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LDRD PROJECT NUMBER: 224483
LDRD PROJECT TITLE: Dual microscopy to explore enhanced atmospheric ice nucleation on multi-component aerosols
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ABSTRACT: Using an optical microscopy setup adapted to in-situ studies of ice formation at ambient pressure, we examined a specific multicomponent mineral, microcline, with the ultimate aim of gaining a more realistic understanding of ice nucleation in Earth's atmosphere. We focused on a perthitic feldspar, microcline, to test the hypothesis that co-existence in some feldspars of K-rich and Na-rich phases are contributing to enhanced ice nucleation [1]. On a sample deliberately chosen to contain lamella, a typical perthitic microstructure, and flat surface regions next to each other, we performed a series of ice formation experiments. We found microcline to promote ice formation, causing a large number of ice nucleation events at around -27°C. The number of ice nuclei decreased from experimental run to experimental run, indicating surface aging upon repeated exposure to humidity. An analysis of 10 experimental runs of identical conditions did not reveal an obvious enhancement of ice formation at the lamellar microstructure. Instead, we find efficient nucleation at various surface sites that produce orientationally aligned ice crystallites with asymmetric shape. Based on this observation we propose that surface steps running along select directions produce microfacets of an orientation that is favorable to enhanced ice nucleation, similar to previously reported for K-rich feldspars [2].

INTRODUCTION AND EXECUTIVE SUMMARY OF RESULTS:

Although it has long been recognized that atmospheric ice nucleation governs most of earth's precipitation (including rainfall) and its radiation balance, the involved nanoscale physics and chemistry are still elusive, making climate prediction less reliable. Some of the most efficient ice nucleators are structurally and chemically very complex. Using optical microscopy adapted to a homemade microliter cloud chamber, we examined a specific multi-component mineral, perthitic feldspar, to finding out what surface property makes this mineral an exceptional ice nucleator. While numerous substances have been found to facilitate ice nucleation, understanding of the involved microscopic processes is insufficient to predict ice-nucleation ability ("ice-nucleability") of a given material. Our microscopy experiments are aimed at filling this gap, thus improving the scientific foundation of climate modelling.

While most aerosols facilitate nucleation of cloud droplets, typically only 1 particle in a million (at -20 Deg°C) is able to do the same for nucleation of (solid) ice [3], making this a rare and inherently difficult to predict event. Numerous recent studies [4] established that feldspar dust particles are extremely efficient in promoting atmospheric ice nucleation strongly effecting global precipitation and Earth's energy balance. More recently, Whale *et al.*[1] reported that the

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co-existence in some feldspars of K-rich and Na-rich phases are contributing to enhanced ice nucleability. These results based on averaging techniques lack direct experimental evidence of where and how ice nucleation takes place on the surface. This lack makes assertions about key mechanisms somewhat speculative. The working hypothesis for our work was that structural features at the boundaries between K-rich and Na-rich phases are the key to enhanced ice nucleation.

After modifying an optical microscopy setup to allow in-situ studies of ice formation at ambient pressure, we examined a specific multicomponent mineral, microcline, to test whether the co-existence of K-rich and Na-rich phases is contributing to enhanced ice nucleation or whether other factors might be more important. Performing a series of ice formation experiments, we confirmed that microcline promotes ice formation, e.g., by causing numerous ice nucleation events at around -27°C. Interestingly, the number of ice nuclei dropped from experimental run to experimental run, providing direct evidence that the mineral surface ages upon repeated exposure to humidity, a process believed to be important in Earth's atmosphere. Our analysis of ten T-drop runs under identical conditions did not confirm our hypothesis of enhanced ice formation at lamellar microstructures rich in domain boundaries. Instead, we find evidence suggesting that microfacets of certain orientations are mostly responsible for enhanced ice nucleation, consistent with previously reports for K-rich feldspars [2] based on experiments performed in (less realistic) vacuum environments.

