Organic matter matters for ice nuclei of agricultural soil origin

Y. Tobo[1,*], P. J. DeMott[1], T. C. J. Hill[1,2], A. J. Prenni[1,], N. G. Swoboda-Colberg[3], G. D. Franc[2,***], and S. M. Kreidenweis[1]**

[1]{Department of Atmospheric Science, Colorado State University, Fort Collins, CO 80523, USA}

[2]{Department of Plant Sciences, University of Wyoming, Laramie, WY 82071, USA}

[3]{Department of Geology and Geophysics, University of Wyoming, Laramie, WY 82071, USA}

[*]{now at: National Institute of Polar Research, Tachikawa, Tokyo 190-8518, Japan}

[**]{now at: Air Resources Division, National Park Service, Lakewood, CO 80225, USA}

[***]{Deceased}

Correspondence to: Y. Tobo (yutaka.tobo@gmail.com)

Abstract

Heterogeneous ice nucleation is a crucial process for forming ice-containing clouds and subsequent ice-induced precipitation. The importance for ice nucleation by airborne desert soil dusts composed predominantly of minerals is widely acknowledged. On the other hand, the potential influence of agricultural soil dusts on ice nucleation has been poorly recognized, despite recent estimates that they may account for up to ~25% of the global atmospheric dust load. We have conducted freezing experiments with various dusts, including agricultural soil dusts derived from the largest dust source region in North America. Here we show evidence for the significant role of soil organic matter (SOM) in particles acting as ice nuclei (IN) under mixed-phase cloud conditions. We find that the ice nucleating ability of the agricultural soil dusts is similar to that of desert soil dusts, but is clearly reduced after either H_2O_2 digestion or dry heating to 300°C. In addition, based on chemical composition analysis, we demonstrate that organic-rich particles are more important than mineral particles for the ice

nucleating ability of the agricultural soil dusts at temperatures warmer than about –36°C. Finally, we suggest that such organic-rich particles of agricultural origin (namely, SOM particles) may contribute significantly to the ubiquity of organic-rich IN in the global atmosphere.

1 Introduction

It has been shown that certain aerosol particles acting as ice nuclei (IN), such as dust, soot, volcanic ash and biological materials, are required to trigger ice nucleation at temperatures warmer than about –36°C (Pruppacher and Klett, 1997; Szyrmer and Zawadzki, 1997; Hoose and Möhler, 2012; Murray et al., 2012). In particular, laboratory and modeling studies suggest that desert soil dusts composed predominantly of minerals are the most important IN sources at temperatures between about –36°C and –15°C because of their ice nucleation properties and abundances in the global atmosphere (Hoose et al., 2010; Murray et al., 2012). In the estimates from these studies, the contribution of other dusts (e.g., agricultural soil dusts) to the global atmospheric IN population has not been taken into account. Although a very large uncertainty remains regarding estimates for the contribution of agricultural emissions to the global atmospheric dust load within the range of 0 to 50% (Mahowald et al., 2004; Tegen et al., 2004; Forster et al., 2007; Ginoux et al., 2012), the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (Forster et al., 2007) and a more recent study (Ginoux et al., 2012) suggest 0-20% and 25% as reasonable estimates, respectively.

So far, some laboratory experiments with samples immersed in supercooled water have shown that soils having higher contents of organic matter may serve as better sources of IN than clay minerals (Schnell and Vali, 1972; Conen et al., 2011; O’Sullivan et al., 2014). Agricultural soils are known to be complex mixtures of minerals, organic matter and so on. However, the chemical composition of individual agricultural soil dust particles capable of nucleating ice has remained uncertain. Also, the focus of these earlier studies has centered on the role of fertile soil dusts as IN at temperatures warmer than about –15°C (Schnell and Vali, 1972; Conen et al., 2011; O’Sullivan et al., 2014), where clay minerals are less effective as IN (Szyrmer and Zawadzki, 1997; Murray et al., 2012).

In this study, we examine heterogeneous ice nucleation by aerosolized agricultural soil dusts under conditions above water saturation at temperatures warmer than about –36°C (i.e., mixed-phase cloud conditions where ice crystals coexist with liquid cloud droplets) and their chemical composition. In particular, we focus on the relative importance of organics (i.e., soil organic matter (SOM)) as nuclei for heterogeneous ice nucleation.

2 Materials and methods

Agricultural soil dusts were prepared using surface soils (0 to 5 cm in depth) collected on 17 May 2011 from sugar beet (42.12878°N, 104.39516°W, 1,270 m above mean sea level) and grass/alfalfa fallow (42.12266°N, 104.38585°W, 1,270 m above mean sea level) fields at the Sustainable Agricultural Research and Extension Center (SAREC) near Lingle (mean annual temperature: 9.3°C), Wyoming, USA. The agricultural fields are located within the largest dust source region in North America (Ginoux et al., 2012). Soil samples were air dried on an aluminum tray in clean conditions and then divided into particles smaller than 45 µm by dry sieving. As a reference for natural desert soil dusts, we used China loess soils (CJ-1) (Nishikawa et al., 2000), which were collected in an arid area in Gansu Province, China. We also used the Clay Minerals Society kaolinite (KGa-1b) (Chipera and Bish, 2001; Murray et al., 2011), for comparison. In addition to the untreated samples, we prepared samples treated with H_2O_2 and ones heated to 300°C. The former samples were prepared by boiling gently in a 30% H_2O_2 solution until almost all organic matter was expected to be digested (i.e., until no visible reaction could be detected by addition of more H_2O_2), followed by rinsing with deionized water and drying. The latter samples were prepared by exposing to dry heat at 300°C for about 2 hours in a muffle furnace.

