Characterization of Water Sorption by Mineral Dust and Nonproteinaceous Biological Particles at Subzero Temperatures

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Abstract

Atmospheric ice-nucleating particles (INPs) from mineral dust and non-proteinaceous biological sources can influence cloud formation, precipitation, and Earth's radiation budget due to their efficient freezing abilities. The ambient aerosol particles from these sources are abundant with ambient concentrations exceeding a few μg m^-3 for each type. Thus, the characterization of INPs and aerosol particles from these sources is important. We typically characterize their specific surface area (SSA), which is the primary variable to estimate their ice-nucleation active surface site density, using a sorbate gas, such as nitrogen. However, it is still uncertain how these particles interact with water vapor under subzero temperatures. To fill this gap, we used the 3Flex instrument (Micromeritics Instrument Corp.) with multiple sorbates to comprehensively characterize the nanoscale surface structure, pore size distribution, and accessibility to water molecules of a commercially available model proxy of mineral dust (illite NX) and cellulose materials. To date, we have completed more than 60 physisorption 3Flex experiments with various sorbates, such as CO_2, H_2O, Kr, and N_2, for each sorbent. In particular, we examined SSA by water vapor sorption at temperatures relevant to atmospheric heterogeneous freezing (~ 0 to -20 °C). We will present our results as physisorption isotherms. In addition, our preliminary results of temperature-dependent SSA observed for micro- and nano-crystalline cellulose materials as well as illite NX will be discussed. Our preliminary result suggests that the SSA of illite NX is less temperature-dependent compared to the cellulose materials, which may be potentially swelling while interacting with water. Therefore, illite NX may be suitable for an INP test proxy.

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Objectives

❖ Characterization of the nanoscale surface properties and accessibility of **sorbate** molecules on atmospherically relevant **sorbents.**

❖ Examining the **water vapor sorption** at temperatures relevant to atmospheric heterogeneous freezing (~0 to -20 °C).

❖ Comparing specific surface areas with various sorbates for each sorbent to understand the role of surface on **ice nucleation**.
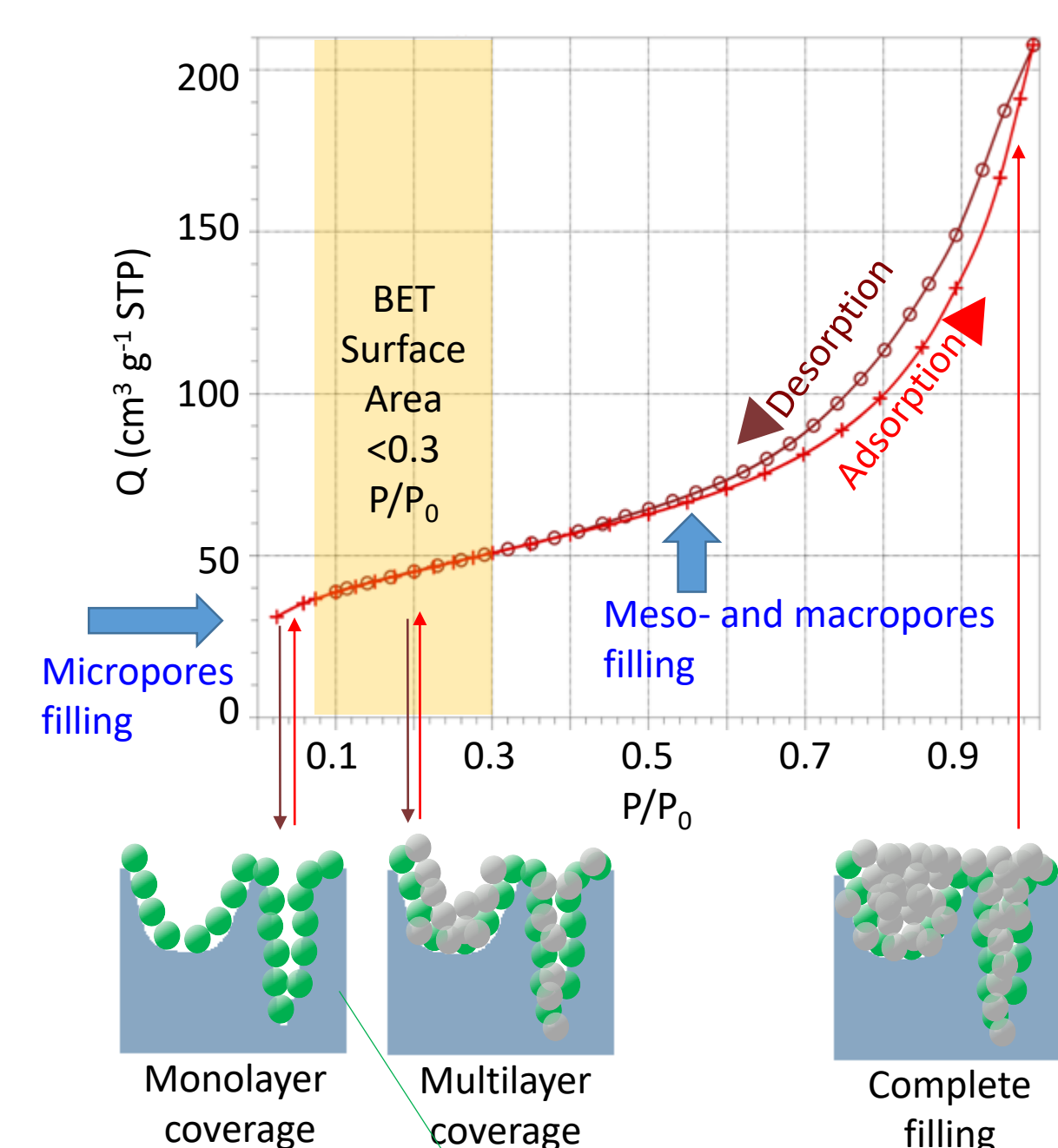
Method