DETAILED DESCRIPTION OF RESEARCH AND DEVELOPMENT AND METHODOLOGY:

The main shortcomings of the currently prevailing techniques are that they mostly either (1) provide averaging information (like the droplet freezing techniques [1,4]), or (2), like Environmental SEM [2], are performed in unrealistic vacuum conditions and use electron beams that potentially damage the sample surface, in particular those of insulating minerals. We used non-destructive optical microscopy to directly examine mineral samples under realistic atmospheric conditions with the goal of finding the specific surface sites at which enhanced ice nucleation occurs. Our experiments were conducted on a specific multi-component mineral, the perthitic feldspar microcline composed of $KAlSi_3O_8$ and $NaAlSi_3O_8$ domains. Samples were prepared in-house by mechanically cleaving small pieces from a microcline rock (Figure 1). Previously we had performed ice experiments in our lab using a homemade mixing chamber described in Refs. [5,6]. Its main limitation was that temperature and humidity could not be controlled completely independently making it difficult to perform series of experimental runs under exactly the same conditions. To make such repetitive reproducible runs possible, we now used a previously acquired commercial microscope setup (vendor: Linkam Inc., shown in Figure 2), featuring a temperature- and humidity-controlled sample stage.

Figure 1: microcline rock from which samples were mechanically cleaved

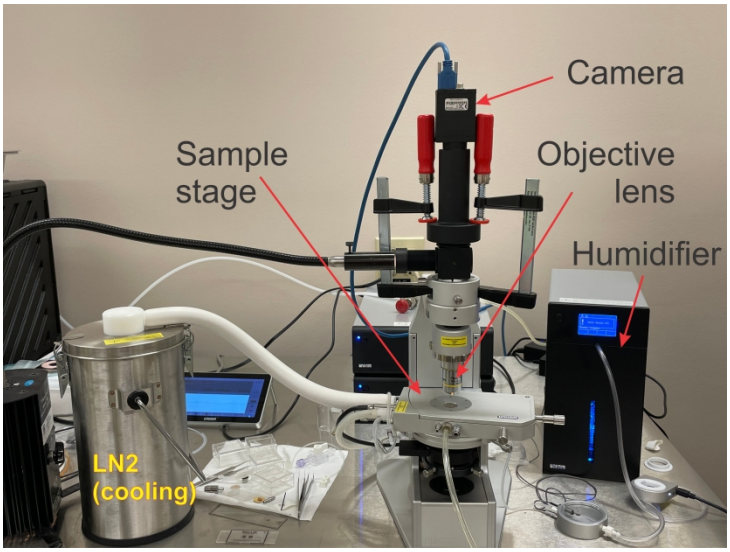

Figure 2: Experimental setup based on commercial optical microscope

In order to conduct ice nucleation experiments, the commercial microscopy setup had to be modified. First, water deposition (liquid or solid) had to be confined to a small volume around the sample so that the experiment is not dominated by uncontrolled drainage of humidity by water sinks outside the field of view of the microscope. To accomplish this, we designed and built a silicone piece that after insertion converts the commercial sample stage into a microliter cloud chamber (Figure 3). This modification in addition to using a gold substrate ensures that ice will form only on the sample (red arrow in Figure 3b).

The second necessary modification addressed the need to detect emerging ice crystallites at an early stage while they are still small, in order to determine the nucleation site with higher accuracy. Due to the transparency of the mineral sample, the initial setup which illuminated the sample from the side made it difficult to distinguish emerging ice crystallites from some features of the microcline substrate. A simple setup where a semi-transparent mirror is inserted into the light path, allowed top-down illumination of the sample surface, resulted in microscopy images which clearly show the ice crystals as conspicuous dark objects (Figure 4).

