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Laboratory Studies of the Cloud Droplet Activation Properties and Corresponding Chemistry of Saline Playa Dust

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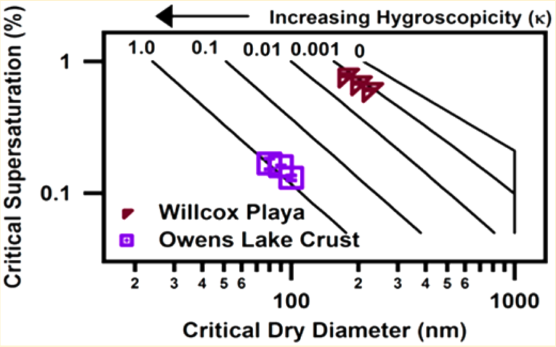
Supporting Information

ABSTRACT: Playas emit large quantities of dust that can facilitate the activation of cloud droplets. Despite the potential importance of playa dusts for cloud formation, most climate models assume that all dust is nonhygroscopic; however, measurements are needed to clarify the role of dusts in aerosol-cloud interactions. Here, we report measurements of CCN activation from playa dusts and parameterize these results in terms of both κ-Köhler theory and adsorption activation theory for inclusion in atmospheric models. κ ranged from 0.002 ± 0.001 to 0.818 ± 0.094, whereas Frankel-Halsey-Hill (FHH) adsorption parameters of $A_{FHH} = 2.20 \pm 0.60$ and $B_{FHH} = 1.24 \pm 0.14$ described the water uptake properties of the dusts. Measurements made using aerosol time-of-flight mass spectrometry (ATOFMS) revealed the presence of halite, sodium sulfates, and sodium carbonates that were strongly correlated with κ underscoring the role that mineralogy, including salts, plays in water uptake by dust. Predictions of κ made using bulk chemical techniques generally showed good agreement with measured values. However, several samples were poorly predicted suggesting that chemical heterogeneities as a function of size or chemically distinct particle surfaces can determine the hygroscopicity of playa dusts. Our results further demonstrate the importance of dust in aerosol−cloud interactions.



1. INTRODUCTION

Dust particles emitted from arid and semiarid regions represent a dominant contributor to the global aerosol burden.[1] One globally significant source of dust is dry lake beds (i.e., playas) that emit high mass concentrations of dust to the atmosphere compared to their small spatial extents.[2,3] Once released into the atmosphere, dust particles affect multiple environmental and climatic processes.[4] Dust can directly scatter or absorb incoming solar radiation,[5,6] impact the production and radiative properties of clouds, and impact precipitation efficiency by acting as ice nuclei[7−11] and cloud condensation nuclei.[12−14] The ability of dust to serve as ice and cloud condensation nuclei is dependent on the size, morphology, and chemical composition of dust particles.[15−17] Most models consider fine dust particles to be inefficient cloud condensation nuclei unless they have acquired coatings or undergone chemical aging in the atmosphere via heterogeneous reactions between dust particles and atmospheric trace gases.[13,18−20] However, observations of warm cloud droplets containing fine, unprocessed dust particles[9,21] have challenged the validity of this assumption. An attempt to model cloud droplet activation from mineral dust has recently been undertaken;[22] however, additional knowledge of the hygroscopicity of complex mineral dusts is needed. In order to improve model parameterizations of dust particles, laboratory and field measurements are required of the water uptake properties of dust particles from a variety of sources.

Several studies have measured the water uptake properties of compounds representative of minerals commonly found in dust. These measurements are typically reported in terms of a single hygroscopicity parameter (κ), which represents the dependence of the water activity of a solution on its chemical composition.[23] Values of κ range from 0, which is representative of wettable but nonhygroscopic particles, up to 1.4 for highly hygroscopic salts, such as sodium chloride

