The role of natural mineral particles collected at one site in Patagonia as immersion freezing ice nuclei

María Laura López[a],[*], Laura Borgnino[b], Eldo E. Ávila[a]

[a] *IFEG-CONCIET-FaMAF, Universidad Nacional de Córdoba, Córdoba, Argentina*
[b] *CICTERRA-CONICET, Universidad Nacional de Córdoba, Córdoba, Argentina*

A B S T R A C T

This work studies the role of mineral particles collected in the region of Patagonia (Neuquén, Argentina) as ice nuclei particles (INPs) by immersion freezing mode. The particle immersion-freezing ability was analyzed under laboratory conditions by using an established drop-freezing technique. Mineralogical composition was characterized by using X-ray diffraction and electron micro probe analysis. Dynamic light scattering was used to determine the grain size distribution of particles, while the N_2 adsorption and methylene blue adsorption methods were applied to determine their specific surface area. Water droplets of different volumes containing different concentrations of particles were cooled until droplets were frozen. For all the analyzed drop volumes, an increase in the freezing temperature of the drops was observed with increasing dust concentration. In the same way, the freezing temperature increased when the drop volume was increased at constant dust concentration. Both behaviors were linked to the availability of active sites in the particles. A plateau in the freezing temperature was observed at high suspension concentration for all the drop volumes. This plateau was related to the aggregation of the particles when the suspension concentration was increased and to the consequent decrease in the number of active sites. The active sites per unit of surface area were calculated and reported. For the studied range of temperature, results are in agreement with those reported for different sites and particles. From the chemical and morphological analysis of the particle components and the results obtained from the literature, it was concluded that even though montmorillonite was the main mineral in the collected sample, the accessory minerals deserve to be analyzed in detail in order to know if they could be responsible for the ability of the collected soil particles to act as INPs. Considering that the region of Patagonia has been identified as an important source of natural mineral particles in the atmosphere, it is important to analyze the ability of these particles to act as INP. As far as we know, this is the first study carrying out this investigation.

1. Introduction

Heterogeneous nucleation is the main process forming ice in the atmosphere, which involves the foreign surfaces of insoluble particles called ice nuclei particles (INP). The chemical and physical characteristics of the aerosol particles acting as INPs are a topic of intense research (e.g. Santachiara et al., 2010; Yang et al., 2014). It has been shown that primary biological particles, mineral dust, metallic particles, soot, and volcanic ash, act as INPs (Fröhlich-Nowoisky et al., 2016; Hazra et al., 2016; Popovicheva et al., 2008; Von Blohn et al., 2005).

There are four modes involving heterogeneous nucleation: deposition nucleation, condensation freezing, contact freezing, and immersion freezing. Deposition nucleation occurs when ice is deposited on the INPs from the vapor phase. For this reason, the environment can be subsaturated with respect to liquid water, but supersaturated with respect to ice. Condensation freezing occurs at temperatures below 0 °C when cloud condensation nuclei act as INPs. During contact freezing, the ice is formed by the collision of interstitial aerosols with cloud droplets. Lastly, immersion freezing occurs when INPs are immersed in aqueous droplets at temperatures below 0 °C (Vali, 1985).

The immersion freezing mechanism is involved in the formation of ice crystals in cirrus and mixed-phase clouds (e.g. Hoose and Möhler, 2012). A review of particles immersed in supercooled droplets acting as INPs has been compiled by Murray et al. (2012). Mineral dust particles play a dominant role in ice formation by immersion freezing (Hoose et al., 2010). At the same time, natural mineral dust particles make the largest mass contribution to aerosol in the atmosphere (e.g. Satheesh and Moorthy, 2005). For this reason, recent works have been focused on understanding the role of mineral particles as INPs by immersion freezing. A recent comparison of the laboratory techniques used to

examine immersion freezing activity was made by Hiranuma et al. (2015). This laboratory studies use commercial particles as surrogates for atmospheric mineral dust particles (e.g. Nagare et al., 2016; Wex et al., 2014) or natural mineral particles. One of the most recent works showing the efficiency of these natural mineral particles in the immersion freezing mode is presented by Kaufmann et al. (2016).

Considering that clay minerals (mainly kaolinite, montmorillonite, or illite) are the main components of mineral dust particles and the most common minerals transported in the atmosphere, they have been intensively studied as INPs by immersion freezing mode (Murray et al., 2012; Boose et al., 2016). However, recently Atkinson et al. (2013) have shown that the feldspar component is more efficient at nucleating ice than other minerals present in higher proportion in desert dusts. Moreover, Harrison et al. (2016) and Kaufmann et al. (2016) showed that the role of feldspar particles promoting the immersion freezing is related to the polymorphic forms of the structures of the feldspars. Thus, the impact of mineral dust aerosols on ice formation depends strongly on their mineralogy, which is largely variable both geographically and spatially (Formenti et al., 2014).

The arid regions around the world have been identified as the most important sources of natural mineral particles in the atmosphere (Prospero et al., 2002; Ginoux et al., 2012). The main arid regions are the global dust belt from the Sahara to the Taklamakan in China, the deserts located in the USA and Mexico, Australia, Botswana, Namibia, Bolivia, and Patagonia in western Argentina (e.g. Formenti et al., 2011). The last five regions are the main sources located in the Southern Hemisphere. Over the last 50 years, the role of mineral dusts from Sahara and arid regions in Asia has been related to heterogeneous nucleation (e.g. Isono et al., 1959; Belosi et al., 2017).

