



Feldspar minerals as efficient deposition ice nuclei

J. D. Yakobi-Hancock, L. A. Ladino, and J. P. D. Abbatt

Department of Chemistry, University of Toronto, Toronto, ON, Canada

Correspondence to: J. D. Yakobi-Hancock (jyakobi@chem.utoronto.ca)

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Abstract. Mineral dusts are well known to be efficient ice nuclei, where the source of this efficiency has typically been attributed to the presence of clay minerals such as illite and kaolinite. However, the ice nucleating abilities of the more minor mineralogical components have not been as extensively examined. As a result, the deposition ice nucleation abilities of 24 atmospherically relevant mineral samples have been studied, using a continuous flow diffusion chamber at -40.0 ± 0.3 °C and particles size-selected at 200 nm. By focussing on using the same experimental procedure for all experiments, a relative ranking of the ice nucleating abilities of the samples was achieved. In addition, the ice nucleation behaviour of the pure minerals is compared to that of complex mixtures, such as Arizona Test Dust (ATD) and Mojave Desert Dust (MDD), and to lead iodide, which has been previously proposed for cloud seeding. Lead iodide was the most efficient ice nucleus (IN), requiring a critical relative humidity with respect to ice (RH_i) of 122.0 ± 2.0 % to activate 0.1 % of the particles. MDD (RH_i 126.3 ± 3.4 %) and ATD (RH_i 129.5 ± 5.1 %) have lower but comparable activity. From a set of clay minerals (kaolinite, illite, montmorillonite), non-clay minerals (e.g. hematite, magnetite, calcite, cerussite, quartz), and feldspar minerals (orthoclase, plagioclase) present in the atmospheric dusts, it was found that the feldspar minerals (particularly orthoclase) and some clays (particularly kaolinite) were the most efficient ice nuclei. Orthoclase and plagioclase were found to have critical RH_i values of 127.1 ± 6.3 % and 136.2 ± 1.3 %, respectively. The presence of feldspars (specifically orthoclase) may play a significant role in the IN behaviour of mineral dusts despite their lower percentage in composition relative to clay minerals.

1 Introduction

Ice clouds affect the earth's energy budget and hydrological cycle, with their impact on climate representing one of the largest uncertainties in the forecasting of future climate (Baker and Peter, 2008; DeMott et al., 2010; Forster et al., 2007; Ramanathan et al., 2001). These clouds influence the radiative properties of the earth by trapping its outgoing infrared radiation and reflecting incoming visible solar radiation, thus having both a warming and cooling effect on the earth (Baker and Peter, 2008). The uncertainty in the impact of ice clouds on radiative forcing arises in part from an incomplete understanding of the formation processes of these clouds (Forster et al., 2007). Additionally, because a large portion of the total precipitation around the globe is initiated by ice formation within mixed phase clouds, the formation of glaciated clouds plays an important role in the exchange of water between the ocean and continents as well as between the planetary surface and the atmosphere (Lau and Wu, 2003; Lohmann and Diehl, 2006).

Ice crystals can form through both homogeneous and heterogeneous nucleation, with the former occurring at temperatures less than about -38 °C (Pruppacher and Klett, 1997). Heterogeneous ice nucleation occurs via atmospheric aerosols that facilitate the formation of ice crystals by lowering the free energy barrier of the nucleation event (Pruppacher and Klett, 1997). A variety of heterogeneous ice nucleation mechanisms has been identified (Vali, 1985): (i) deposition nucleation, where water vapour deposits directly onto a solid as ice; (ii) condensation freezing, which occurs when liquid water condenses on ice nuclei (IN) to form a liquid droplet at temperatures where it then rapidly freezes; (iii) immersion freezing, where an ice nucleus becomes immersed in a liquid droplet within which ice formation eventually occurs; and (iv) contact freezing, in which ice nuclei

collide with supercooled liquid droplets to cause ice nucleation.

Mineral dusts and their main components (clay minerals including kaolinite and illite) are commonly acknowledged to be efficient ice nuclei that can facilitate the formation of high-altitude ice clouds (Hoose and Möhler, 2012; Pruppacher and Klett, 1997; Cziczo et al., 2013). The ice nucleation properties of these substances have been investigated through several methods including cloud chambers, cold stages, vacuum chambers, expansion chambers, continuous flow diffusion chambers, and the examination of snow crystal residues (e.g. Archuleta et al., 2005; Broadley et al., 2012; Kanji and Abbatt, 2006; Kumai, 1961; Möhler et al., 2006; Welti et al., 2009; Zuberi et al., 2002). Due to the use of widely differing experimental methods, previous studies have varied both in their sensitivity to nucleation events and in their experimental conditions. For instance, it has been established that the efficiency of a tested material can vary as a function of temperature, particle size, and the presence of soluble material that may be redistributed to enhance the hygroscopicity of insoluble particles (Fletcher, 1958; Koehler et al., 2007; Ladino and Abbatt, 2013; Lohmann and Diehl, 2006; Phebus et al., 2011; Wheeler and Bertram, 2012). In addition, the identification of an ice formation onset is highly dependent on the sensitivity of the observation technique, with some experiments (such as those conducted on cold stages) often sensitive to a single nucleation event out of a large surface area sample, whereas diffusion chambers are less sensitive, referring to the onset of a larger fraction of a smaller surface area sample. As a result of these experimental variations, it is challenging and indeed, at times, unhelpful to attempt to compare the IN efficiencies of substances from different studies.