The overview of the setup for dust aerosol generation and sampling is illustrated in Fig. 1. Dry dust particles were generated using a self-built flask dust generator (nitrogen flow for dust generation: ~2 L min^{-1}) and then passed through a cyclone (cut-point diameter: 3.5 µm at 2 L min^{-1}) and ^{210}Po neutralizers. It has been reported that while the number-size distributions of airborne soil dust particles vary depending on the source area conditions (e.g., surface wind speed, soil characteristics) and long-range transport regimes, the mode diameters during their long-range transport typically range from ~2 µm down to submicrometer (Formenti et al., 2011; Kok, 2011). Here, we prepared particles with a mobility diameter of 600 nm selected in a differential mobility analyzer (DMA; Model 3081, TSI Inc.; sheath flow: 4.5 L min^{-1}, sample flow: 1 L min^{-1}). A condensation particle counter (CPC; Model 3010, TSI Inc.) was used to measure number concentrations of the total aerosol particles. A Colorado State University continuous flow diffusion chamber (CFDC; Rogers et al., 2001; sheath flow: 8.5 L min^{-1}, sample flow: 1.5 L min^{-1}) was used to measure number concentrations of IN active under conditions above water saturation (105.0±0.5% relative humidity with respect to liquid water) at temperatures warmer than about –36°C. Under such conditions, heterogeneous ice nucleation processes including deposition nucleation (ice formation on the surfaces of insoluble nuclei from ice-supersaturated water vapor) and condensation/immersion freezing (ice formation during or following the condensation growth of aqueous droplets containing insoluble nuclei) are expected to be activated (Sullivan et al., 2010a, b; Tobo et al., 2012; Wex et al., 2014). In particular, we expect the predominance of immersion freezing in this regime, since the relative humidity is high enough to activate cloud droplet formation. Following such a particle nucleation/growth section, the CFDC has a droplet evaporation section where only ice saturation exists. Since cloud droplets cannot survive though the evaporation section unless the relative humidity with respect to liquid water in the particle nucleation/growth section exceeds ~108% (Sullivan et al., 2010a, b), only particles that form ice crystals are counted as IN with an optical particle counter at the outlet. The IN data were collected every second and then averaged for 150-180 sec. The total dust aerosol particles and IN active at given temperatures were collected on a butvar film supported by Ni grids (EM Japan Co., Ltd.) using impactors. The dust aerosol particles were collected using a two-stage jet impactor (Matsuki et al., 2010a, b; Tobo et al., 2010). We used only the second stage of the impactor, because the 50% cutoff aerodynamic diameters of the first and second stages at a sample flow of 1 L min^{-1} are estimated to be 1.6 and 0.2 µm, respectively, and the mobility diameter of the particles is 600 nm (= 0.6 µm). For the IN sampling, the particles that nucleated ice and were grown to ice crystal sizes were collected using a single jet impactor (Prenni et al., 2013; Tobo et al., 2013) installed at the outlet of the CFDC. The 50% cutoff aerodynamic diameter at a sample flow of 1.5 L min^{-1} is estimated to be 2.9 µm. Then, the size, morphology and elemental composition of individual particles were analyzed manually after Au-coating (coating thickness: 2-3 nm) using a Quanta FEG MK2 scanning electron microscope (SEM; FEI Company) combined with an energy dispersive X-ray analyzer (EDX; Model 51-XMX0005, Oxford Instruments America Inc.). After the SEM images of individual particles were taken, the X-ray spectra from the particles were acquired for 20 sec of live time at an acceleration voltage of 20 kV.

3 Results and discussion

3.1 Freezing experiments

In Fig. 2a, we show the number fraction of particles capable of nucleating ice as a function of temperature. The results show that the ice nucleation properties of agricultural soil dusts obtained from sugar beet and grass/alfalfa fallow fields in Wyoming are similar to each other. Treatment with H_2O_2 is a commonly used technique to oxidize organic matter from soils and to obtain the remaining minerals (Conen et al., 2011; O'Sullivan et al., 2014). After H_2O_2 treatment, both agricultural soil dusts experienced a significant reduction in their ice nucleating ability at temperatures warmer than about –36°C, suggesting that they contain specific ice nucleation active constituents that can be removed by H_2O_2 treatment (most likely, organic matter). To evaluate the possibility that the ice nucleation properties of some mineral components might be affected by H_2O_2 treatment, we conducted freezing experiments with China loess soil dust (desert loess; a proxy for Asian natural soil dusts (Nishikawa et al., 2000)) and kaolinite (Chipera and Bish, 2001) in the same manner. The results indicate that the impact of H_2O_2 treatment on their ice nucleating ability is relatively small (within the range of error). Dry heating is also known as a technique to remove and/or deactivate organic matter in soils. For example, Fernández et al. (1997) reported that soils heated at 150°C exhibit no significant loss of organic matter, whereas those heated at 490°C lose almost all the organic matter. As for the ice nucleation properties, we confirmed that dry heating to 300°C has a similar impact to H_2O_2 digestion (Fig. 3).

In Fig. 2b, we compare the experimental data for agricultural soil dusts collected in Wyoming with the parameterizations for various dusts based on the number of ice nucleation active sites per unit surface area (i.e., ice nucleation active site density: n_s). Their surface area is estimated assuming that all particles are spherical (the n_s parameterizations for the samples presented in Fig. 2a are summarized in Fig. A1a). The results show that the n_s values for the original Wyoming agricultural soil dusts are relatively similar to those for desert and agricultural soil dusts from various locations in the world, at least in the temperature range examined. After H_2O_2 digestion, however, the n_s values for the Wyoming agricultural soil dusts are reduced to an almost comparable level to those for kaolinite. The n_s values for the kaolinite presented here are relatively similar to those reported by Murray et al. (2011) and Wex et al. (2014), but are more than one order of magnitude lower than those reported by Kanji et al. (2013) at temperatures warmer than about –30°C despite the use of the same Clay Minerals Society kaolinite (Fig. A1b). The difference may be related to different experimental technique; however, further speculation concerning this issue is beyond the remit of this study and is not pertinent to the major conclusions drawn from the comparison of our experimental results obtained using the CFDC. Around –36°C (near to the limit for homogeneous freezing temperature of water in droplets, Koop et al., 2000), all samples presented here show relatively similar n_s values.