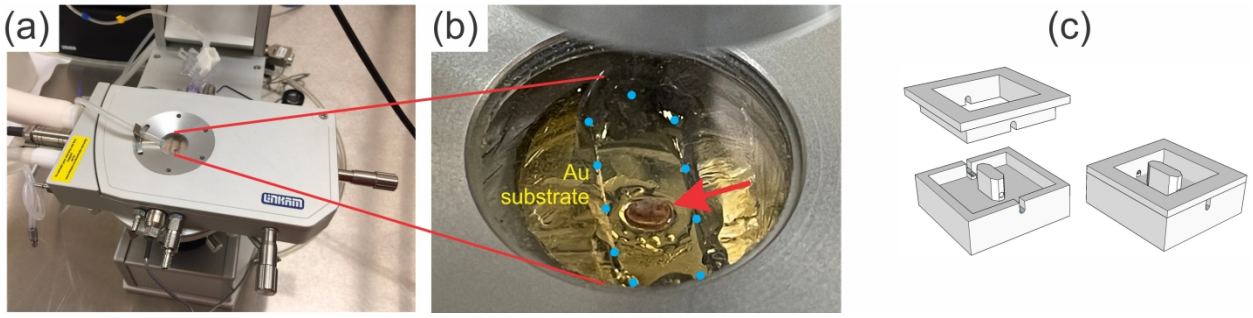

Figure 3: (a) temperature regulated sample stage (b) zoom into area around the sample (red arrow). A silicone insert produced using the mold shown in (c) confines the humidity to the small volume (marked blue) around the sample.

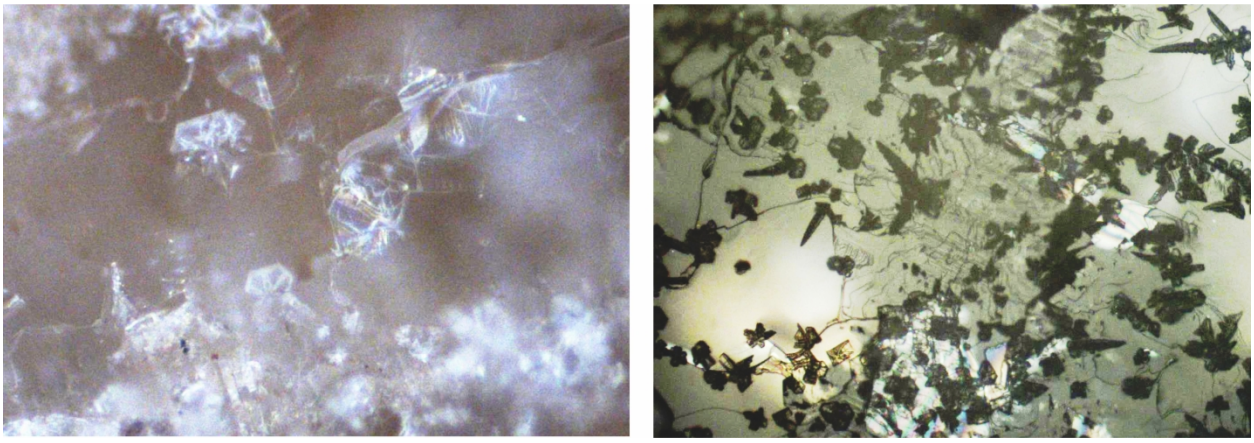

Figure 4: Effect of illumination. The initial configuration produces images that make distinguishing ice from surface features of the mineral substrate difficult (left). Top-down illumination renders the emerging ice crystallites very dark and easy to detect (right).

Temperature-drop tests performed on various samples or just the Au substrate alone confirmed that this modified microscopy setup is capable of performing well controlled and highly reproducible ice nucleation experiments.

RESULTS AND DISCUSSION:

With the goal of testing the hypothesis that structural features at the boundaries between K-rich and Na-rich phases are the key to enhanced ice nucleation of perthitic feldspar, we produced multiple microcline samples attempting to find one that exhibits lamella structures surrounded by flat surface regions. This would allow a direct comparison of the ice nucleation ability ("ice

nucleability") of the classic perthitic microstructure, lamellae, with that of flat regions containing few or no domain boundaries. Figure 5(a) taken from Ref. [7] depicts such lamella microstructure, and Figure 5(b) shows our choice of sample surface, on which all the experiments described below were performed.