While the IN properties of the main components of mineral dusts have been examined before, the IN activities of the more minor mineralogical components have not been extensively studied in a controlled manner, with the most recent being studies by Atkinson et al. (2013) and Zimmermann et al. (2008). Firstly, Atkinson et al. (2013) focussed on the immersion IN properties of feldspar minerals, and, secondly, Zimmermann et al. (2008) used environmental scanning electron microscopy to observe ice growth on a number of mineralogical components. In addition to clay minerals, mineral dusts from Asia, Africa, and Arizona can be composed of other minor minerals which include varying amounts of feldspars, quartz, hematite, and carbonates (e.g. Broadley et al., 2012; Jeong, 2008; Linke et al., 2006). Finally, Cziczo et al. (2013) identified metal-containing particles as another dominant component of the residual particles of cirrus ice crystals.

As a contrast to the naturally occurring minerals, an anthropogenic material, lead iodide (PbI_2), has been predicted to be an efficient ice nucleus based on the similarity of its crystal lattice to that of ice. Not only do both substances exhibit hexagonal lattice systems, but lead iodide was also

found to possess lattice constants (4.54 \AA , 8.86 \AA) that were nearly equal to those of ice along the a axis (4.535 \AA , 7.41 \AA) (Barnes, 1929; Schaefer, 1954; Vonnegut, 1947). Due to this similarity, early studies were conducted in the immersion/condensation and deposition regimes (Baklanov et al., 1991; Harris et al., 1963; Morgan, 1967; Reischel, 1975; Schaefer, 1954), and it was proposed as a cloud seeding compound by Schaefer (1966), Morgan and Allee (1968), and Parungo and Rhea (1970). However, no studies using modern experimental techniques have been conducted on this compound.

The focus of this study is to use the same experimental approach to compare the relative ice deposition nucleating abilities of many minor mineralogical components of mineral dusts in addition to the major components. By controlling the particle size selection approach, temperature, particle preparation method, and the criterion for ice onset, we hope to identify in a relative sense the species that are most important in making mineral dust efficient deposition ice nuclei. In addition, the IN abilities of these substances are compared to that of lead iodide.

2 Experimental procedure

Experiments were conducted on particles size selected at 200 nm using the University of Toronto Continuous Flow Diffusion Chamber (UT-CFDC) at a temperature of $-40.0 \pm 0.3 \text{ }^\circ\text{C}$, as illustrated in Fig. 1 (Kanji and Abbatt, 2009). Prior to experimentation, each compound was washed twice using Millipore water ($18.2 \text{ M}\Omega \text{ cm}$). A selection of compounds (TiO_2 , orthoclase, Arizona Test Dust (ATD), Mojave Desert Dust (MDD)) was not washed prior to experimentation in order to compare the IN properties of the washed and unwashed forms of these samples. The purpose of the washing was twofold. Firstly, it allowed a relative ranking system of the IN properties of minerals to be created without interferences from soluble contaminants that may be present at the particles' surfaces. If such materials are present, either through handling, laboratory contamination, or from the manufacturer, then they may affect the underlying abilities of the pure compounds to nucleate ice. Secondly, it allowed the behaviour of these minerals to be compared to the multicomponent mixtures (ATD and MDD), which were washed as well, without interference from such material. We note that the washing procedure may also affect the surface composition of pure compounds; however, the research community is unclear about this. As well, the degree to which dust particles are "washed" in the environment is variable, depending on whether they undergo liquid water cloud processing or whether they experience rain when still on the ground.

Each compound was tested at least three times over the course of two or more days in order to ensure reproducibility. In the UT-CFDC, aerosol is continuously passed between

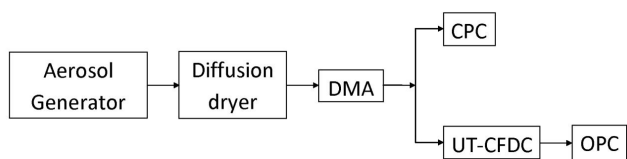


Fig. 1. Schematic of the main components of the experimental set-up.

two horizontal, ice-coated copper plates that regulate the relative humidity (RH) and temperature (T) of the chamber; in particular, the different temperatures of the plates lead to a supersaturation with respect to ice in the centre of the chamber where the particle flow was injected (0.3 L min^{-1}), in between a particle-free sheath flow (2.6 L min^{-1}). After the UT-CFDC, an optical particle counter (OPC, Climet CI-20) measured the number concentration of ice crystals greater than $5 \mu\text{m}$ that exited the chamber. As particles larger than $5 \mu\text{m}$ were not introduced into the UT-CFDC, these values were measurements of ice nuclei number concentrations, after low levels of background counts within the chamber were subtracted. By maximizing the residence time of particles within the chamber (12 s), the degree to which ice nucleation may occur is also maximized. We refer the reader to Kanji and Abbatt (2009) for a full description of the UT-CFDC.

The total organic carbon level of the Millipore water used to wash the samples was extremely low (i.e. less than 5 ppb) as it was exposed to an ultraviolet light source for purification. In particular, the samples were washed with 500 to 1000 mL of water, the particles were allowed to settle, and then the supernatant liquid was poured off. This procedure was then repeated before addition of more water prior to atomization. To monitor the effectiveness of this procedure, the critical relative humidity with respect to ice (RH_i) values of washed and unwashed TiO_2 , orthoclase, ATD, and MDD samples were compared by measuring the conductivity, and therefore the amount of soluble ionic material in each solution, using a conductivity meter (VWR 89094-958).

