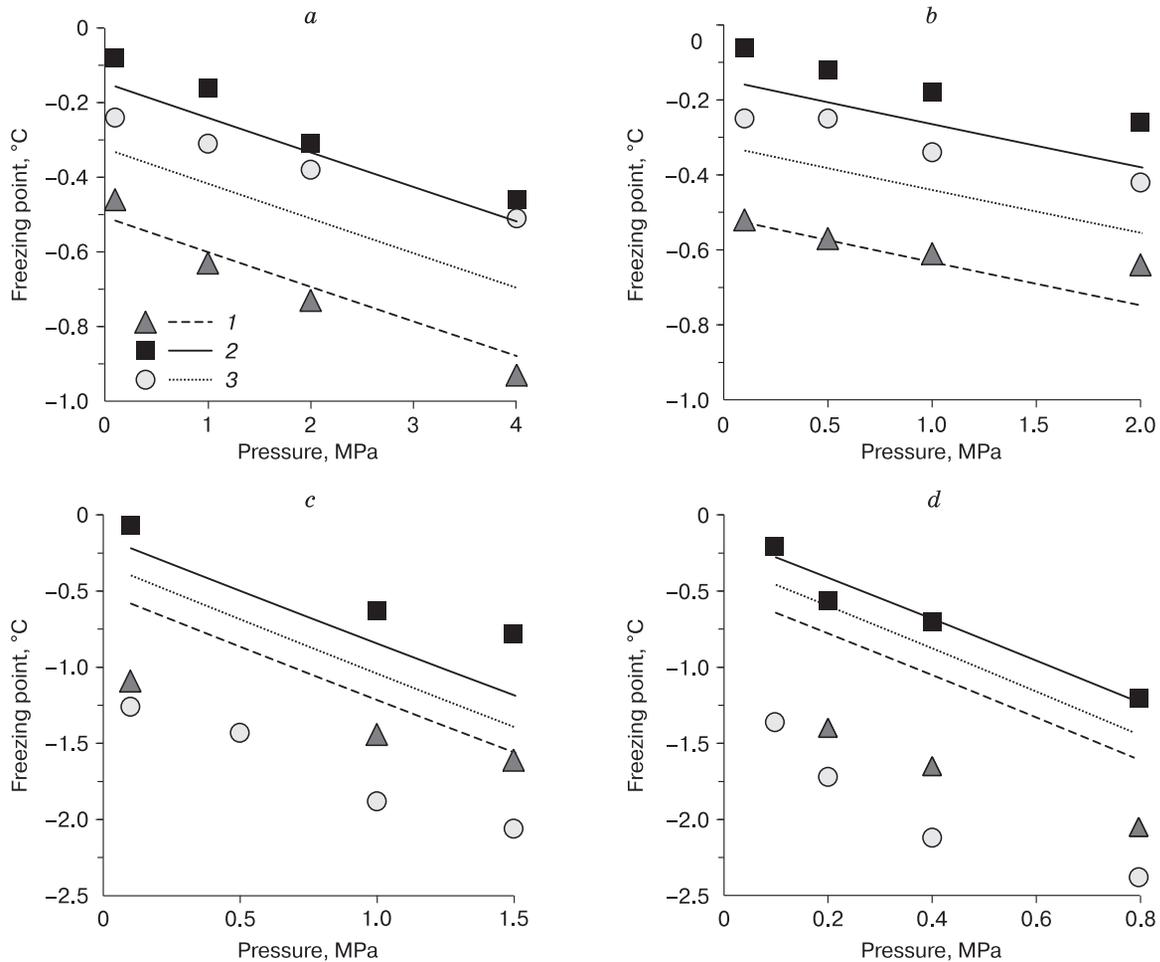
$$b = a(1 - x_g) \exp\left(-\frac{\Delta V(p - p_0)}{R \cdot 273.15}\right),$$

where  $t_{fr}$  is the freezing point of pore fluid;  $p$  is the external pressure (gas pressure in our case), MPa;  $p_0 = 0.101325$  MPa is the atmospheric pressure;  $x_g$  is

the molar fraction of all dissolved gases,  $x_g = \sum_{i=1}^N x_i$ ;  $x_i$

is the molar fraction of the  $i$ -th dissolved gas;  $R$  is the universal gas constant,  $R = 8.3146$  J/(mol·K);  $a$  is the experimentally estimated pore water activity in saline pore fluid (electrolyte) at atmospheric pressure  $p_0$ ;  $\Delta V = 1.63$  cm<sup>3</sup>/mol is the difference of water and ice molar fractions. Thermodynamic equation (1) allows calculating the freezing temperature  $t_{fr}$  of a gas-saturated saline fluid at different gas pressures  $p$  for different gases and salinities.

The experimental and calculation results agree well for nitrogen- and methane-saturated samples (Fig. 3): the difference in freezing temperatures does not exceed 0.1 °C for sand and 0.15–0.20 °C for silt. In the case of samples saturated with a CH<sub>4</sub> + CO<sub>2</sub> mixture and CO<sub>2</sub>, the misfit may reach 0.4–0.5 °C for sand and 0.8–1.2 °C for silt because CO<sub>2</sub> reacts with salt ions in pore fluids, and their chemistry control the CO<sub>2</sub> solubility. This effect has been so far overlooked in the thermodynamic model, which thus requires updating for the gases that are highly soluble in water.



**Fig. 3.** Freezing point of pore water in gas-saturated sediments as a function of gas pressure, for different gas compositions, from physical experiments (dots) and thermodynamic calculations (lines).

*a:* N<sub>2</sub>; *b:* CH<sub>4</sub>; *c:* 50 % CH<sub>4</sub> + 50 % CO<sub>2</sub>; *d:* CO<sub>2</sub>; 1 – sand 1; 2 – sand 2; 3 – silt.

### CONCLUSIONS

The reported experiments allowed improving the method for estimating the freezing point of pore water in pressurized gas-saturated soil as a function of gas composition and pressure.

They have provided estimates for the gas pressure-induced freezing point reduction for sand and silt saturated with nitrogen, methane, carbon dioxide and a mixture of 50 % CH<sub>4</sub> + 50 % CO<sub>2</sub>.

The freezing point of pore water in sand and silt saturated with poorly solvable gases (N<sub>2</sub>, CH<sub>4</sub>) became 0.2 °C lower on average as the gas pressure increased to 2 MPa. The reduction was especially notable in the presence of solvable CO<sub>2</sub>: it reached 0.5–0.6 °C at a gas pressure of 1.5 MPa for samples saturated with CH<sub>4</sub> + CO<sub>2</sub> and 1 °C at 0.8 MPa in the case of pure CO<sub>2</sub>. The CO<sub>2</sub>-bearing pore fluid in sand and silt samples freezes at 0.5–1.0 °C lower temperatures than that with methane or nitrogen.

The average reduction coefficients of pore water freezing point experimentally estimated for pressure effects of different gases are about 0.1 °C/MPa for poorly solvable gases (N<sub>2</sub> and CH<sub>4</sub>) and 1.36 °C/MPa for CO<sub>2</sub>.

The experimental results agree well (within 0.1–0.2 °C) with thermodynamic calculations based on pore water activity in the case of methane and nitrogen saturation but the misfit is greater in samples saturated with CH<sub>4</sub> + CO<sub>2</sub> and CO<sub>2</sub>: 0.4–0.5 °C or up to 0.8–1.2 °C in silt. Thus, the thermodynamic model has to be updated.

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