❖ **3Flex instrument** [1] characterizes the specific surface area, nanoscale surface structure, pore size distribution of samples based on physisorption isotherms [2].

  ➢ **Sorbates**: CO_2, N_2, Kr, and H_2O

  ➢ **Sorbents**: illite NX, micro-crystalline cellulose, (MCC), and cellulose nano fiber (CNF) as dust and biological particle proxies

Sorption Isotherm & BET Theory

▼ **Illite NX Sorption Isotherm**

$$Q = \frac{1}{\left[\left(\frac{P_0}{P}\right)-1\right]\left[\frac{C-1}{V_m c}\left(\frac{P}{P_0}\right)+\frac{1}{V_m C}\right]}$$

where Q is the quantity of gas adsorbed (g/cm³), P/P_0 and P_0/P the relative pressure, C the BET (Brunauer-Emmett-Teller) constant, V_m the quantity of gas adsorbed when the entire surface is covered with a monolayer of molecules, $\frac{C-1}{V_m c}$ the slope of the linear portion of the isotherm, and $\frac{1}{V_m C}$ the y-intercept of the isotherm. NOTE: In the case of using water molecules as sorbates (i.e., $P/P_0 = RH_w$), we introduce a k constant to correct for the sorption state of the sorbed molecules beyond the first layer, so their character lies somewhere between the strongly bound first layer and the totally free liquid [3].