An aerosol generator (TSI 3076) was used to produce aerosol from a slurry, which was then dried with two silica gel drying tubes, size selected at a mobility diameter of 200 nm with a differential mobility analyzer (DMA, TSI 3081), and then passed into both a condensation particle counter (CPC, TSI 3010) for number concentration measurements, and the UT-CFDC. The slurries' concentrations were adjusted in order to produce number concentrations of 50–200 particles cm^{-3} as measured by the CPC. Particle size selection was accomplished with the DMA at 200 nm, with at most 25 % of the total number of particles exiting the DMA being multiply charged particles larger than 200 nm. For example, in the case of Al_2O_3 , the fraction of particles that were multiply charged was only 7 %, whereas it was 25 % for ATD. The percentage of total surface area that cannot be attributed to 200 nm particles was between 13 % and

60 % for Al_2O_3 and ATD, respectively. We note that the dry dispersal system available in our laboratory does not give clean monodispersed particle distributions when coupled to a DMA with a number of large particles being transmitted (see Ladino and Abbatt, 2013), whereas good size selection was always achieved with wet atomization. Since our primary goal is to establish a relative ranking of the IN abilities of these different species (i.e. free from the effects of particle size on the results), this was an additional reason for using wet atomization throughout.

All reported measurements are for a temperature of $-40.0 \pm 0.3 \text{ }^\circ\text{C}$. To calculate the activated fraction (AF), the number of ice crystals recorded by the OPC was normalized by the total number of injected aerosol particles counted by the CPC, after accounting for dilution by the CFDC sheath flow. The RH_i was calculated using Eq. 1 based on Murphy and Koop (2005).

$$\text{RH}_i = \frac{e}{e_s(T)} \cdot 100\%, \quad (1)$$

where e is the partial pressure of water vapour (Pa) in the centre of the chamber and e_s is the saturated vapour pressure over ice. The critical RH_i was defined in this work as the RH_i at which 0.1 % of the total number of injected aerosol particles had nucleated ice (i.e. formed $5 \mu\text{m}$ crystals). The uncertainty in RH_i is approximately $\pm 4 \%$ (Kanji and Abbatt, 2009).

The samples studied and their sources are listed in Table 1. The electrical conductivity (μS) of the suspensions is indicated in parentheses for MDD, ATD, orthoclase, and TiO_2 after the sample names. Most of the samples were obtained commercially with the exception of K-feldspar (herein referred to as orthoclase), Ca/Na-feldspar (herein referred to as plagioclase), and calcium carbonate (herein referred to as calcite), which were obtained as individual mineral crystals from the Department of Earth Sciences, University of Toronto. These samples originated from the Bancroft area of Ontario, Canada, and were ground into sufficiently fine particles using a mortar and pestle.

2.1 Mineral structures

2.1.1 Clay minerals

Kaolinite is a 1 : 1 clay mineral in which one layer consists of an octahedral alumina sheet and a tetrahedral silica sheet that share a plane of oxygen atoms (Bear, 1964). The layers are held together by hydrogen bonds, and the surface consists of an alumina/hydroxyl sheet (Bear, 1964; Frost, 1998). As a result, the surface hydroxyl groups may be able to form hydrogen bonds with water molecules, thus causing kaolinite to be an efficient ice nucleus. Additionally, due to a low degree of isomorphic substitution of a fraction of the metal ions in the lattice by metals of lower charge, this clay carries a small net negative charge (1–10 mequiv/100 g of clay) which

Table 1. Tested substances in order of increasing critical RH_i for deposition activation of 0.1 % of 200 nm particles at −40 °C. The electrical conductivity (μS) of the suspensions is indicated in parentheses for MDD, ATD, orthoclase, and TiO₂ after the sample names.

Sample	Critical RH _i (%)	Category	Source
PbI ₂	122.8 ± 2.0	Anthropogenic	Sigma-Aldrich, 99 %
MDD unwashed (70 μS)	125.4 ± 1.8	Mineral dust	Peters et al. (2008)
MDD (50 μS)	126.3 ± 3.4	Mineral dust	Peters et al. (2008)
Orthoclase (K-feldspar) (18 μS)	127.1 ± 6.3	Feldspar mineral	Department of Earth Sciences, University of Toronto
ATD (30 μS)	129.5 ± 5.1	Mineral dust	Powder Technology Inc., 0–5 μm
ATD unwashed (89 μS)	132.9 ± 0.5	Mineral dust	Powder Technology Inc., 0–5 μm
Orthoclase (K-feldspar) unwashed (50 μS)	135.0 ± 3.6	Feldspar mineral	Department of Earth Sciences, University of Toronto
Plagioclase (Na/Ca-feldspar)	136.2 ± 1.3	Feldspar mineral	Department of Earth Sciences, University of Toronto
Kaolinite	136.4 ± 1.9	Clay mineral	KGa-1b, Clay Minerals Society, Source Clays Repository
Montmorillonite	139.3 ± 1.0	Clay mineral	K10, Sigma-Aldrich
Illite	142.5 ± 2.3	Clay mineral	IMt-1, Clay Minerals Society, Source Clays Repository
Pyrite (FeS)	142.9 ± 0.8	Metal sulfide	Sigma-Aldrich, technical grade
Corundum (Al ₂ O ₃)	143.2 ± 3.2	Metal oxide	Sigma-Aldrich, ≥98 %
Calcite (CaCO ₃)	144.3 ± 0.9	Metal carbonate	Department of Earth Sciences, University of Toronto
Magnetite (Fe ₃ O ₄)	144.4 ± 2.2	Metal oxide	Sigma-Aldrich, < 5 μm, 95 %
Quartz (SiO ₂)	144.7 ± 1.5	Metal oxide	Alfa Aesar, 99.9 %
Gypsum (CaSO ₄ ·2H ₂ O)	144.8 ± 1.2	Metal sulfate	Sigma-Aldrich, ≥99 %
Galena (PbS)	145.0 ± 1.0	Metal sulfide	Sigma-Aldrich, 99.9 % trace metal basis
Anglesite (PbSO ₄)	145.1 ± 1.3	Metal sulfate	Sigma-Aldrich, 98 %
Zn	145.4 ± 0.6	Pure metal	Atlantic Equipment Engineers, 99.8 %
Massicot (PbO)	145.5 ± 1.3	Metal oxide	Sigma-Aldrich, ≥99.0 %
Calcite (CaCO ₃)	145.8 ± 1.4	Metal carbonate	Sigma-Aldrich, ≥99.0 %
Rutile (TiO ₂) unwashed (10.8 μS)	146.3 ± 1.0	Metal oxide	Sigma-Aldrich, 99–100.5 %
Bunsenite (NiO)	146.5 ± 0.8	Metal oxide	Sigma-Aldrich, 99 %
Cerussite (PbCO ₃)	146.7 ± 0.6	Metal carbonate	Sigma-Aldrich, ACS reagent grade
Rutile (TiO ₂) (1.4 μS)	147.4 ± 0.4	Metal oxide	Sigma-Aldrich, 99–100.5 %
ZnS	147.7 ± 1.5	Metal sulfide	Sigma-Aldrich, ≥97.0 %
Zincite (ZnO)	148.6 ± 0.2	Metal oxide	Sigma-Aldrich, ≥99.0 %
Hematite (Fe ₂ O ₃)	148.8 ± 1.0	Metal oxide	Sigma-Aldrich, < 5 μm, 99+ %