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(NaCl). Several minerals found in dust exhibit low hygroscopicity including calcite ($CaCO_3$, $\kappa \sim 0.001$) and clays such as illite, kaolinite, and montmorillonite ($\kappa \sim 0.001-0.003$).[24−27] A few studies have characterized the water uptake properties of dust generated from soil samples including Arizona Test Dust ($\kappa \sim 0.003$), Chinese loess ($\kappa \sim 0.007$), and dust from the Saharan desert ($\kappa \sim 0.023$).[25,28−30] However, these dusts are not comprised of playa materials. Recently, the water uptake properties of dust generated from a sample from the Owens (dry) Lake Basin in Inyo County, California were measured. This sample exhibited high hygroscopicities that varied as a function of particle size with the highest hygroscopicities measured for the smallest sized particles (i.e., κ ranged from 0.04 to 1.07 with an average $\kappa \sim 0.7$).[31] The highly hygroscopic nature of dust from the Owens (dry) Lake Basin is due to the fact that this region is a playa, which contains high amounts of saline material derived from groundwater or dissolved minerals in surface water that evaporate leaving behind a salt-rich, erodible crust.[32−35] The erodible surface formed on playas is a significant source of mineral aerosols. The saline nature of dust generated from playas, such as Owens (dry) Lake, suggests that playa dusts can potentially serve as efficient cloud condensation nuclei in the atmosphere. Using single-particle mass spectrometry, Pratt et al.[36] detected playa dust particles in individual cloud droplets further suggesting that playa dusts are efficient cloud condensation nuclei. Because playas can emit some of the highest regional concentrations of particulate matter observed in the atmosphere[32,37] and dust-emitting playas are ubiquitous in many arid and semiarid regions of the world,[3,35,38,39] quantifying the hygroscopic properties of playa dust particles is critical in order to understand the role that dust plays in aerosol-cloud-climate interactions around the globe.

Here we present measurements of the water uptake properties of dust particles generated from playa soil samples collected from southwestern North America. The bulk and single-particle chemical compositions of dust generated from these samples were also measured in order to determine relationships between dust mineralogy, the presence of soluble salts, and the cloud nucleating properties of playa dust. We explore whether diverse values of κ exist for different dusts or whether a single, average value of κ is appropriate for dust aerosols. The potential for playa dusts to efficiently seed cloud droplets is discussed.

2. EXPERIMENTAL SECTION

Generation of Dust Particles. Surface samples were obtained from saline playas in southwestern and western North America known to be intense dust emitters including: the Black Rock Desert (Nevada),[40] Owens (dry) Lake (California),[32−34] Lordsburg Playa (New Mexico),[41] Salt Flat Basin (Texas),[42] Willcox Playa (New Mexico),[41] and near the Great Salt Lake (Utah).[42] Photos of some of the sediment samples are shown in Figures S1−S3 of the Supporting Information (SI). When necessary, sediment samples were manually ground with a mortar and pestle to produce smaller particles for analysis. For the Owens (dry) Lake samples, both atmospheric dust and surface soil were collected (referred to here as Owens Lake Dust and Owens Lake Crust, respectively). The dust sample was collected in the atmosphere at 10 cm above the playa surface during a dust storm on March 23, 1993 using Big Spring Number Eight (BSNE) samplers,[32] and a second sample was collected from the playa surface when a powdery white crust was present. Samples were aerosolized by dry generation as detailed previously by Sullivan et al.;[27] further details of this method can be found in the SI. Commercially purchased salts were used to generate salt aerosols of known compositions. Predicted and observed values of κ for the salt standards are discussed in the Table S1 of the SI.

Chemical Analysis of Dust Using ATOFMS. The chemical composition of individual aerosolized particles was measured using an aircraft aerosol time-of-flight mass spectrometer (A-ATOFMS).[43] The A-ATOFMS measured, in real-time, the vacuum aerodynamic diameter (d_{va}) and dual-polarity mass spectra of individual particles from ∼100−1500 nm (d_{va}). After exposure to a ^{210}Po neutralizer, particles are focused in an aerodynamic lens system. Then particles are optically detected by two continuous wave 532 nm lasers spaced 6.0 cm apart, providing particle velocity and, thus, d_{va}. Polystyrene latex spheres of known physical diameter from 95 to 1500 nm were used for the particle size calibration. The timing circuit used to determine the particle velocity was also used to time the firing of a 266 nm laser (∼0.6−0.85 mJ/laser pulse) used to induce laser desorption/ionization, which produced positive and negative ions from individual particles that were detected using a dual polarity, time-of-flight mass analyzer. No significant chemical differences were observed for the particle sizes detected within the size range of the A-ATOFMS, likely due to grinding the samples; thus, average mass spectral signatures are discussed herein.