Monolayer coverage   Multilayer coverage   Complete filling

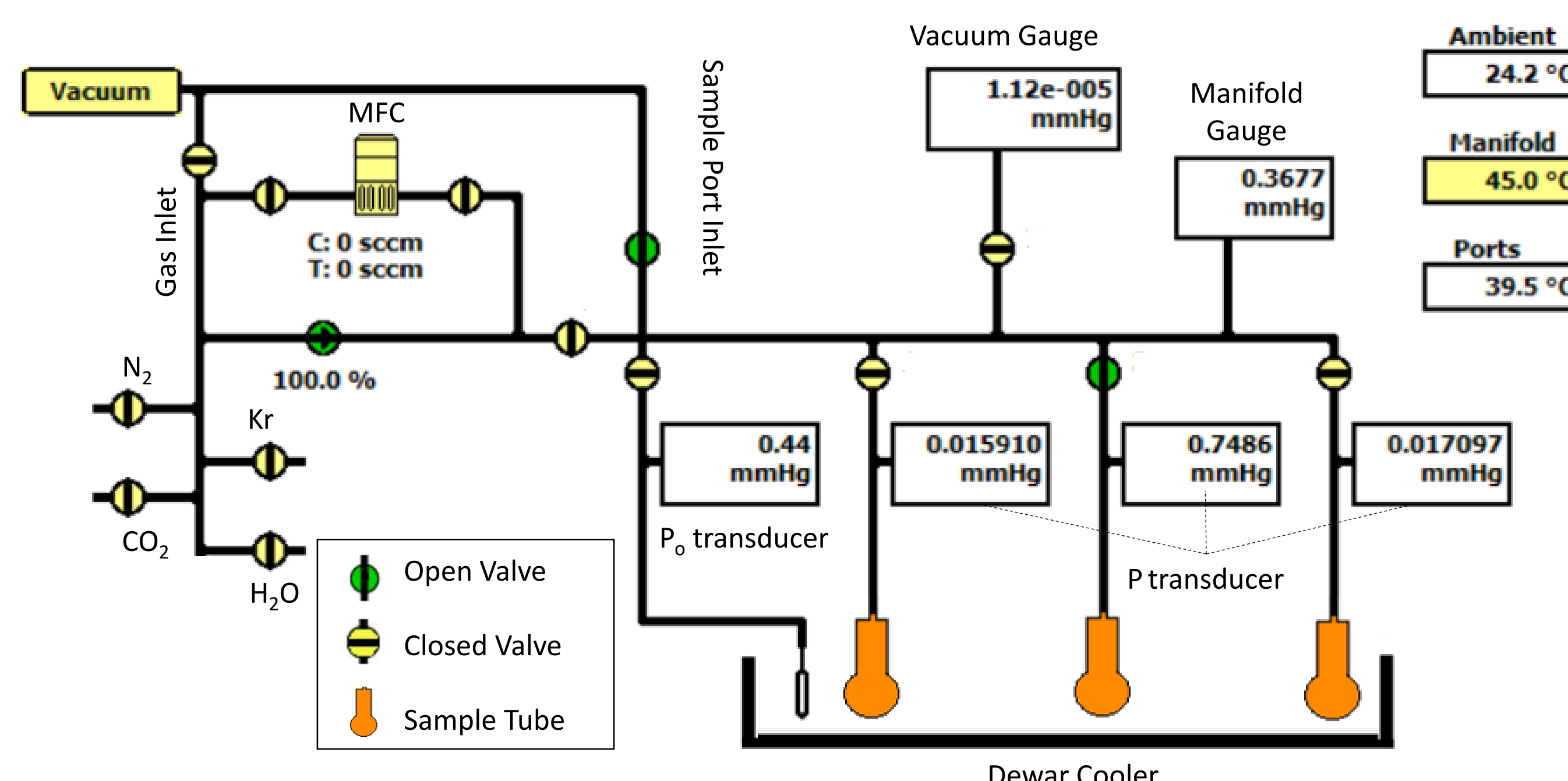$$S = \frac{V_m \sigma N_A}{m V_0}$$

where S is specific surface area (m² g⁻¹), σ is the area of surface occupied by a single adsorbed gas molecule (m²/molecule), N_A is the Avogadro constant (6.023 x 10²³ molecules/mole), m the mass of the sorbents (g), and V_0 the molar volume of the gas (cm³/mole). e.g., for nitrogen, σ is 16.2 Å² or 16.2 x 10⁻²⁰ m² & V_0 is 22414 cm³.

Gas adsorption (0.3 nm – 300 nm)

Micropores (<2 nm) Mesopores (2-50 nm) Macropores (> 50 nm)

CO_2 < N_2, Kr, and H_2O

Adapted from: PennState MCL web [4]

Pore Volume Estimation

$$V_p = \left[\frac{(S_1 - S_2)(t_1 - t_2)}{2}\right] K \qquad where\ t = 3.54\left[\frac{V_a}{V_m}\right]$$

in which, V_p is the volume of pores per a unit mass (cm³ g⁻¹), S_1 and S_2 the surface areas obtained at condition 1 and 2 (e.g., P/P_0 or other associated parameters), t the thickness of the adsorbed layer at different conditions, K the constant converting gas volume (STP) to liquid volume and Å to cm, and V_a the quantity of gas adsorbed at pressure P.

