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Investigating water adsorption onto natural mineral dust particles: Linking DRIFTS experiments and BET theory

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ABSTRACT

The adsorption of water molecules on natural mineral dusts was investigated employing *in situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). The natural dust samples originated from North and West Africa, Saudi Arabia and Gobi desert regions. Furthermore, the hygroscopicity of commercially available Arizona Test Dusts (ATDs) and Icelandic volcanic ash were examined. N_2 sorption measurements, X-ray fluorescence and diffraction (XRF and XRD), as well as Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analyses were performed to determine the physicochemical properties of the particles. The water adsorption experiments were conducted in an optical cell, at room temperature under the relative humidity (RH) range of 1.9–95%. Results were simulated using a modified three-parameter Brunauer-Emmett-Teller (BET) equation. Water monolayer (ML) was formed in the RH range of 15–25%, while additional water layers were formed at higher RH. Besides, the standard adsorption enthalpies of water onto natural mineral dust samples were determined. A thorough comparison of two commercially available ATD samples indicated that size distribution and/or porosity should play a key role in particle hygroscopicity. Regarding the natural mineral particles, Ca/Si ratios, and to a lesser extent Al/Si, Na/Si, Mg/Si ratios, were found to impact the minimum RH level required for water monolayer formation. These results suggest that the hygroscopic properties of investigated African dusts are quite similar over the whole investigated RH range. Furthermore, one of the major conclusions is that under most atmospheric relative humidity conditions, natural mineral samples are always covered with at least one layer of adsorbed water.

1. Introduction

According to recent estimates around 1600 Tg of mineral dust particles are released to the atmosphere each year, representing a dominant source of particulate matter at the global scale (Andreae and Rosenfeld, 2008; Satheesh and Krishna Moorthy, 2005). Although the primary sources are arid regions (e.g. Saharan and Gobi deserts contributing around 70% of global emissions), mineral dust undergoes long-range transportation to remote areas, (Engelstaedter et al., 2006; Moosmüller et al., 2009; Prospero, 1999).

The mineralogy of dust particles is complex, and depends on the primary emission sources (Fitzgerald et al., 2015; Formenti et al., 2014; Formenti et al., 2011; Journet et al., 2014; Klaver et al., 2011; Perlwitz et al., 2015a,b; Romanías et al., 2016; Scheuvens et al., 2013; Usher et al., 2003). The most abundant elements of mineral dusts and soils are Silicon (Si) and Aluminum (Al) (Goudie and Middleton, 2006; Scheuvens et al., 2013). Si is mainly present in SiO_2 phases (e.g. quartz, cristobalite) and in various aluminosilicate minerals. Aluminosilicates such as feldspars and clays (illite, kaolinite, montmorillonite, etc.) are the major aluminum-bearing minerals (Goudie and Middleton, 2001; Goudie and Middleton, 2006; Scheuvens et al., 2013). Al is also present in the crystalline polymorphic phases of aluminum oxide Al_2O_3. Calcium (Ca) is also an important component of mineral dust mainly present in the form of calcite, calcium oxide, aragonite, and dolomite. Besides the abovementioned elements, others such as K (K-feldspar, white mica, illite), Na (albite feldspar, smectite clay minerals), Fe (in mineral oxides e.g. hematite, magnetite), Ti (TiO_2 phases of anatase and rutile) and Mg (dolomite) are also found in mineral dust and source sediments (Formenti et al., 2014; Journet et al., 2014; Klaver et al., 2011; Lafon et al., 2006; Scheuvens et al., 2011; Scheuvens et al., 2013). However, it should be noted that the mineralogical composition of airborne dust particles also depends on the size fractionation during emission and

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transport (Journet et al., 2014). To be able to account for these fractionation effects, Journet et al. specified the chemical composition of the finer textural classes of soils in the silt (2–63 μm) and clay (<2 μm) fractions. The silt fraction contains primary minerals such as quartz, feldspars and mica while other minerals such as clays and iron oxides are mostly found in the clay fraction (Journet et al., 2014).

The impact of mineral dust on Earth's atmosphere is manifold. Dust particles have a direct effect on the radiative budget of the atmosphere, by absorbing and scattering the radiation, thus they impact Earth's climate. On the other hand, due to their potential to interact with water vapor in the atmosphere, mineral dust can act as cloud condensation nuclei (CCN) and ice nuclei (IN) leading to cloud formation (Creamean et al., 2013; DeMott et al., 2003; Gaston et al., 2017; Levin et al., 2005; Pratt et al., 2009; Twohy et al., 2009; Wurzler et al., 2000). Beside their climatic impact, dust surfaces may provide the seedbed for specific interactions with trace gas molecules, and therefore, could play a key role in the transformation and environmental fate of many atmospheric species (Bedjanian et al., 2013; Zein et al., 2014). Recent laboratory studies have shown that the water content of aerosols significantly influences the adsorption properties, as well as the heterogeneous reactivity and photoreactivity of mineral particles (Bedjanian et al., 2013; Crowley et al., 2010; Zein et al., 2014). Water on the surface of mineral aerosol can (i) enhance its photo-reactivity by acting as a source of surface radical species (Romanias et al., 2012; Zein et al., 2014) or (ii) inhibit its adsorption efficiency by occupying the available adsorption sites (Bedjanian et al., 2013; El Zein et al., 2013; Romanias et al., 2016). Therefore, it is particularly important to determine the hygroscopic properties of natural mineral aerosols (Cwiertny et al., 2008; Dentener et al., 1996; Krueger et al., 2003; Tang et al., 2012; Usher et al., 2003). In parallel, it is challenging from a fundamental point of view to study the water sorption capacity of natural samples that originate from different regions of the planet and investigate to what extent the sample origin, and hence its physicochemical properties, could influence the corresponding hygroscopic properties.