3.2 Identification of particle types

To identify particle types in the agricultural soil dusts used here, we examined the elemental composition of individual particles using SEM/EDX analysis. A major difficulty in the EDX analysis of submicron particles is their high transparency for the primary electron beam (Laskin and Cowin, 2001). Since the electron beam penetrates the entire particle, the EDX spectrum from the particle projection area contains the background signal from the butvar film supported by Ni-grids as well as the signal of the particle coated with Au. For this reason, as illustrated in Fig. 4, we compare the EDX spectrum of the particle projection area with that from the particle-free area. We found that the majority of the analyzed particles can be classified as either “organics” or “minerals”. The major elements of particles categorized as organics are C, N and S (some of the elements found in smaller amounts: O, F, Na, Cl, K). It has long been known that SOM serves as a reservoir of nutrients, such as N, P and S (Paul, 2007). As for the samples analyzed here, all the particles categorized as organics contained both N and S, but P was not found. It should also be noted that we classify carbonaceous particles lacking N and S (e.g., soot-like particles as shown in Fig. 4e) as “others” and not organics. The major element of particles categorized as minerals is Si (some of the elements found in smaller amounts: C, O, F, Na, Mg, Al, Cl, K, Ca, Mn, Fe, Ti). We consider that the detection of the C peak in particles categorized as minerals may be attributable to the presence of carbonates (e.g., $CaCO_3$, $CaMg(CO_3)_2$). In this study, only particles containing the major elements of both organics and minerals (i.e., C, N, Si and S) are categorized as “organo-mineral mixtures”. Therefore, the possibility remains that Si-rich particles containing N- and S-free organics or very small amounts of organics are categorized as minerals and not organo-mineral mixtures.

In Fig. 5a, we summarize the results of SEM/EDX analysis for the total dust aerosol particles (n = 95) and IN active at temperatures of –36°C, –30°C and –24°C (n = 58, 52 and 68) in the untreated sugar beet soil dust particles. The results show that mineral particles account for more than half of the total aerosol population and organic-rich particles for about 40%. However, the number fraction of mineral particles in the IN population decreases dramatically with increasing freezing temperatures. Correspondingly, the fraction of organic particles increases, accounting for nearly 90% of the IN population at around –24°C. The fraction of organo-mineral mixture particles or other particles (mainly, soot-like and/or Na-rich particles) is only 2-7% in both the total aerosol and IN populations.

Furthermore, we estimated the fractions of organic and inorganic particles in the agricultural soil dust IN, based on the results of freezing experiments with the soil dusts before and after H_2O_2 treatment. Here, we assume that organic and inorganic particles account for 40% and 60% of the total agricultural dust aerosol particles, respectively (this assumption is based on the results of the SEM/EDX analysis) and that all organic compounds can be digested and removed via H_2O_2 treatment, but inorganic components are not altered by H_2O_2 treatment. The calculation method is detailed in Appendix A1. The temperature-dependent changes in the fractions of organic and inorganic IN estimated from this calculation (Fig. 5b) are roughly consistent with the results from the SEM/EDX analysis (Fig. 5a). If H_2O_2 treatment can cause a certain reduction in the ice nucleating ability of inorganic components, the possibility remains that the results in Fig. 5b may somewhat overestimate the fractions of organic IN. We have not exhaustively analyzed the influence of H_2O_2 treatment on all known minerals that may be present in the soil dusts. Nevertheless, the results presented here indicate that the reduction of the ice nucleating ability of the agricultural soil dusts after H_2O_2 treatment (Fig. 2) can be explained mainly by the removal of organic matter.

Based on these results, we propose organic-rich particles (namely, SOM particles) as the most important component of agricultural soil dusts for ice nucleation in the temperature regime examined. We note that while phosphorus is known to be one of the major biological markers (Pósfai et al., 2003; Pratt et al., 2009; Creamean et al., 2013; Cziczo et al., 2013), no P-containing particles were found in all of the analyzed particles. This may suggest that there was no measurable contribution of microorganisms (e.g., fungal spores, bacteria) to the numbers of the agricultural soil dusts or IN examined here, although the possibility of the presence of some P-free microorganisms or plants (or their fragments) cannot be ruled out. Organic matter in soils is composed of a variety of macromolecules, such as lignin, cellulose, hemicellulose, protein, lipids, humic-like substances (e.g., humic acid, fulvic acid) and so on (Paul, 2007). So far, freezing experiments with certain standard humic-like substances have indicated that while they can act as IN under mixed-phase cloud conditions (Fornea et al., 2009; Wang and Knopf, 2011; Knopf and Alpert, 2013; Rigg et al., 2013; O'Sullivan et al., 2014), they are much less effective as IN than fertile soil dusts (O'Sullivan et al., 2014). In addition, although the potential importance of ice nucleation by other macromolecules like protein (Hartmann et al., 2013), cellulose (Hiranuma et al., 2014) or fragments of pollen grains (Pummer et al., 2012; Augustin et al., 2013) has been suggested, it still remains unclear what materials are responsible for the major source of SOM particles having very high ice nucleating ability.

It is noteworthy that although agricultural soil dusts collected in Wyoming have similar ice nucleating abilities to those collected in England (Fig. 2b), the major component responsible for ice nucleation at temperatures between about –36°C and –15°C has been interpreted in different ways. Our results demonstrate that the presence of organic compounds (i.e., SOM particles) has a significant influence on the ice nucleating ability of the Wyoming soil dusts throughout the entire temperature range down to –36°C. In contrast, O'Sullivan et al. (2014) suggested that mineral components are more important than biogenic components for the ice nucleating ability of the England soil dusts at temperatures colder than about –15°C. The suggestion by O'Sullivan et al. (2014) was based on the results from freezing experiments with the soil dusts before and after wet heating to 90°C. It is expected that wet heating to 90-100°C deactivates only certain organic matter (e.g., heat-sensitive proteins or proteinaceous compounds, Christner et al., 2008). In fact, it has been reported that wet heating to 90-100°C is less effective than H_2O_2 digestion in reducing the ice nucleating ability of fertile soil dusts (Conen et al., 2011; O'Sullivan et al., 2014). In this study, we applied treatments designed to remove and/or deactivate almost all organic matter (i.e., H_2O_2 digestion or dry heating to 300°C). Thus, although the possibility remains that the soil dusts from Wyoming and England are very different in composition, we speculate that the different interpretations of the major component responsible for ice nucleation are in part attributable to the different experimental approaches.