3Flex Schematics

▲ The operation of 3Flex is governed by automated control of 15 solenoid valves, 1 MFC, 1 vacuum pump unit, 2 pressure gauges, and 4 pressure transducers for 3 sample tubes in a dewar cooler.

Preliminary Results

❖ Our N_2 and Kr sorption BET values for individual sorbents are comparable to the BET values from previous studies; illite NX 124.4 m² g⁻¹ [5] and MCC 1.44 m² g⁻¹ [6].

❖ Our CNF (Nippon Paper Industries, CM-CNF powder 94.8 wt%) [7] exhibited a much lower BET specific surface area than nano crystalline cellulose (Melodea, 3wt%) [6], perhaps due to a fundamental difference in surface properties of CNF and NCC.

❖ We examined 0.2 – 1.4 g of MCC, and varying the mass did not impact our BET values (<4% variation).

❖ We also examined the influence of degassing process on the N_2 sorption analyses of MCC and CNF (<16% variation).

❖ For the analyses with Kr, CO_2, and H_2O, we made sure to degas our samples before each sorption measurement begins.

❖ 3Flex was calibrated by a known composition standard (Carbon Black ~21.5 m² g⁻¹) and examined only for C > 10 [2].

❖ The measured BET of CO_2 sorption is slightly higher than N_2 sorption for CNF, suggesting the presence of micro(nano-)pores.

❖ The resultant specific surface area of illite NX at 0 °C ≈ the result of N_2 sorption.

❖ We observed a slight suppression of water-based BET in the temperature range of -5 to -15 °C for illite NX (reason unknown).

❖ MCC and CNF exhibited much higher BET values through water sorption across the examined temperatures, presumably due to the physical alteration of sorbents while adsorbing water on the surface and absorbing bulk water (e.g., swelling) but likely not through liquid water condensation or phase change.

❖ The pore volume of illite NX is much larger than that of MCC and CNF. Illite NX might contain mesopores, which provides high specific surface area.
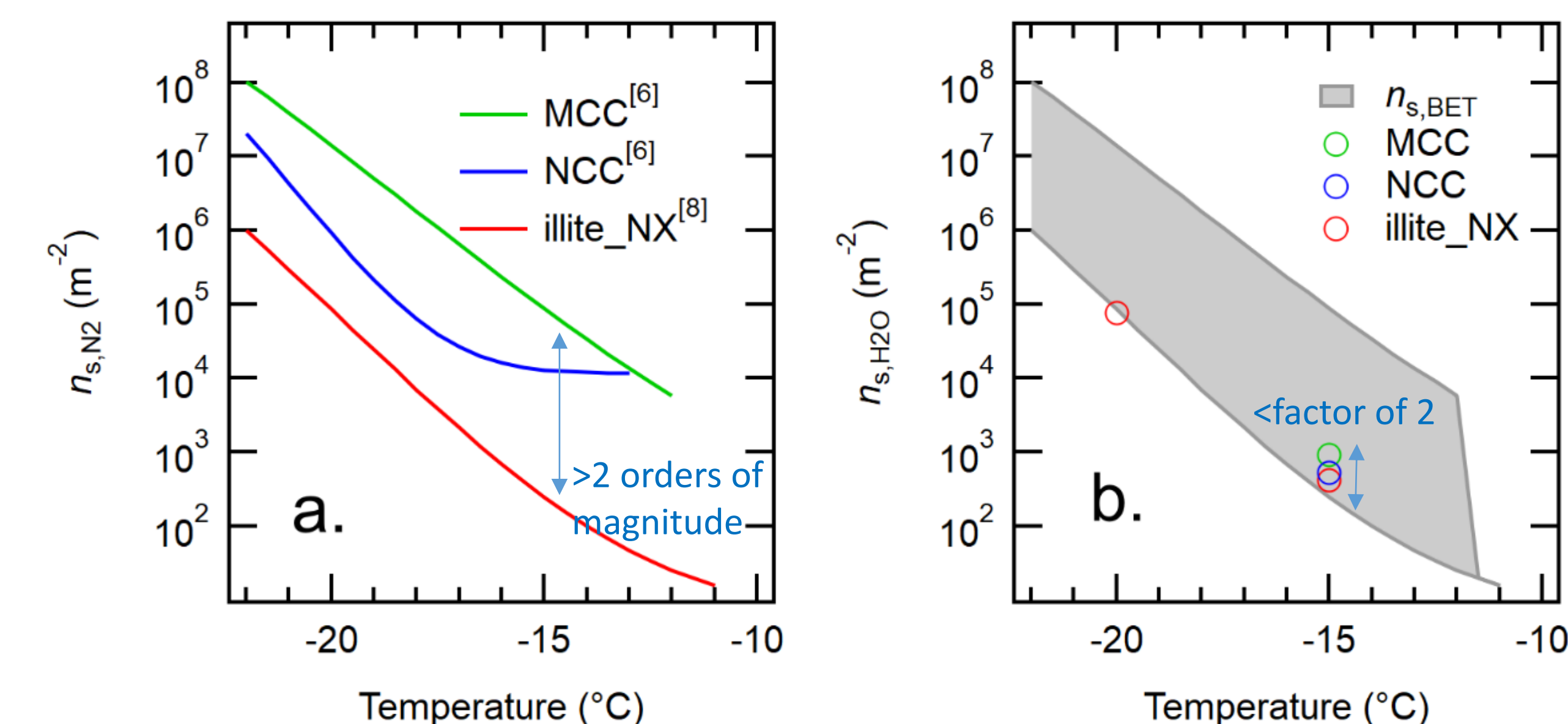
▼ Summary of BET specific surface area and pore volume of each sorbent