Measurements of Dust Hygroscopicity. The hygroscopicity of each aerosol sample was measured by aerosolizing particles, passing them through a ^{85}Kr neutralizer, and then size-selecting the aerosol using a differential mobility analyzer (DMA, Model 3081, TSI Inc.). Three mobility diameters, ranging from 50 to 250 nm, were chosen for each sample depending on its hygroscopicity. Total particle concentrations were measured by a condensation particle counter (CPC, model 3010, TSI Inc.) and compared to the number concentrations of particles that activated cloud droplets within a miniature cloud condensation nuclei counter (CCNc) at supersaturations between 0.1 and 1.1%.[44] The supersaturation of the CCNc is a function of the column temperature gradient (dT), which was calibrated using $(NH_4)_2SO_4$ (Aldrich, 99.999% purity). Activation curves of CCN/CN ratios, referred to herein as f_{CCN}, were generated by scanning through supersaturations (column dT) at a fixed dry diameter. The critical supersaturation (S_c) is defined as CCN/CN = 0.5. The contribution of multiply charged particles was corrected using the method of Rose et al., 2008.[45] Herein, CCN activity is presented as the single hygroscopicity parameter kappa (κ),[23] which was determined by plotting S_c for each dry diameter (D_d) on a log−log plot with the different S_c-D_d pairs for each sample falling on κ-isolines. Herein we report (i) experimentally measured values of κ, hereafter referred to as apparent κ or simply κ and (ii) predicted values of κ ($\kappa_{predict}$) using a simple mixing rule described in the next section for multicomponent aerosols. Uncertainty in κ is primarily due to the stability of the column dT and the transmission efficiency of the DMA, which affects calibrations of the column dT in the CCNc and the accuracy of size-selected monodisperse aerosols.[45]

Ion Chromatography Analysis and Thermodynamic Predictions of Hygroscopicity. Ion chromatography (IC) was performed to quantify soluble ions and to predict κ for each aerosol sample. Samples were prepared by adding 10 mg of

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Table 1. Measured and Predicted Values of κ (i.e., κ, $\kappa_{predict}$) and the FHH Adsorption Coefficients A_{FHH} and B_{FHH} for Each Playa Dust Sample

sample	soluble V_f	κ	$\kappa_{predict}$	A_{FHH}	B_{FHH}
Owen's Lake Crust	52.66%	0.818 ± 0.094	0.688		
TX Salt Basin Site S3	2.67%	0.052 ± 0.004	0.001	3.15 ± 0.20	1.14 ± 0.02
Great Salt Lake "Puffy Soil"	33.14%	0.041 ± 0.006	0.374	2.48 ± 0.07	1.13 ± 0.01
Great Salt Lake "Salt Crust"	29.89%	0.033 ± 0.004	0.348	2.10 ± 0.05	1.12 ± 0.02
Owen's Lake Dust #12	14.53%	0.030 ± 0.003	0.148	2.42 ± 0.20	1.14 ± 0.02
TX Salt Basin Site S63	4.21%	0.029 ± 0.002	0.033	2.11 ± 0.05	1.13 ± 0.01
Lordsburg Playa #8	0.36%	0.006 ± 0.001	0.002	2.20 ± 0.18	1.32 ± 0.01
Black Rock Desert Dust	0.54%	0.004 ± 0.001	0.002	2.70 ± 0.35	1.33 ± 0.04
Lordsburg Playa #2	0.63%	0.002 ± 0.001	0.001	1.50 ± 0.12	1.40 ± 0.04
Willcox Playa	0.05%	0.002 ± 0.001	0.001	1.17 ± 0.05	1.47 ± 0.03

crushed dust or sediment to 30 mL of milli-q water (>18 MΩ), sonicating the solution for 75 min in a water bath heated to 60 °C to ensure that all of the soluble material had dissolved, and filtering the solution using a 0.2 μm Supor membrane syringe filter (Acrodisc, Pall Life Sciences) similar to the method described in Padró et al., 2010[46] and Kumar et al., 2011.[47] Two different IC systems were used to quantify anions (F^-, Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}); the details of the IC instruments can be found in the SI. All samples were run in triplicate. Sample blanks were obtained by filtering milli-q water in the absence of dust particles and performing IC using the same method. Mass fractions of Na_2SO_4, $NaNO_3$, NaCl, $CaSO_4$, $Ca(NO_3)_2$, K_2SO_4, KCl, $CaCl_2$, $MgCl_2$, and $MgSO_4$ were estimated using the ISORROPIA-II model.[48] The following inputs were used: total mass concentration of each ion measured from the IC assuming a temperature of 293 K and 5% relative humidity. Mass fractions were converted to volume fractions using the reported densities of each compound.[27,31,46,47] Excess Na^+ and Ca^{2+} were assumed to form carbonates, consistent with available data on the mineralogy of Owens (dry) Lake[49−51] where most of the excess cations were observed. The remaining (insoluble) mass fraction for each sample was assumed to have $\kappa \sim 0$ and is likely composed of aluminosilicates. κ for each aerosol sample was then calculated using eq 1:[47]