Our results also indicate that agricultural and desert soil dusts have similar ice nucleating abilities and are more efficient IN than kaolinite over the wide temperature range examined (Fig. 2b). However, since treatments to remove and/or deactivate organic matter have a small impact on the ice nucleating ability of China loess soil dust, the key ice nucleation active sites contained in desert soil dusts are presumed to be related to inorganic compounds. In this regard, a recent study reported that the feldspar (in particular, K-feldspar) component can explain higher n_s values for desert soil dusts than clay minerals (Atkinson et al., 2013). It is likely that the ice nucleating ability of the feldspar component is resistant to H_2O_2 treatment (O'Sullivan et al., 2014). It may also be important to note that dust-productive soils in China tend to have much higher contents of feldspar than those in North America (Nickovic et al., 2012). Since we have not evaluated the feldspar content in dust samples used here, further investigations are required to verify the hypothesis concerning the contribution of the feldspar component to their ice nucleating abilities. Nevertheless, our results clearly demonstrate that the key IN type is quite different between agricultural and desert soil dusts.

3.3 Atmospheric implications

In order to estimate the contribution of agricultural soil dusts to the IN population in the atmosphere, we combined a global simulation of atmospheric concentrations of different aerosol particle types at the 600 hPa pressure altitude (Hoose et al., 2010; Murray et al., 2012) with experimentally derived n_s values. The calculation method for potential IN number concentrations is detailed in Appendix A2. The n_s values used in the calculation are based on the parameterizations for desert soil dusts (Niemand et al., 2012) and for agricultural soil dusts derived from this study. In Fig. 6a, we show the estimates of potential number concentrations of soil dust IN, based on the classical view that all dusts are of natural origin and that desert soil dusts are representative of natural dusts (Murray et al., 2012). In addition, we provide the estimates of potential number concentrations of soil dust IN by assuming that agricultural soil dusts account for either 5% (Tegen et al., 2004) or 25% (Ginoux et al., 2012) of the total soil dust emissions (Fig. 6b). In these cases, agricultural soil dusts represent a relatively small but non-negligible contribution to the IN population, as compared with natural soil dusts. Given the results of immersion freezing experiments showing that soils having higher contents of organic matter can serve as efficient IN even at temperatures warmer than about –15°C (Schnell and Vali, 1972; Conen et al., 2011; Hill et al., 2013; O'Sullivan et al., 2014), the contribution of agricultural soil dusts to the IN population at these temperatures may exceed that of natural soil dusts (not shown here). The influence of biological IN on ice clouds is also a controversial topic (Pratt et al.., 2009; Creamean et al., 2013; Cziczo et al., 2013). In this regard, the results in Fig. 6b suggest that the contribution of agricultural soil dusts to the IN population may be more significant than that of microorganisms, as exemplified by certain well-known fungal spores (Iannone et al., 2011;

Murray et al., 2012), at least at temperatures below about –18°C and on a global scale. However, further studies will be necessary to understand the contribution of various other microorganisms or their fragments. Considering that SOM particles play the dominant role in the ice nucleating ability of agricultural soil dusts at temperatures warmer than about –36°C (Fig. 5), the results in Fig. 6b suggest the possibility that SOM particles of agricultural origin may contribute strongly to the global atmospheric IN population.

The results presented here offer a possible explanation for the presence of organic-rich particles found in residues within ice clouds and ice-phase precipitation. For example, previous field studies have indicated that organic/sulfate/nitrate particles account for about 5-25% of the nuclei involved in heterogeneous ice nucleation in ice-containing clouds, whereas mineral particles always predominate (DeMott et al., 2003; Richardson et al., 2007; Pratt et al.., 2009; Creamean et al., 2013; Cziczo et al., 2013). Previous filed studies have also pointed out the possibility of heterogeneous ice nucleation by urban anthropogenic organic particles at temperatures as warm as –20°C (Knopf et al., 2010; Wang et al., 2012b), although the composition of individual IN has not been examined. It has been suggested that certain sulfates (e.g., ammonium sulfate) and oxidized organics exist as anhydrous salts or glassy solids at relatively cold temperatures and hence act as effective IN (Abbatt et al., 2006; Murray et al., 2010; Wang et al., 2012a). On the other hand, this theory cannot readily explain heterogeneous ice nucleation at temperatures warmer than about –30°C (Abbatt et al., 2006; Murray et al., 2010; Wang et al., 2012a). Here, we speculate that SOM particles of agricultural origin can be regarded as a possible source for the organic/nitrate/sulfate particles found in residues within ice clouds. This idea may also be supported by recent work showing that most organic matter contained in hailstones originated from soils (Šantl-Temkiv et al., 2013), leading to speculation that SOM particles might participate in ice nucleation as well as be scavenged by ice-phase precipitation. Further field, laboratory and modeling studies will therefore be necessary to validate the hypothesis that SOM particles of agricultural origin are indeed an important source of nuclei for atmospheric ice nucleation.