is compensated by the presence of counter cations (Swartzen-Allen and Matijevic, 1974).

In contrast to kaolinite, illite is a 2:1 clay mineral possessing one octahedral alumina sheet between two tetrahedral silica sheets in each layer (Swartzen-Allen and Matijevic, 1974). Due to a high degree of isomorphic substitution, this clay carries a large net negative charge (80–100 mequiv/100 g of clay) which is compensated by the presence of counter cations (Swartzen-Allen and Matijevic, 1974). The interlayer spaces are filled with counter cations, the majority of which are potassium ions (Hu et al., 2003). In addition to cations being present in the inter-layer space, they are also present at the clay's surface.

2.1.2 Feldspar minerals

Feldspars are a mineral class found commonly in igneous rocks, which make up a large fraction of the earth's crust (Carlson, 1920). Members of the feldspar mineral family consist of silica tetrahedra with varying degrees of Al–Si substitution, which results in surface charges and the presence of counterions within the crystal lattice (Papike and Cameron, 1976). While the counterion found in orthoclase is typically K⁺, those associated with the members of the plagioclase family are Na⁺ and Ca²⁺ (Colville and Ribbe, 1968; Fitz Gerald et al., 1986; Phillips et al., 1971; Wenk et al., 1980).

3 Results and discussion

As examples, three activated fraction curves are shown in Fig. 2, plotted as a function of RH_i. It can be seen that more inactive species (e.g. ZnS) have a better defined critical relative humidity which is close to water saturation, whereas the better IN (e.g. orthoclase and illite) have an activation spectrum spread across a wider range of RH_i, reflecting a range of active sites on the particles that have differing ice nucleating efficiencies. Note that the activation curves typically plateau at activated fractions close to 0.1, which is a common occurrence in CFDCs. Incomplete activation of all particles is attributed to the depletion of water vapour within the chamber when many ice crystals have formed, as well as possibly to the depositional settling of ice crystals.

Indicated in Table 1 are the IN efficiencies of the tested samples, which fall into nine categories: anthropogenic substances, mineral dusts, feldspar minerals, clay minerals, metal carbonates, metal oxides, metal sulfates, metal sulfides, and pure metals. While the discussion will focus primarily on the mineral components of MDD and ATD, several other pure minerals are included in Table 1 to make a more complete comparison of minerals that may be present in other types of mineral dusts. In the following discussion Sects. 3.1 and 3.2 will focus on the relative IN properties of the washed samples, while Sect. 3.3 will compare the relative

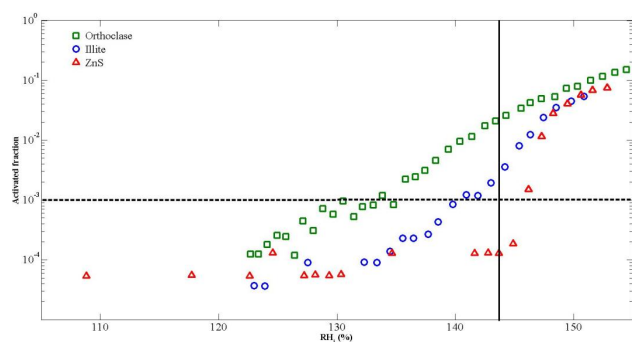


Fig. 2. Activated fraction as a function of RH_i for orthoclase (green square), illite (blue circle), and ZnS (red triangle). The dashed black line represents an activated fraction of 0.001, and the solid black line represents water saturation.

IN properties of a selection of washed and unwashed samples (TiO₂, orthoclase, ATD, MDD)

3.1 IN properties of pure single component samples

The most efficient classes of pure atmospheric substances were the clay and feldspar minerals, whereas the least efficient were metal oxides, carbonates, sulfates, sulfides, and the pure metal. Clay minerals including kaolinite and illite have been presented as the most important components of mineral dusts when considering their IN properties (Hoose and Möhler, 2012; Pruppacher and Klett, 1997). In accordance with this, the results of this study showed that these minerals were efficient IN relative to many of the other pure compounds that were investigated. Indeed, it is striking how many of the non-clays nucleate ice near water saturation (i.e. 146.2 % RH_i at -40°C). There is clearly a distinction to be made between the feldspars and clays, on the one hand, and the other compounds on the other hand.