H_2O adsorption on solid surfaces is a key issue in material and atmospheric sciences since it may impact any heterogeneous process or surface analysis of the considered material (Adolphs and Setzer, 1998). Numerous models and approximations have been developed in the literature to simulate H_2O adsorption isotherms (Adolphs, 2007; Khalfaoui et al., 2003; Ryu et al., 2001; Tang et al., 2016; van Erp and Martens, 2011). One of the primary studies that attempted to investigate the hygroscopic properties of atmospherically relevant surfaces was published by Goodman et al. (Goodman et al., 2001). The authors used transmission FTIR spectroscopy to probe H_2O adsorption on individual metal oxide surfaces (i.e. SiO_2, α-Al_2O_3, TiO_2, γ-Fe_2O_3, CaO, and MgO). The obtained results were well-simulated using a three-parameter BET equation that allowed determining the number of water layers formed as a function of relative humidity (RH). Furthermore, Gustafsson et al. have investigated the adsorption of H_2O on commercially available nominal 0–3 μm Arizona Test Dust (ATD) and on calcite ($CaCO_3$) (Gustafsson et al., 2005). Thermogravimetric analysis (TGA) experiments were performed to obtain quantitative results about H_2O monolayer (ML) formation. Based on TGA measurements the first H_2O ML on ATD is formed at ca. ~12% RH while up to four H_2O layers are formed at ca. ~80% RH. The hygroscopic behavior of individual metal oxides (i.e. SiO_2, Al_2O_3, Fe_2O_3, MgO and TiO_2) has also been studied employing DRIFT spectroscopy (Ma et al., 2010). H_2O adsorption followed a type-III isotherm model and the authors suggested that the three-parameter BET equation was compliant with water adsorption fitting. In addition, Hatch et al. investigated the water adsorption on clay minerals as a function of relative humidity (Hatch et al., 2012), in which the classical two-parameter BET and the Freundlich adsorption models were applied to simulate their experimental observations. One of their major conclusions was that the Freundlich adsorption model was found to fit the data well over the entire RH range, while the classical two-parameter BET failed to adequately describe adsorption phenomena at high RH conditions. The failure of classical BET equation to simulate the adsorption of water was also reported previously by Goodman et al. (Goodman et al., 2001) and other literature studies (see also Section 2.6).

Beside the abovementioned publications, several studies have been performed on natural mineral dust particles and mineral proxies probing the water uptake properties under sub- and super-saturated conditions employing either infrared spectroscopy (Hatch et al., 2014; Navea et al., 2010; Schuttlefield et al., 2007), or humidified tandem differential mobility analysis (HTDMA) (Garimella et al., 2014; Gustafsson et al., 2005; Herich et al., 2009; Koehler et al., 2009; Koehler et al., 2007; Kumar et al., 2009; Kumar et al., 2011; Sullivan et al., 2010; Vlasenko et al., 2005; Yamashita et al., 2011). A very recent review (Tang et al., 2016) summarizes the efforts carried out over the past 15 years to determine the water sorption properties of individual mineral oxides, natural and commercially-available samples.

The aim of the current study is to determine the hygroscopic properties of natural mineral dust samples originating from different arid regions on Earth. DRIFT spectroscopy was employed for the *in situ* monitoring of the adsorbed water on mineral particles. First, the experimental setup was validated by measuring and cross-checking the water adsorption behavior on pure SiO_2 that has been extensively studied in the literature (Tang et al., 2016). Then, water adsorption measurements were carried out on natural mineral dusts. Experiments were performed at room temperature, atmospheric pressure and within the relative humidity range 1.9–95%.

2. Materials and methods

2.1. Dust samples

Natural mineral dust samples were collected from various regions of the Earth in order to encompass a large diversity of hygroscopic properties (Fig. S1). African samples were collected close to the oases of Nefta (Tunisia) and Bordj (Algeria), and the city of M'Bour (Senegal), corresponding to three different regions of North and West Africa. The objective was to identify a wide range of hygroscopic properties with location points extending from the eastern part of North Africa to the west. Two other natural samples were collected from China (Gobi desert) and Saudi Arabia (Rawdat arid region), respectively. The Saharan and Rawdat dusts were soil samples manually collected with a shovel at around 20 cm depth. On the contrary Gobi dust was an aeolian sample. The hygroscopic properties were studied only for the smallest sieved size fraction of the natural dust samples (<100 μm) that can be suspended in air. In particular, a mechanical dust sifter was used to fractionate (just by weak hand-shaking) the natural mineral samples into different classes. Then, the finest fraction collected (<100 μm) was used for the experiments. Nevertheless, it should be acknowledged that sieved soil samples could have different physicochemical properties than those naturally resuspended. Besides, two commercially available ATD samples (Powder Technology Inc.) were also included. The ATD samples correspond to different collection dates and possibly to different sieving processes to obtain (a) nominal 0–3 μm ATD collected in October 2010, and (b) ISO 12103–1, A1 ultrafine ATD (3–22 μm, where ~97% is below 11 μm) collected in June 2013. Finally, an Icelandic volcanic ash topsoil sample (<100 μm) was collected after the