4 Conclusions

In this study, we highlight the role of agricultural soil dusts as IN under mixed-phase cloud conditions. Our results indicate that the ice nucleating ability of agricultural soil dusts is comparable to that of desert soil dusts, but is reduced to almost the same level as clay minerals after treatments to remove and/or deactivate almost all organic matter (i.e., H_2O_2 digestion or dry heating to 300°C). Based on chemical composition analysis of individual IN, we demonstrate that the presence of SOM particles, rather than mineral particles, is largely responsible for the ice nucleating ability of the agricultural soil dusts at temperatures warmer than about –36°C. In addition, we suggest the possibility that SOM particles of agricultural origin may be regarded as a possible significant source influencing the ubiquity of organic-rich IN and also residues found within ice clouds and ice-phase precipitation.

Appendix A

A1 Estimation of the composition of ice nuclei of agricultural soil origin

Here, we explain how to estimate the fraction of organic and inorganic IN of agricultural soil origin as shown in Fig. 5b, based on the n_s parameterizations obtained from freezing experiments. The number concentration of IN active at a given temperature T, $N_{IN}(T)$, can be described by (Murray et al., 2012):

$$N_{IN}(T) = N_{total}\,(1-\exp(-n_s(T)\,s)) \tag{A1}$$

where N_{total} is the number concentration of total particles, $n_s(T)$ is the ice nucleation active site density and s is the surface area of a single particle. Similarly, the number concentrations of IN of agricultural soil origin, $N_{IN\,[agri.\,soil\,dust]}(T)$, can be expressed as:

$$N_{IN\,[agri.soil\,dust]}(T) = N_{total\,[agri.soil\,dust]}\,(1-\exp(-n_{s\,[agri.soil\,dust]}(T)\,s)) \tag{A2}$$

where $N_{total\,[agri.\,soil\,dust]}$ is the number concentration of agricultural soil dust particles, $n_{s\,[agri.\,soil\,dust]}(T)$ is the n_s value for untreated agricultural soil dust particles presented in Fig. A1a. When calculating s, all soil dust particles are assumed to be spherical particles having a diameter of 600 nm. Also, if only inorganic particles exist after the removal of organic matter by H_2O_2 treatment, the number concentration of inorganic IN of agricultural soil origin, $N_{IN\,[inorganic]}(T)$, can be expressed as:

$$N_{IN\,[inorganic]}(T) = N_{total\,[inorganic]}\,(1-\exp(-n_{s\,[inorganic]}(T)\,s)) \tag{A3}$$

where $N_{total\,[inorganic]}$ is the number concentration of inorganic particles of agricultural soil origin, $n_{s\,[inorganic]}$ is the n_s value for H_2O_2-treated agricultural soil dust particles presented in Fig. A1a. To obtain $N_{total\,[inorganic]}(T)$ in Eq. (A3), we assume that inorganic (mostly, mineral) particles account for 60% of the total agricultural soil dust particles (i.e., organic:inorganic ratio = 4:6; see the top-left pie chart in Fig. 5b), with the choice of the ratio guided by in the elemental composition analysis of individual 600 nm particles from the total population (i.e., the top-left pie chart in Fig. 5a):

$$N_{\text{total [inorganic]}} = 0.6\, N_{\text{total [agri.soil dust]}} \tag{A4}$$

By combining Eqs. (A2), (A3) and (A4), the fractions of both inorganic and organic particles in the agricultural soil dust IN, $f_{\text{IN [inorganic]}}(T)$ and $f_{\text{IN [organic]}}(T)$, respectively, can be estimated:

$$f_{\text{IN [inorganic]}}(T) = \frac{N_{\text{IN [inorganic]}}(T)}{N_{\text{IN [agri.soil dust]}}(T)} \tag{A5}$$

$$f_{\text{IN [organic]}}(T) = 1 - f_{\text{IN [inorganic]}}(T) \tag{A6}$$

A2 Estimation of the number concentrations of ice nuclei of agricultural soil origin

Here, we describe a possible method to estimate the global mean number concentrations of IN of agricultural soil origin under mixed-phase cloud conditions as shown in Fig. 6. According to modeling estimates, the zonal annual mean number concentrations of soil dusts (1 μm in diameter) at the 600 hPa pressure altitude range from 0.1 to 50 cm^{-3} (Hoose et al., 2010; Murray et al., 2012). If soil dusts in the global atmosphere can be regarded as consisting of only desert and agricultural soil dusts, then the zonal annual mean concentration of soil dusts, $N_{\text{total [soil dust]}}$ (= 0.1 to 50 cm^{-3}), may be expressed as:

$$N_{\text{total [soil dust]}} = N_{\text{total [natural soil dust]}} + N_{\text{total [agri.soil dust]}} \tag{A7}$$

where $N_{\text{total [natural soil dust]}}$ is the number concentration of natural soil dust particles. Recently, Murray et al. (2012) estimated the zonal annual mean number concentration of IN of natural soil origin, $N_{\text{IN [natural soil dust]}}(T)$, using the formula:

$$N_{\text{IN [natural soil dust]}}(T) = N_{\text{total [natural soil dust]}}\ (1 - \exp(-n_{\text{s [desert soil dust]}}(T)\ s)) \tag{A8}$$

where $n_{\text{s [desert soil dust]}}(T)$ is the n_{s} value for desert soil dusts (Niemand et al., 2012). In this calculation, Murray et al. (2012) assumed that all dusts are of natural origin (i.e., $N_{\text{total [natural soil dust]}}$:$N_{\text{total [agri. soil dust]}}$ = 100:0) and that natural soil dusts can be regarded as desert soil dusts. The results are shown in Fig. 6a. On the other hand, in Fig. 6b, we provide two estimates of the global mean number concentrations of both natural and agricultural soil dust IN by assuming that agricultural soil dusts account for 5% ($N_{\text{total [natural soil dust]}}$:$N_{\text{total [agri. soil dust]}}$ = 95:5) and 25% ($N_{\text{total [natural soil dust]}}$:$N_{\text{total [agri. soil dust]}}$ = 75:25) and by combining Eqs. (A2), (A7) and (A8).