3.1.1 IN properties of clay minerals

Kaolinite's critical RH_i ($136.4 \pm 1.9\%$) was greater than that reported by Salam et al. (2006), which was 118 % at -40°C , where the critical RH_i was the value at which ice crystals were first detected. This low value may be attributed to the use of 1–2 μm particles by Salam et al. (2006) because ice nucleation efficiency increases as a function of particle size (Archuleta et al., 2005; Kanji and Abbatt, 2006; Welti et al., 2009; Wheeler and Bertram, 2012). Welti et al. (2009) reported an onset RH_i of 115 % at -40°C when using 200 nm particles produced by a fluidized bed aerosol generator (i.e. generated in a different manner). An older study used a cold stage method to report that an RH_i of 120 % was necessary for a first ice nucleation event to occur at temperatures lower than -1°C (Roberts and Hallett, 1967). Similarly to Salam et al. (2006), the low RH_i value may be attributed to the use of large kaolinite particles having diameters of 0.5–3 μm .

Due to illite's highly charged surface, this clay mineral may experience electrostatic interactions with the dipole moment of water, resulting in its fairly low critical RH_i of $142.5 \pm 2.3\%$. While this RH_i is one of the lower values in Table 1, it is still much higher than the onset RH_i of 110 %, which was reported by Welti et al. (2009) for 200 nm particles at -40°C ; however, the studies differed with respect to the illite sources, ice crystal sizes for onset determination, and sample preparation methods. Welti et al. (2009) used an NX Nanopowder illite sample obtained from Arginotec, detected ice crystals described as being a few micrometres in size, and produced aerosol using a fluidized bed.

Due to the presence of counterions on the surfaces of clay minerals, there has been a significant amount of investigation regarding the effect of counterions on the adsorption of water by clays. It has been reported that clays possessing polyvalent counterions adsorb more water vapour than those having univalent counterions (Swartzen-Allen and Matijeic, 1974). Therefore, it may be hypothesized that the kaolinite sample possessed more highly charged counterions than the illite samples. In addition, both the charge and ionic size of counterions have been reported to influence the strength of their interactions with clay surfaces (Swartzen-Allen and Matijeic, 1974). As a result, the degree of preferential H^+ adsorption to clay surfaces has been investigated. However, this work has been inconclusive as various studies have found different preferences for H^+ adsorption (Swartzen-Allen and Matijeic, 1974). Because of the limitations of this study and the inconclusiveness of past work, we can only make a general conclusion that the electrostatic interactions between the charged clay surfaces, counterions, and the dipole moment of water may be influencing the IN properties of clays.

3.1.2 IN properties of feldspar minerals

While the clay minerals were identified as efficient IN as predicted, the surprising results are the very high efficiencies of the feldspars. It has been reported that the outermost K^+ ions of orthoclase are removed upon contact with deionized water, and dangling Si atoms become attached to O or OH (Fenter et al., 2000). As a result, the surface would be prone to interact with water molecules through hydrogen bonding, as is the case for kaolinite, which was the more active clay mineral (critical RH_i $136.4 \pm 1.9\%$). Incidentally, the critical RH_i values of orthoclase and kaolinite were not significantly different according to Student's t test, which is used to determine whether two data sets significantly differ from one another.

In addition, as plagioclase minerals have a similar crystal structure to orthoclase, it may be that they also have the ability to form hydrogen bonds with water molecules. Therefore, it was not surprising that the critical RH_i values of plagioclase and kaolinite were also not significantly different according to Student's t test. This implies that their interaction with water molecules may be similar. Additionally, the

charged crystal lattice of feldspars may also allow electrostatic interactions to occur between their surfaces and the dipole moment of water, as is the case for illite. The differing activities of the two feldspar samples may be due to different degrees of hydrogen bonding and electrostatic interactions that are exhibited by each sample.

In contrast with the clay minerals, the feldspar mineral class has been poorly studied by the ice nucleation community, with reports being for feldspar-containing soil and illite samples, as well as for pure feldspar samples, that acted as IN in the deposition, contact, and immersion modes (Broadley et al., 2012; Roberts and Hallett, 1967; Rosinski and Nagamoto, 1976a, b; Rosinski et al., 1971, 1974; Zimmermann et al., 2008). Additionally, older reports have investigated the IN properties of pure feldspar samples in unknown modes (Isono and Ikebe, 1960; Mason and Maybank, 1958). In one study a cold chamber was used to report that 72.4 % of 40–60 μm soil particles containing 5 % feldspar nucleate ice in the immersion mode at temperatures below -20°C (Rosinski and Nagamoto, 1976b). In a second paper it was reported, using the same instrument and soil samples, that about 40 % of one of the samples having diameters of 5–20 μm functioned as IN in the contact mode at about -16°C (Rosinski and Nagamoto, 1976a). More recently, a study by Broadley et al. (2012) examined the IN activity of illite-rich powder (NX illite), containing about 8 % feldspar, using a cold stage. Immersion freezing was found to occur primarily below the median freezing temperature of -27°C . While all three of these studies identified the feldspar-containing particles as being fairly efficient IN in various modes, none of them identified the feldspar component as the source of the IN activities. In addition, because the methods, soil particle sizes, definition of activity, IN modes, and feldspar-containing samples themselves differed from those used in this study, a comparison with this past work is very challenging. In addition, Zimmermann et al. (2008) investigated the IN properties of two types of feldspars (albite and microcline) in the deposition mode with the use of a cold stage. At -25°C , 1–10 μm albite and microcline particles were found to nucleate ice at critical RH_i values of about 114 % and 118 %, respectively. Critical RH_i values corresponded to 1–3 % activation. The difference between these critical RH_i values and those reported here is to be expected because of the difference in experimental conditions. However, it should be noted that of the nine minerals examined by Zimmermann et al. (2008), the feldspars were found to be among the more active minerals, which supports the conclusions of this study. Most recently, a concurrent study by Atkinson et al. (2013) found that while clay minerals dominate the composition of mineral dusts, it is the feldspar minerals that dominate their immersion IN properties. This work is very much in agreement with our conclusions, with respect to the excellent deposition IN abilities of feldspars.