Regarding the Southern Hemisphere, even though some recent works have analyzed the heterogeneous nucleation on natural particles collected in Botswana, Namibia, Bolivia, and Australia (Kaufmann et al., 2016; Boose et al., 2016), there is still a lack of measurements in this area. Indeed, studies of natural dust particles as INPs from Patagonia have never been reported. This area is worth analyzing because Patagonia is the most important source of dust in South America (Prospero et al., 2002) and because the particles can even reach Antarctica (Gassó et al., 2010), where ice formation is important since clouds are prevalently mixed or cold (e.g. Belosi et al., 2014).

In this context, the aim of the present study was to characterize the ability of soil mineral particles collected in the region of Patagonia to act as ice nuclei particles by immersion freezing mode. As far as we know, this is the first work studying the role of Patagonian soil particles as INP.

2. Materials and methods

2.1. Mineral dust particles

Patagonia is located between latitudes 38° and 52°, stretching over about 700,000 km^2 and covers practically the whole of south Argentina. The climate is controlled by the dynamics of westerly winds, which blow from the South Pacific Ocean. Since most of their moisture is discharged on the Andes, they continue as dry winds to the east. As a consequence, rainfall in the region is low, with a mean annual precipitation of 100–180 mm (National Weather Office). The monthly mean velocity of the western winds is 30 km h^{-1}. The maxima are recorded during October (spring time), when wind velocity can be over 100 km h^{-1}. Winds blowing from the east (Atlantic Ocean) are calmer, except during some storms concentrated mainly in July. The dust storms are very frequent in Patagonia and they are mainly related to the western winds from the Andes (Ramsperger et al., 1998a, 1998b).

The semi-arid plateau of northern Patagonia is almost treeless, with vegetation covering around 30%. The combination of sparse vegetation, high wind velocity and low water content in soil becomes an important soil erosion factor and the transport of aerosol particles in the

atmosphere (Tegen and Fung, 1994). In fact, Patagonia and Australia constitute the predominant sources of dust delivered on the surface of the South Atlantic Ocean (e.g. Johnson et al., 2010; Gaiero et al., 2003). Prospero et al. (2002) showed that the main source of dust in Patagonia is located between 38° S and 48° S. Within this region, they identified a particular source in the province of Neuquén, on the flanks of the Andes, and in western Río Negro. In this area, which is part of the Neuquén Basin, there are many bentonite deposits (e.g. Domínguez et al., 2001) which extends to the extra-Andean Region at the provinces of Río Negro, La Pampa and Neuquén (around 120,000 km^2). For the present work, this area was selected to collect natural mineral samples. Even bentonites are present along all the Patagonia region (e.g. McCartney, 1934), they were formed in different geological periods. In the present work, sample was collected in the province of Neuquén, in northern Patagonia. The area of collection is in the surroundings of a hill called Cerro Bandera located at latitude 38.75° S and longitude 70.33° W, and 1103 m a.s.l., where deposits of bentonite occur with 2 to 15 m in thickness (Impiccini and Vallés, 2002). Thus, the collected sample would correspond to a bentonite from the Tertiary period (Impiccini and Vallés, 2002; Domínguez et al., 2001). Then, we estimate the collected sample is representative of an approximate area of 6000 km^2. The collection site was selected because it is located in an area identified as the main source of dust in Patagonia region (Prospero et al., 2002). This choice was also based in the results from Gaiero et al. (2004). From the analysis of the rare earth element (REE) signature of dust, topsoil and riverine sediments in Patagonia, they showed that eolian dust exhibits REE compositions similar to Patagonian topsoils. This is why Patagonian topsoils has been identified as important contributors to the eolian dust, which is delivered to the South Atlantic Ocean (Gaiero et al., 2003, 2004).

The sample was collected from a sediment profile, in the bottom section located at 1 m from the surface in order to avoid the organic matter contamination. XRD and EDX analysis were used to verify the sample was only composed by mineral matter. Fig. 1 shows a map of the study area and the location of the sampling site. In order to characterize the collected particles, the X-ray diffraction and electron micro probe analysis techniques were used to analyze the chemical composition of the particles. The specific surface area of the particles was measured by the N_2 adsorption and methylene blue adsorption methods. The grain size distribution of the collected particles was measured by using the dynamic light scattering method.

2.1.1. X-ray diffraction

Powder X-ray diffraction (XRD) was used to determine the main minerals present in the sample. XRD patterns were recorded on a Philips X'Pert PRO X-ray diffractometer, using CuK radiation (30 kV-15 mA). Data were obtained in the 2θ range of 4 to 70° (step size: 0.01; 6 seg $step^{-1}$). The reflection assignments were carried out using the Panalytical X'Pert High Score software. Fig. 2 shows the XRD spectrum of the analyzed sample. The presence of the 001 reflection at 7.01 2θ corresponding to a basal spacing d_{001} of 12.6 Å is typical for a Na exchanged montmorillonite (Borgnino et al., 2009). Other mineral phases (quartz and feldspar) are also present as accessory minerals, which lead us to classify the collected sample as a bentonite in agreement with previous mineralogical studies (Impiccini and Vallés, 2002).

2.1.2. Electron micro probe analysis

The chemical composition of the sample was determined by electron micro probe analysis (EMPA). A JEOL JXA 8230 microprobe at the LAMARX laboratory of the National University of Córdoba, operating in wavelength-dispersive mode (WDS) was used. Before analysis, samples were gently disaggregated with a pestle and mortar and then mixed with Epofix resin and hardener. After that, the samples were placed in a pressure vessel for 12 h, then backfilled with araldite resin and dried in an oven (50 °C, ≥ 4 h). To perform the measures, the samples were polished and subsequently carbon coated before being measured. The