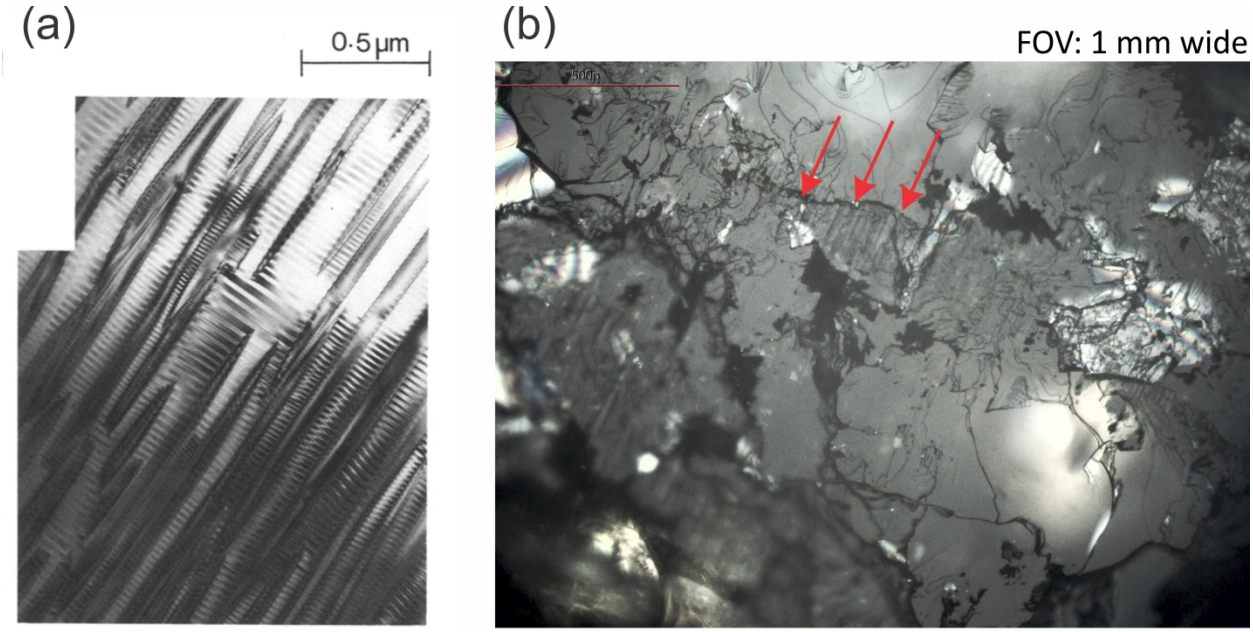

Figure 5: (a) Exsolution lamellae: the classic perthitic microstructure, taken from Ref.[7], (b) Our choice of microcline sample, exhibiting co-existance of lamella structures and flat regions. All experiments included in our analysis were performed on this sample.

On the surface region shown in Figure 5 (b) we performed multiple ice nucleation experiments. The following analysis was done on a series of 10 experimental runs under identical conditions. The sample cell was fed with clean nitrogen humidified to a level of relative humidity at room temperature of RH=1%. Maintaining absolute humidity, the sample cell was cooled down at a constant rate of 2°C/min until the microcline sample is decorated by a large number of ice crystallites at around ~-35°C. The surface evolution was recorded by the microscope camera at a frame rate of 10/s. After each run the cell temperature was raised above ~+20°C to completely evaporate any ice and water deposits.