3.1.3 IN properties of other pure compounds

In contrast with the more structurally complex minerals having ionic surfaces, other minerals found in mineral dusts have lower capacities to interact with water molecules through electrostatic and hydrogen bonding interactions. In particular, of the minerals present in MDD and ATD, hematite and cerussite were found to be the least efficient minerals as they were activated above water saturation. Similarly, magnetite, calcite, and quartz were very poor ice nuclei in the deposition regime. These results are somewhat surprising, as Cziczko et al. (2013) found that in addition to mineral dust, metallic particles are a dominant component of ice crystal residuals in cirrus clouds.

In general, species such as magnetite (Fe_3O_4), hematite (Fe_2O_3), and quartz (SiO_2) are stable oxides that will either have metal-O bonds at their surfaces, or perhaps some metal-OH groups; for example, alumina is known to have hydroxyl functional groups present under some conditions (Swartzen-Allen and Matijevic, 1974). Similarly, hydroxyl groups may be present at the surface of quartz, which would allow hydrogen bonding to occur between quartz and water molecules (Schlegel et al., 2002, and references therein). However, its poor IN activity may be attributed to its lack of structural charge. To compare, orthoclase has hydrogen bonding abilities due to the presence of surface Si-OH groups; however, this is due to the removal of potassium ions from its surface (Fenter et al., 2000). This also results in the exchange of potassium ions with protons or hydronium ions upon exposure to water (Fenter et al., 2000, and references therein). Therefore, the IN properties of orthoclase may be due to the presence of a surface charge and ions, as well as to its hydrogen bonding abilities.

Lastly, as expected based on the similarities between the crystal structures of lead iodide and ice, lead iodide was reported to be the most efficient ice nucleus of those considered here (critical RH_i of $122.8 \pm 2.0\%$). Harris et al. (1963) observed a deposition onset RH_i of approximately 143 % at -35°C when using a cold chamber, where the onset RH_i was defined as the first observed nucleation event. The particle size used in this study was 0.1–2 mm, and nucleation events were recorded by eye with the use of a Vickers projection microscope, which may have caused some of the very early nucleation events to be overlooked. Baklanov et al. (1991) reported that 3×10^{16} ice crystals per kg of PbI_2 formed when 40–100 nm PbI_2 particles were injected into an isothermal cloud chamber at -10°C .

3.2 IN properties of mineral dusts

Figure 3a shows the critical RH_i at which 0.1 % of the ATD and Mojave Desert Dust (referred to as Mojave Mars Simulant, or MMS in previous studies) particles activated at a temperature of $-40.0 \pm 0.3^\circ\text{C}$. For reference, the results for lead iodide are also shown.

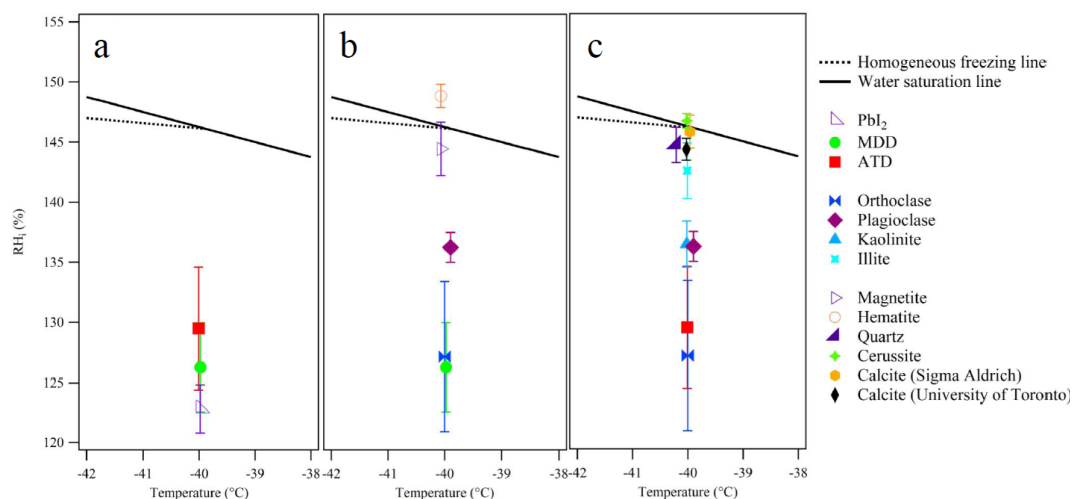


Fig. 3. Critical RH_i at which 0.1 % of particles were activated at a temperature of -40.0 ± 0.3 °C. The solid black line represents the water saturation line and the dotted black line represents the homogeneous freezing line (Koop et al., 2000; Murphy and Koop, 2005). The three panels are as follows: (a) ATD, MDD, and PbI_2 ; (b) MDD and its mineral components (orthoclase, plagioclase, magnetite, hematite); (c) ATD and its mineral components (orthoclase, plagioclase, kaolinite, illite, quartz, and carbonates such as calcite and cerussite). The error bars represent the standard deviation of the critical RH_i measured in individual experiments, of which each point is the average of at least three scans.

Mojave Desert Dust is very efficient with a critical RH_i of 126.3 ± 3.4 %. It is striking that the IN efficiency of this natural dust is nearly comparable to that of an artificial IN, such as lead iodide which was identified for its very close crystal match to that of ice. The value for MDD is in agreement with the previously reported value of $RH_i = 123$ % from our group at a temperature of -53 °C and particle diameter of 240 nm (Ladino and Abbatt, 2013). Motivated by ice cloud nucleation on Mars, this past study also indicated that there is a strong temperature dependence on this onset value, with it rising substantially at temperatures lower than -50 °C (Ladino and Abbatt, 2013).