Sorbent	Sorbate	T (°C)	BET (m² g⁻¹)	Pore Volume (cm³ g⁻¹)
illite NX	N_2	-196	148.28 ± 47.39	3.73 x 10⁻¹ ± 7.29 x 10⁻² **
	H_2O	0	130.34 ± BDL*	N/A
	H_2O	-5	92.63 ± 0.67*	N/A
	H_2O	-15	74.84 ± 0.94*	N/A
	H_2O	-20	139.02 ± 1.52*	N/A
MCC	N_2	-196	0.96 ± 0.11	3.59 x 10⁻³ ± 1.95 x 10⁻³ **
	Kr	-196	1.27 ± 0.15	N/A
	H_2O	0	142.69 ± 15.91*	N/A
	H_2O	-5	99.59 ± BDL*	N/A
	H_2O	-15	136.56 ± 2.43*	N/A
CNF	N_2	-196	0.65 ± 0.10	4.39 x 10⁻³ ± 4.13 x 10⁻⁴ **
	Kr	-196	0.64 ± 0.01*	N/A
	CO_2	0	0.76 ± 0.18	1.63 x 10⁻⁴ ± 4.93 x 10⁻⁵ ***
	H_2O	0	74.26 ± 1.49*	N/A
	H_2O	-5	37.93 ± 2.76*	N/A
	H_2O	-15	193.93 ± 90.25*	N/A

*single measurement ± 3Flex inset error; **BJH method applied [2]; ***DFT method applied [2]; BDL: Below detection limit

Implication in Atmospheric Ice Nucleation

❖ Adapting the water sorption-based BET values for different ice-nucleating particles (INPs) yields a similar ice nucleation efficiency at -15 °C for examined INPs.

❖ The observed agreement is within a factor of two in terms of ice nucleation active surface site density, $n_{s,BET}(T) = n_m(T) / BET$ [8]. Note: n_m = concentration of INP scaled to a unit mass (g⁻¹).

▲ Ice nucleation efficiency of illite NX, MCC, and NCC in terms of n_s as a function of temperature based on (a) N_2 sorption BET and (b) H_2O sorption BET

Summary & Outlook

✓ Our test sorbents have different surface properties – illite NX possesses high specific surface area with mesopores while cellulose materials come with low specific surface area with micropores.

✓ We observed different affinities of water on our test sorbents as a function of temperature.

✓ **Understanding a total sorption properties (i.e., surface and bulk) via temperature-dependent water sorption (rather than a surface gas sorption) is key in understanding the physics of atmospheric ice nucleation on insoluble aerosol particles (confirmed hypothesis).**

❑ Surface analysis of other INPs and heterogeneous mixture of water-insoluble sorbents with water sorption, as well as their $n_{s,BET}(T)$ examination might lead to developing a simple ice nucleation parameterization (expected outcome).

❑ The molecular dynamics level process of water sorption BET suppression at certain temperatures must be understood (future study).

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