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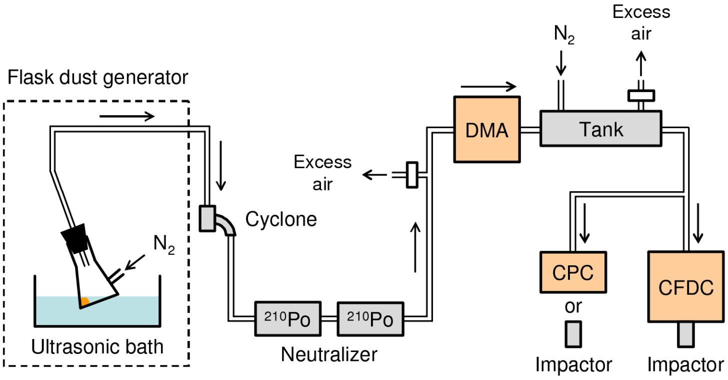

Fig. 1. Schematics of freezing experiment systems. Dry dust particles were generated from the flask dust generator. The DMA selected particles with a mobility diameter of 600 nm for analysis by the CPC and CFDC. Impactors were used for direct sampling of the total particles and ice-nucleating particles.

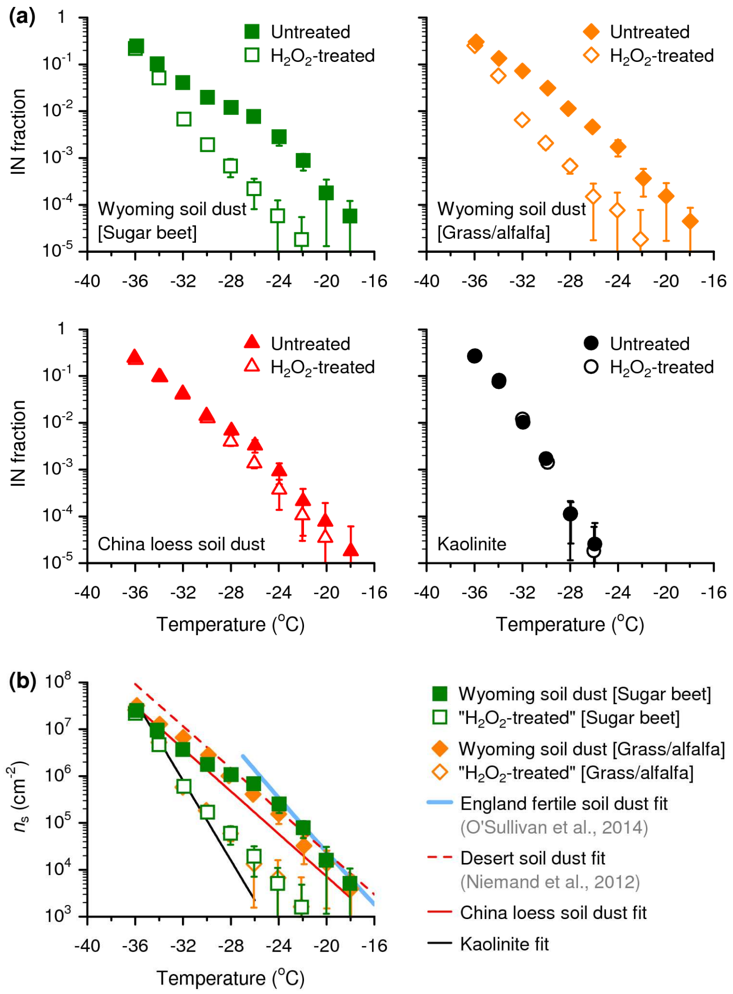

Fig. 2. Ice nucleating ability for various dusts under mixed-phase cloud conditions. **(a)** Fraction of 600 nm particles capable of nucleating ice. The data for untreated and H_2O_2-treated samples are shown in each figure. **(b)** Ice nucleation active site densities for various dusts. The n_s parameterizations for various dusts are compared with the data for agricultural soil dusts (before and after H_2O_2 treatment) collected in Wyoming. The n_s parameterizations for China loess soil dust and kaolinite are based on the data presented in Fig. A1a. The n_s parameterizations for fertile soil dusts collected in England (O'Sullivan et al., 2014) and desert soil dusts (Niemand et al., 2012) are also shown. Error bars represent standard deviations.

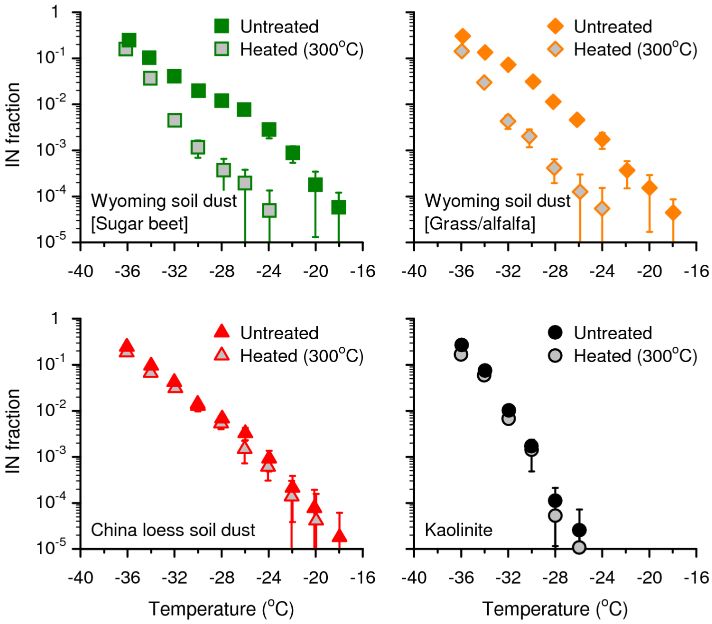

Fig. 3. Same as Fig. 2a, but for the data for untreated and heated samples.