Figure 6 (a) shows a histogram of the activation temperatures of ice nucleation events aggregated over all 10 experimental runs. With nucleation starting at ~-25°C and peaking at ~-27°C, the microcline clearly promotes ice formation, as expected, as the comparison with homogeneous nucleation, i.e., without help from a substrate or a dust particle, reveals. More interestingly, we find that the ice nucleability of microcline varies with time, as seen in Figure 6 (b). During the first experimental run the number of ice nuclei detected within the field of view of our microscope was the highest (45). This number of ice nuclei gradually decreased from

experiment to experiment levelling off at around 15-20 nuclei after the 4th run. This observation showcases the aging upon humidity exposure of the mineral surface with respect to ice nucleability, a process believed to be important for the fate of mineral dust aerosols in Earth's atmosphere.

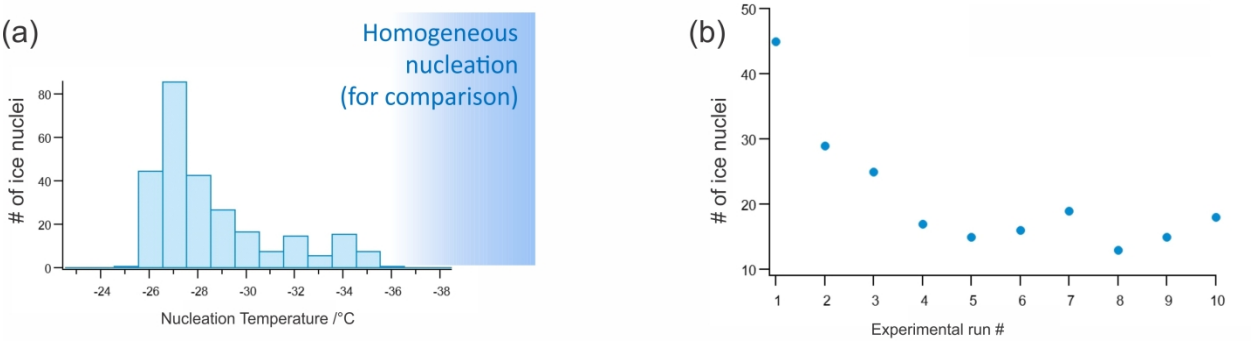

Figure 6: (a) Histogram of activation temperatures (b) Evolution of microcline's ice nucleability

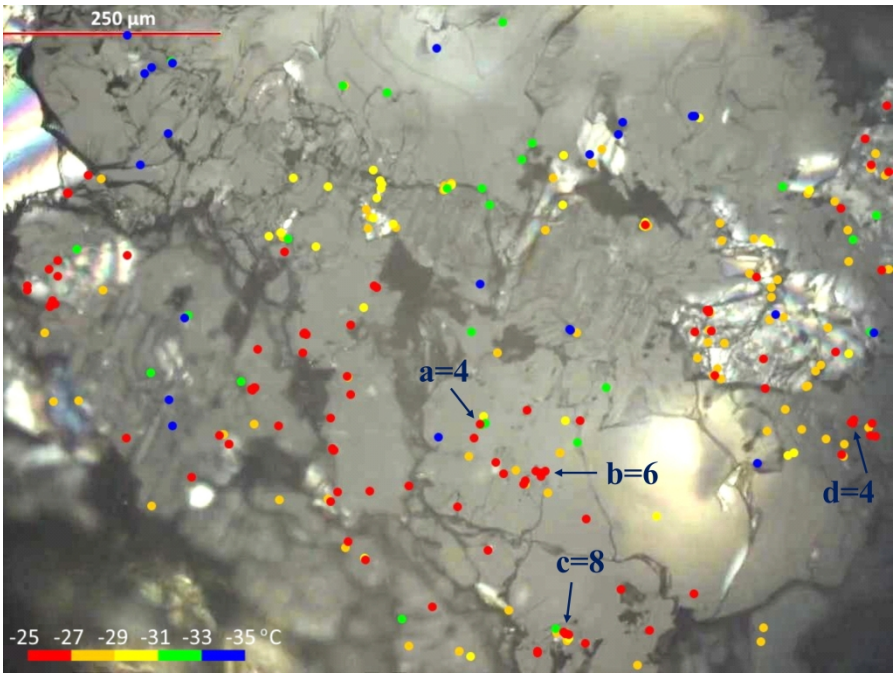

Figure 7: Map of nucleation site efficiency. Nucleation sites are marked by dots, which are color coded according to the nucleation temperature.