$$\kappa_{predict} = \sum_i V_{f,i}\kappa_i \tag{1}$$

where $\kappa_{predict}$ is the predicted κ for each sample derived from the sum of κ for each compound (κ_i) reported in this work and in previous work[27,46,47,52] and multiplied by the volume fractions of each compound ($V_{f,i}$) calculated from eq 2:[47]

$$V_f = \frac{m_i/\rho_i}{\sum m/\rho} \tag{2}$$

where m_i and ρ_i refer to the mass and density of each measured substance (i) and the denominator refers to the total volume of the sample, which includes both soluble and insoluble material. Table S2 lists all of the densities and κ values for the standard compounds used in this work. Values of $\kappa_{predict}$ for each aerosol sample are compared to κ and discussed in this work.

The water uptake properties of the dust samples were also predicted using Frankel-Halsey-Hill (FHH) adsorption theory[53−56] because adsorption has also been shown to be important for predicting the water uptake properties of aerosols with low amounts of soluble material. The water activity of the aerosol is parametrized using a multilayer adsorption framework and combined with the Kelvin term (A) to solve for the equilibrium saturation ratio over a droplet (S) using eq 3:[56]

$$S = \exp\left(\frac{A}{D}\right)\exp[-A_{FHH}\Theta^{-B_{FHH}}] \tag{3}$$

where D is the droplet diameter, Θ is the surface coverage of adsorbed water molecules, and A_{FHH} and B_{FHH} are adsorption coefficients. eq 3 is explained in greater detail in the SI. Here we report values of the adsorption coefficients A_{FHH} and B_{FHH} that yielded the best fits to our experimental data and compare them to previously reported values for other dust samples.[47]

3. RESULTS AND DISCUSSION

Hygroscopicity of Playa Particles. Table 1 presents the values of κ, $\kappa_{predict}$, and the adsorption parameters A_{FHH} and B_{FHH} for each playa dust/sediment sample. Average values of $A_{FHH} = 2.20 \pm 0.60$ and $B_{FHH} = 1.24 \pm 0.14$ were observed with values of B_{FHH} decreasing with increasing hydrophilicity of the dust sample. The values reported herein are similar to the values of $A_{FHH} = 2.25 \pm 0.75$ and $B_{FHH} = 1.20 \pm 0.10$ reported for unprocessed mineral dust samples.[55] Because the Owens (dry) Lake crust sample is well-described by κ-Köhler theory (e.g., $\kappa > 0.2$), A_{FHH} and B_{FHH} adsorption parameters are not reported for this sample. Both Figure 1 and Table 1 present the measured values of κ for each sample. The most striking feature in both Figure 1 and Table 1 is the widespread of hygroscopicities measured for playa surface and dust particles. κ ranged from 0.002 ± 0.001 up to 0.818 ± 0.094. For simplicity, the observed values of κ are grouped into three categories: (i) "highly hygroscopic" samples with $\kappa \geq 0.1$; (ii) "slightly hygroscopic" with $0.01 \leq \kappa \leq 0.1$, similar to values obtained for some organic compounds[23] and a dust sample from the Sahara Desert;[25,28] and (iii) "low hygroscopicity" with $\kappa \leq 0.01$, similar to the water uptake measured for aluminosilicate clays.[24−26,57] For comparison, water-soluble salts exhibit $\kappa > 0.5$,[23,27,52] water-soluble organic compounds can have values of κ up to 0.3,[46,58,59] and organic compounds with low degrees of oxygenation can exhibit $\kappa < 0.1$.[60] "Highly hygroscopic" samples include model salts and the Owens Lake Crust sample; "slightly hygroscopic" samples include two samples from the Great Salt Lake Basin, the two sediment samples from the Salt Flat Basin (Texas), and the Owens Lake Dust sample; the "low hygroscopicity" samples include both sediment samples from the Lordsburg Playa, the Black Rock Desert playa sample, and sediment from the Willcox Playa. It is notable that the hygroscopicities of the dust sample and the sediment sample taken from Owens (dry) Lake differ by over an order of magnitude (i.e., the Owens Lake Crust sample has κ