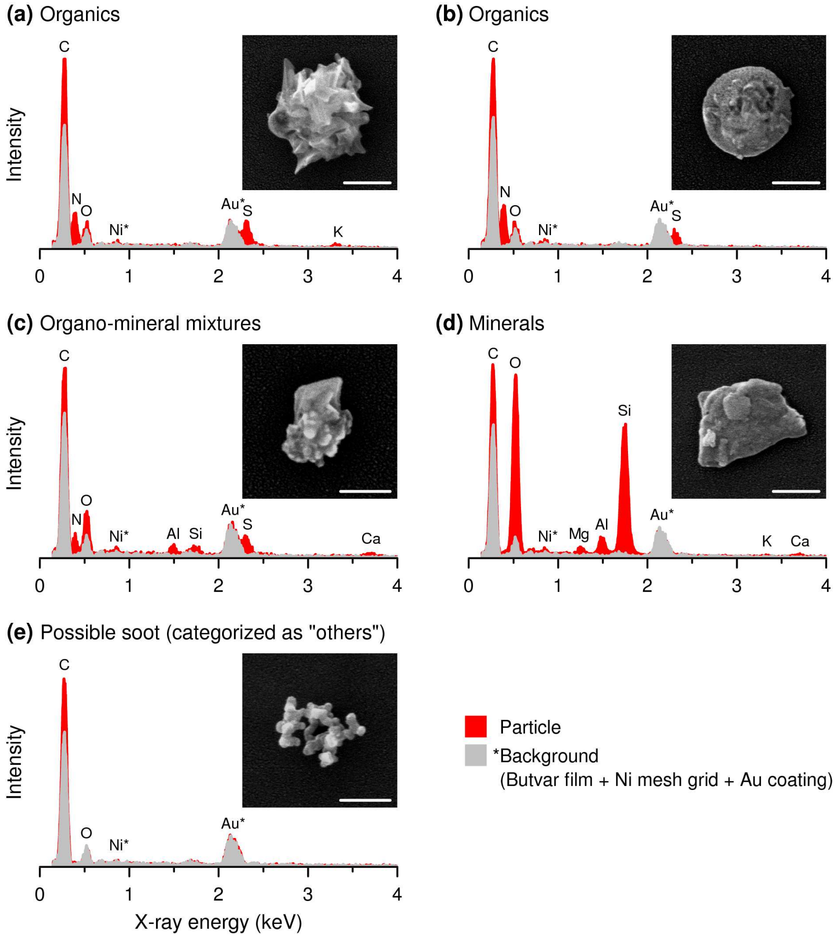

Fig. 4. Exemplary SEM/EDX images of sugar beet soil dust particles. **(a)** Organic particle (crystalline-shape type). **(b)** Organic particle (amorphous-shape type). **(c)** Organo-mineral mixture particle. **(d)** Mineral particle. **(e)** Soot-like particle. The SEM/EDX images were acquired after Au-coating. Scale bars, 300 nm. Red X-ray spectra show the elemental composition of each particle, and grey X-ray spectra represent the background signal caused by a butvar film supported by Ni mesh grids and Au-coating.

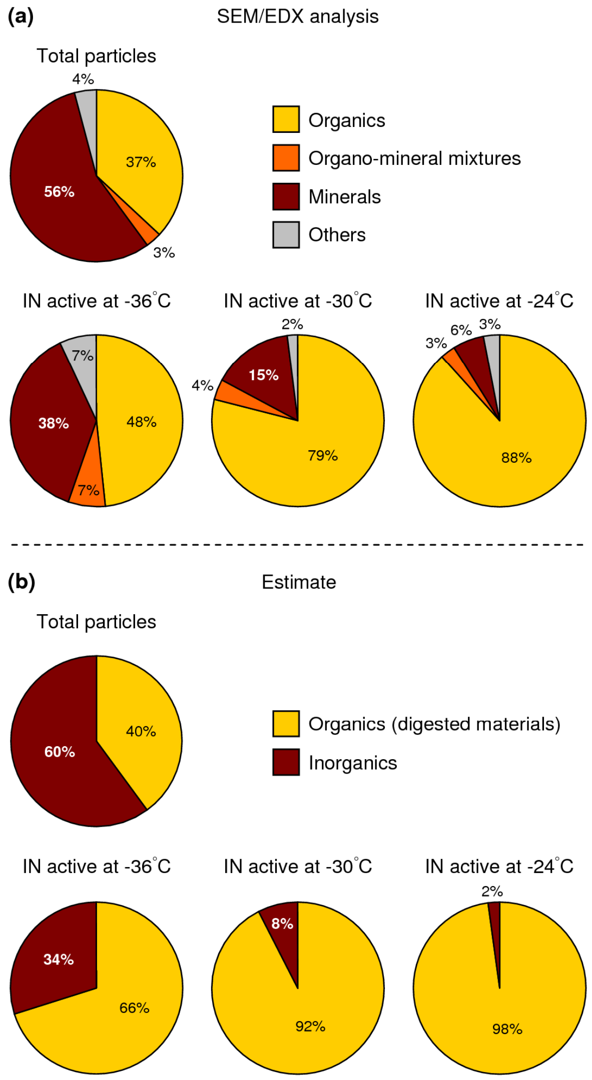

Fig. 5. Relative contributions of different particle types to agricultural soil dusts. **(a)** Compositions of the total dust aerosol particles (*n* = 95) and IN active at –36°C, –30°C and –24°C (*n* = 58, 52 and 68) determined by SEM/EDX analysis. Untreated sugar beat soil dust particles are used. **(b)** Compositions of the IN active at –36°C, –30°C and –24°C estimated from the freezing experiments with untreated and H_2O_2-treated agricultural soil dusts. In this calculation, the percentages of organic and inorganic particles in the total dust aerosol particles are set to 40% and 60%, respectively, and then the n_s parameterizations presented in Fig. A1a are used to estimate the number fractions of organic and inorganic IN.