Arizona Test Dust was found to be less efficient as an ice nucleus (critical RH_i 129.5 ± 5.1 %) under the investigated conditions. As ATD is a standard sample in the ice nucleation community, several studies have been conducted to investigate its activity using a CFDC (Archuleta et al., 2005; Koehler et al., 2010; Welti et al., 2009). Welti et al. (2009) and Koehler et al. (2010) reported critical RH_i values of about 118 % and 128 %, respectively, where these values corresponded to the activation of 1.0 % of ATD particles at -40 °C and 200 nm in size. These values were not in agreement with each other; however, the value reported by Koehler et al. (2010) agreed well with the value from this study. The disagreement with Welti et al. (2009) may be attributed to their detected ice crystal sizes, which were described as being a few microns. Because the ice crystals detected in this study were relatively large (5 μ m), a higher RH_i would be required for their formation. This divergence in the literature results for not only ATD, but many other substances as well,

emphasizes the need for this study that uses the same experimental protocol for all samples, in order that the relative nucleating abilities of these materials be established.

ATD has been reported to contain about 30 % feldspar minerals (e.g. plagioclase, orthoclase), and more minor amounts of kaolinite, illite, illite–smectite, quartz, carbonates (e.g. calcite, cerussite) and other unidentified clay minerals, in varying amounts (Broadley et al., 2012). On the other hand, MDD consists of mainly feldspars, hematite, and minor amounts of magnetite, without the same contributions of clay minerals or carbonates as in ATD (Peters et al., 2008). Indeed, it is due to its more igneous nature and relative lack of weathered and sedimentary components, such as clays and carbonates, that it has been used as a simulant for Mars dust.

Because these mineral dusts consist of several pure minerals, it is reasonable to hypothesize that the overall IN ability of the dusts may be understandable in terms of the IN activities of their individual components. Figure 3b shows the critical RH_i at which 0.1 % of aerosol particles of MDD and its main mineralogical components (hematite, magnetite, feldspar) were activated. As the RH_i values of hematite and magnetite were 148.8 ± 1.0 % and 144.4 ± 2.2 %, respectively, they are unlikely to contribute to the IN abilities of MDD. Rather, the most efficient components of MDD were the feldspar minerals orthoclase and plagioclase, supporting the hypothesis that the feldspars (specifically orthoclase) are likely contributors to the IN properties of the mineral dusts. Of course, we cannot rule out that the mixing of these constituents to form an MDD particle (i.e. its specific morphology) may also result in the formation of active sites or

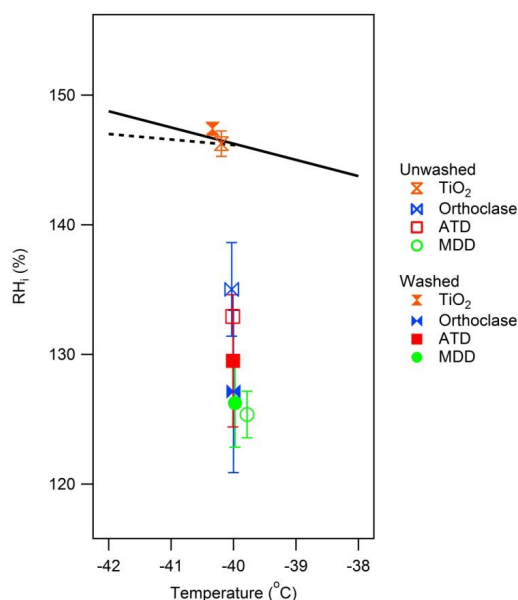


Fig. 4. Critical RH_i at which 0.1 % of particles were activated at a temperature of -40.0 ± 0.3 °C. The solid black line represents the water saturation line, and the dotted black line represents the homogeneous freezing line (Koop et al., 2000; Murphy and Koop, 2005). The solid markers indicate washed samples while the empty markers indicate unwashed samples of TiO_2 , orthoclase, ATD, and MDD. The error bars represent the standard deviation of the critical RH_i , each of which is the average of at least three scans.

physical imperfections that facilitate ice formation (Pruppacher and Klett, 1997).

Figure 3c shows the critical RH_i at which 0.1 % of aerosol particles of ATD and its main mineralogical components were activated at a temperature of -40.0 ± 0.3 °C. Once again, the minerals having more complex crystal structures (kaolinite, plagioclase, and orthoclase) were found to be more efficient deposition ice nuclei. The similarity of the orthoclase and ATD activities suggests that the efficiency of ATD may also be primarily explained by the presence of orthoclase despite the large fraction of clays in ATD (Broadley et al., 2012). As MDD was found to activate at very low RH_i values more consistently than ATD, it may be that MDD particles contain orthoclase more consistently than do ATD particles.

3.3 Unwashed and washed samples

As described above, washing was performed to remove soluble impurities that might affect our ability to rank the different species by their IN ability. An attempt was made to assess the effects of washing the samples prior to studying their IN properties. Shown in Fig. 4 are the critical RH_i values of washed and unwashed TiO_2 , orthoclase, ATD, and MDD samples. According to Student's *t* test, the RH_i values of the washed and unwashed samples for each of the four ma-

terials considered were not significantly different from one another. Therefore, we conclude that washing does not alter the general conclusions about whether a particle is a good IN or not. These effects may be due to the removal of soluble material that would otherwise affect their IN properties, either by promoting ice nucleation through additional electrostatic interactions or inhibiting it by blocking active sites. In contrast with orthoclase, ATD, and MDD, TiO_2 is an example of a synthetically manufactured pure chemical compound having greater than 99 % purity. Consequently, a relatively small amount of soluble material was present regardless of the number of washings. Indeed, based on the electrical conductivity measurements (see Table 1) of the supernatant water after washing, we estimate that there are fewer than 5×10^3 soluble ions per particle present. To do this calculation, we use the measured conductivity of the atomizer slurry (1.4 μ S) to estimate its ion content, assuming the constituents are NaCl, and then calculated the number of ions in each atomized droplet, assuming these to be 1.2 μ m in size. Upon drying, these ions then will become part of the dried 200 nm particle. It is not surprising that such a low level of constituents has no effect on the IN abilities of the particles. The other three washed samples contained a greater amount of soluble ions (6×10^4 – 2×10^5 soluble ions per particle), which was less than a monolayer of ions (5×10^5 soluble ions per particle, assuming that a monolayer coverage is 5×10^{14} soluble ions cm^{-2}). The unwashed MDD, ATD, and orthoclase samples all contained a greater concentration of soluble ions than their washed counterparts.