The overall nucleation behavior is summarized in Figure 7 showing a map of the efficiency of nucleation sites throughout the 10-run series. The dots marking those sites are color coded according to the temperature at which a given site activates, i.e., causes an ice

nucleus to form. The most efficient ones are the red ones, causing ice to emerge at the highest temperatures. Some of those efficient ones are labelled a,b,c, or d with the number indicating how many times that particular site activated in the course of the 10-run series. The fact that there is no obvious enhancement of ice formation at the lamellar microstructure (marked in Figure 5 b) suggests that perthitic domain boundaries do not dominate ice formation. This statement comes with the caveat that the analysis was limited to the surface regions (~70 % of the total area) that allowed reliable determination of the nucleation sites, i.e., the areas close to the focal plane excluding a few of the dark patches.

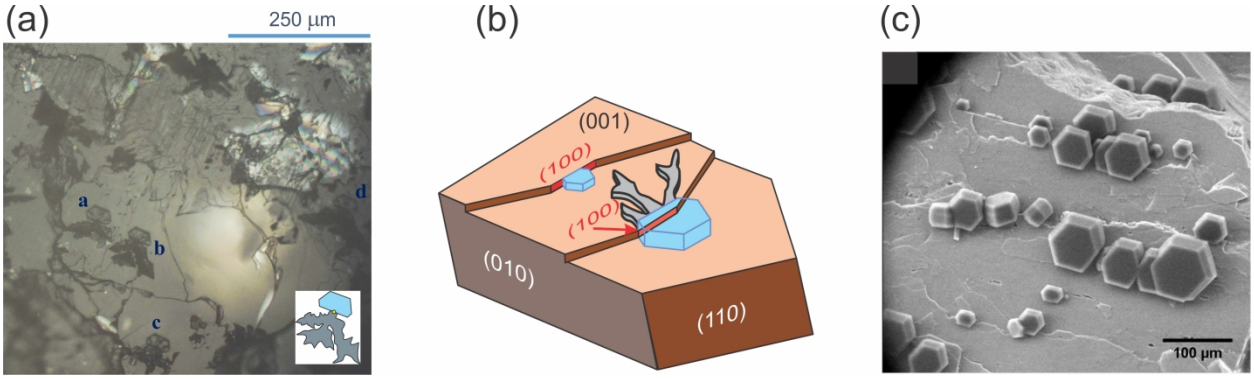

Figure 8: (a) frame acquired shortly after ice nucleation occurred at the most efficient sites labeled a-d in figure 7. The insert schematically shows the shape of the ice features emerging from these sites. (b) illustrates the proposed scenario producing those ice features. (c) aligned ice crystallites grown on K-rich feldspar in vacuum observed with ESEM, image taken from Ref. [2].

To learn about the nature of the most efficient nucleation sites labelled a-d in Figure 7, we examine a microscopy frame acquired shortly after nucleation (Figure 8(a)). It reveals that the ice crystallites emerging from these sites all share a rather peculiar asymmetric shape and the same azimuthal orientation, as illustrated in the insert of Figure 8(a). The schematic in Figure 8 (b) illustrates the mechanism we propose to be associated with the ice formation at these special substrate locations. The observed asymmetry can straightforwardly be accounted for by the inherently asymmetric surface steps, which are always bound by an upper and a lower surface terrace. A step riser of a step segment running along a certain direction can constitute a microfacet on which ice nucleation is very efficient. Kiselev et al.'s observation for K-rich feldspar with ESEM in vacuum (Ref.[2] and Figure 8(c)) had identified the (100) facet as an extremely efficient ice nucleator. Ice crystals growing epitaxially on these facets would automatically be oriented the same way, which straightforwardly explains the observed azimuthal alignment of the ice crystal emerging from the sites a,b,c, and d. (Once the height of the crystallite exceeds that of the step riser, water can attach from the upper side of the surface step, causing the ice feature to start growing onto the upper terrace. The difference in shape, i.e., dendritic versus hexagonal platelet, might be caused by a directional bias of the flow of water molecules). Unfortunately, confirmation that the highly efficient nucleation sites in our