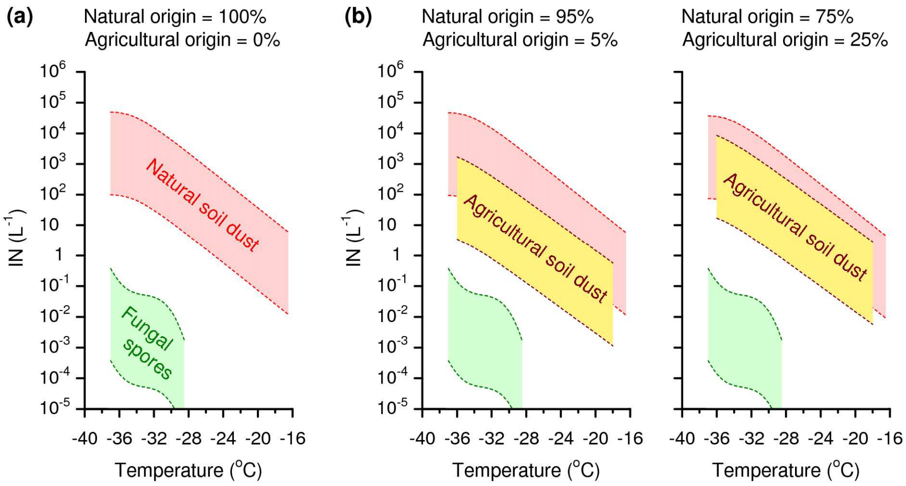

Fig. 6. Estimates of global mean number concentrations of IN active under mixed-phase cloud conditions. **(a)** IN number concentrations for soil dusts, assuming that all dusts are of natural origin (i.e., desert origin). **(b)** IN number concentrations for agricultural and natural soil dusts, assuming that 5% and 25% of all dusts are of agricultural origin. Calculations are performed using the n_s parameterizations for desert soil dusts (Niemand et al., 2012) and for untreated agricultural soil dusts (Fig. A1a) and the range of the zonal annual mean concentrations of dusts at 600 hPa (lower and upper limits) (Hoose et al., 2010; Murray et al., 2012). Also provided for comparison are IN number concentrations for fungal spores estimated using the n_s parameterization for *Cladosporium* spores (Iannone et al., 2011; Murray et al., 2012) and the range of the zonal mean concentrations of fungal spores at 600 hPa (lower and upper limits) (Hoose et al., 2010; Murray et al., 2012).

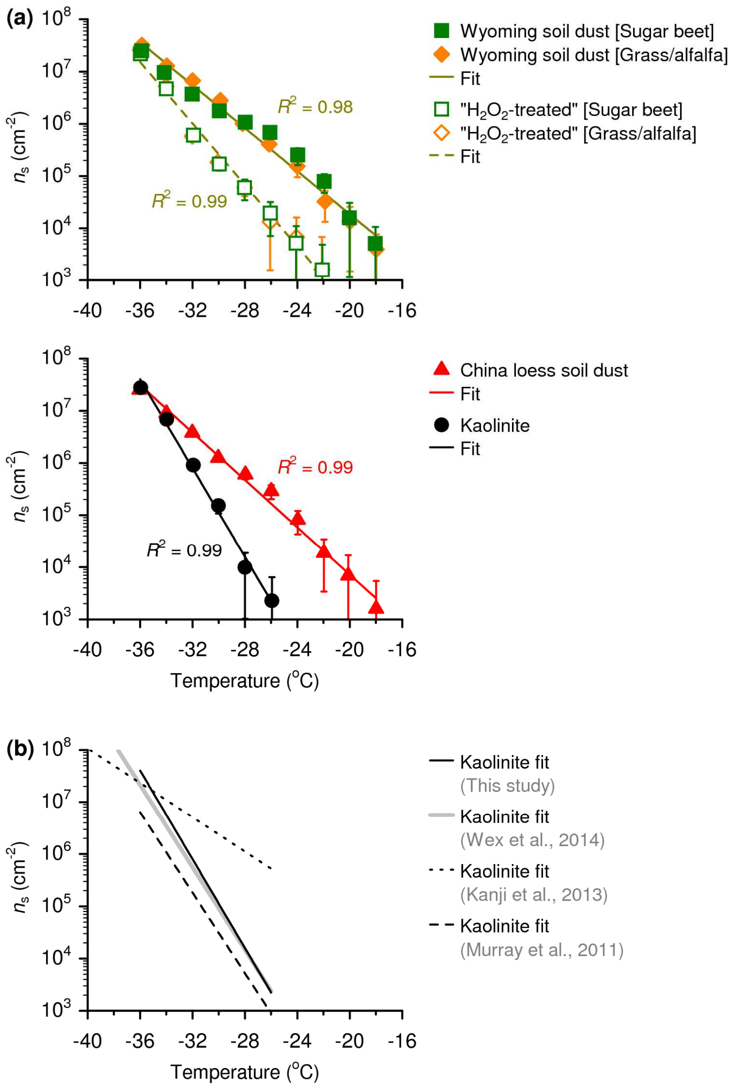

Fig. A1. Fit to ice nucleation active site densities for various dusts. **(a)** Parameterizations of n_s for untreated agricultural soil dusts ($\ln(n_s) = -0.4736T + 0.3644$; validity range: $-36°C < T < -18°C$) and for H_2O_2-treated agricultural soil dusts ($\ln(n_s) = -0.6773T - 7.8436$; validity range: $-36°C < T < -22°C$). Parameterizations of n_s for untreated China loess soil dust ($\ln(n_s) = -0.5230T - 1.5767$; validity range: $-36°C < T < -18°C$) and for untreated kaolinite ($\ln(n_s) = -0.9803T - 17.7764$; validity range: $-36°C < T < -26°C$) are also shown. Error bars represent standard deviations. **(b)** Comparison of the n_s parameterizations for kaolinite from this study, Murray et al. (2011), Kanji et al. (2013) and Wex et al. (2014).