It is well known that clay minerals undergo exchange between soluble cations and hydronium ions in solution, which may then affect their surface compositions, and hence IN activity. It is difficult to assess the importance of this effect for natural samples, making it hard to claim that wet atomization or dry dispersal is the best method for particle preparation in laboratory studies. On the one hand, through the action of rain all natural samples are exposed on the ground to water prior to dispersion as an aerosol. As well, most particles are thought to pass through regions of water saturation before reaching altitudes at which cirrus clouds form (Wiacek et al., 2010). On the other hand, it is quite possible that the few trajectories that do not pass through water saturation are those that deliver the best IN to the upper troposphere. The work of Cziczo et al. (2013) indicates that the particles with the fewest soluble impurities appear to be the best IN. Thus, while each aerosol preparation method has its merits, it is difficult to claim that either dry dispersal or wet atomization is universally the most atmospherically appropriate method.

An important additional point to make, as described by Koehler et al. (2007), is that atomized multicomponent mixtures such as MDD and ATD may lose some atmospheric relevancy due to the redistribution of soluble material, if there is a lot of soluble material present. However, for the goals of our paper (i.e. to compare the ice nucleating abilities of single component minerals to multicomponent mixtures), all of the

samples were washed prior to atomization in order to remove as much soluble material as possible before making this comparison. As a result, their soluble material that may otherwise have been redistributed on the multicomponent mixtures was removed prior to atomization.

4 Conclusions and atmospheric implications

This study represents the first examination of the deposition ice nucleating abilities of a wide number of mineral substances where the experimental procedure has been kept constant throughout, leading to a better understanding of the most important ice forming materials. The major findings from this work are that the feldspar minerals are the most active natural minerals studied, rivalling the anthropogenic material lead iodide, which has a good crystallographic match with ice (Schaefer, 1954; Vonnegut, 1947). Consistent with this, the MDD dust sample, which is thought to have a much lower weathered rock component than ATD, was found to be the more active dust sample. Of the three clay minerals tested, illite and montmorillonite were not as active as the feldspar minerals themselves, especially orthoclase, or the feldspar-containing dusts. In contrast, kaolinite was found to have higher activity than the other clays, closer to that of the feldspar minerals. This indicates that the efficiency of IN may be attributed to either hydrogen bonding or ionic interactions between the IN surface and water molecules. The least active materials were the metal oxides, carbonates, sulfates, sulfides, and pure metal. By working with the same experimental protocol throughout, this study isolates the ice nucleating substance itself as the determinant of the onset for nucleation, and removes factors such as temperature, particle size, ice crystal detection technique, and the definition of ice onset. Given that all the samples were wet atomized in this work, it would be interesting to determine the relative ranking using dry dispersed particles of the same size.

We note that the minerals (e.g. quartz, calcite, hematite, magnetite) lacking a surface charge are poor IN, whereas those that are good IN are able to bond strongly with hydrogen via the presence of surface hydroxyl groups (kaolinite, feldspars), or possess a net charge in their crystal lattice (illite, feldspars). The ability to participate in electrostatic interactions may then be added as a characteristic of a good IN, beyond the ability to bond simply with hydrogen (Pruppacher and Klett, 1997). Indeed, it may be for this reason that soluble salts, such as ammonium sulfate and sodium chloride, have been shown to show deposition IN abilities, provided that the temperature is below their eutectic (Abbatt et al., 2006; Wise et al., 2012).

The most striking example of this effect in this study is demonstrated by orthoclase (i.e. K-feldspar), which was identified as the most active component of both of the mineral dusts. This conclusion has now been made by this study in the deposition mode, which nicely matches the findings

from the concurrent study of Atkinson et al. (2013) for the immersion mode. Together, plagioclase and orthoclase feldspars have been reported to represent 5 % to 16 % of African and Asian dust particles that reach the atmosphere (Shi, 2005; Jeong, 2008; Awadh, 2012). In comparison, 48 % of Asian dust particles have been identified as clay aggregates (Jeong, 2008). Although the presence of feldspars in dust particles is less than that of clay minerals, their effect may still be substantial as some may be significantly more active as IN in the deposition mode. For this reason it is important that these feldspar-containing particles be further investigated in order for their effects to be appropriately incorporated into global climate models. One issue to consider is the degree to which such good IN are removed by cloud processing prior to reaching the upper troposphere, where much cirrus cloud formation occurs.

Another conclusion from this work is that many species, such as metal oxides and carbonates, are poor deposition IN. Given that many metal oxides are formed by mining and smelting activities (Aragón Piña et al., 2000; Fernández et al., 2000; Swaine, 2000; Li and Thornton, 2001; Burt et al., 2003), it seems unlikely that there is an anthropogenic effect on ice nucleation through the release of such species to the atmosphere. On the other hand, if cloud seeding were to proceed under deposition mode conditions, for example in the seeding of cirrus clouds, it appears that feldspar minerals would be a good option.

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