experiments constitute (100) microfacets was beyond the scope of this project. Nevertheless, the experimental evidence presented above makes us confident that the basic mechanism underlying enhanced ice nucleation in our ambient-pressure experiments are the same as the one reported by Kiselev et al. [2] for their in-vacuum experiments.

ANTICIPATED OUTCOMES AND IMPACTS:

This work successfully addressed a capability gap in climate science: the ability to gain microscopic information about minerals' surface properties responsible for their efficiency as ice nucleating particles in the atmosphere. While currently prevailing techniques [1,4] either mostly provide averaging information, or in the case of Environmental SEM [2] are performed in unrealistic vacuum conditions and employ electron beams that potentially damage the mineral surface, we developed and demonstrated a non-destructive optical microscopy setup capable of directly examining mineral samples under realistic atmospheric conditions to reveal the surface sites that dominate ice nucleation. Overcoming limitations of a previous setup [5,6], we are now capable of controlling temperature and humidity independently to performing highly reproducible ice nucleation experiments. Such reproducibility will be vital for envisioned future projects that compare atmospheric ice nucleation on various mineral substrates under a multitude of atmospheric conditions.

While we were able to provide evidence for the importance of microfacets for atmospheric ice nucleation on multi-component feldspar, which had previously only been shown under vacuum conditions [2], the next logical step would be to put this finding onto firmer ground by conducting a larger-scale study involving other microscopy techniques like AFM and SEM-EDS. Such a study should be performed on a larger range of minerals to obtain the critical mass of information needed to make the implementation of ice nucleation in DOE's Energy Exascale Earth system model (E3SM) more realistic, e.g., by replacing CNT-based on droplet geometry, or adding more realistic aerosol tracers for feldspar dust. Our initial results described above give us confidence that such a study would lead to multiple high-impact publications.

Another area where further research is likely to yield results that can be implemented into E3SM or other large-scale climate models, concerns how "aging" of mineral aerosols upon atmospheric exposure affects their ability to nucleate ice. We have demonstrated our capability to examine aging upon exposure to humidity (see Figure 6(b)) and see no unsurmountable obstacles to investigate exposure to other relevant substance like volatile organic compounds (VOCs), or even exposure to real atmosphere employing ARM's tethered balloon systems. Such research could produce "aging factors" to be applied to the ice nucleabilities of mineral dust tracers implemented in E3SM or other climate models.

CONCLUSION:

During this project we created the ability to perform reliable reproducible ice nucleation experiments under realistic atmospheric conditions using non-destructive microscopy. We

demonstrated the potential of this capability on a complex mineral, the perthitic feldspar microcline. We observed how its efficiency in nucleating ice quickly drops and then saturates upon repeated exposure to humidity, thus demonstrating the need and our ability to conduct further studies of mineral aging. Our experiments did not yield evidence for enhanced ice nucleation at boundaries between K-rich and Na-rich feldspar domains, although we cannot exclude this possibility in general. Our results suggest that nucleation is dominated by surface step-related microfacets, as had previously been observed under unrealistic vacuum conditions [2]. Further studies are needed to generate actionable knowledge for improving the implementation of atmospheric ice nucleation in DOE's Energy Exascale Earth system model (E3SM) or similar climate models.

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