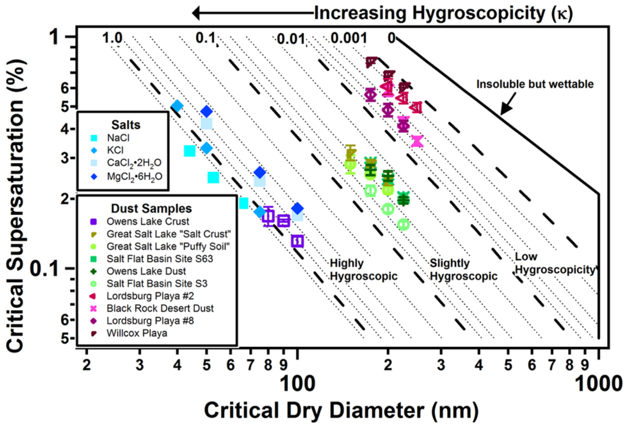

Figure 1. Critical supersaturation (S_c) and the estimated activation diameter (D_c) for salt standards and playa dust samples are plotted along with κ-isolines. The diameter shown along the *x*-axis is the mobility diameter. Closed blue symbols denote salt particles atomized from solutions containing commercially available standards, whereas open symbols denote particles derived from dry generated dust samples. "Highly hygroscopic" samples are shown in purples, "slightly hygroscopic" samples are shown in greens, and "low hygroscopicity" samples are shown in reds.

= 0.818 ± 0.094, while the Owens Lake Dust sample has κ = 0.030 ± 0.003) despite being collected from within the same dried lake bed. The likely explanation for the differing values of κ is the different types of material that were collected and analyzed in this work. The Owens Lake Crust sample was a white, powdery sediment taken from the top of the dried lake bed consistent with a highly saline-rich crust that is persistent after the playa has been recharged from an underlying brine pool. The Owens Lake Dust sample was beige in color and was comprised of dust collected from the atmosphere, representing a mixture of materials eroded from both the immediate efflorescent salt surface and the salt-silt-clay crust directly underneath it.[32−34,61−63] Thus, the Owens Lake Crust sample is expected to contain much higher concentrations of hygroscopic evaporites, while the Owens Lake Dust sample contains a mixture of hygroscopic evaporites and poorly hygroscopic clays, which explains the differences in κ.

It is also important to note that the playa sample appearance is not always indicative of its hygroscopic properties. For example, the two samples from the Great Salt Lake were very different in appearance, hence the distinction between a "salt crust" sample that contained a distinct powdery white crust and the "puffy soil" sample, which was fluffy yet contained no distinct powdery crust (see Figure S1 for photos of the two samples). Despite these differences in appearance, their respective values of κ did not exhibit major differences (i.e., κ = 0.041 for the "puffy soil" sample and κ = 0.033 for the "salt crust" sample). Overall, these results highlight the range of hygroscopicities that playa dust and sediment grains exhibit as a consequence of precipitation, hydrological, and geophysical phenomena including saline inputs to the playa surface from underlying groundwater and the generation and differentiation of dust (in the atmosphere) from sediment (on the land surface). These factors are not necessarily reflected in the morphological appearance of the soil or dust.[33]

Single-Particle Composition and Mineralogy of Playa Aerosols. In order to probe the relationship between dust/playa mineralogy, soluble salts, and κ, single-particle mass spectrometry was used to determine the chemical composition of individual playa/dust particles. The hygroscopic properties of each sample were correlated with individual particle mineralogy. Figure 2 shows the average single-particle mass spectra for the most and least hygroscopic samples—Owens Lake Crust and Willcox Playa, respectively (see Figure S4 for the average mass spectra corresponding to the other samples). Dominant ion peaks found in dust generated from the Willcox Playa sediment sample and most of the "low hygroscopicity" and "slightly hygroscopic" playa sediment/dust samples include silicates ($^{60}SiO_2^-$, $^{76}SiO_3^-$, etc.), metals ($^{7}Li^+$, $^{27}Al^+$, etc.), and metal oxides ($^{43}AlO^-$) indicative of clastic minerals including aluminosilicates and quartz. The values of κ for the "low hygroscopicity" samples are consistent with hygroscopicities derived from clay minerals suggesting that little additional soluble material was present in most of these samples.[25] The ion peak at m/z + 56 frequently detected in the "low hygroscopicity" samples corresponds to $^{56}CaO^+$, indicative of calcite ($CaCO_3$),[64] a typical constituent of playa sediments and dust aerosols in southwestern North America. These samples also contain a large peak at $^{40}Ca^+$ further supporting the assignment of m/z + 56 to calcite. This ion peak does not correspond to $^{56}Fe^+$ due to the lack of an isotope pattern at m/z + 54, 57, and 58.

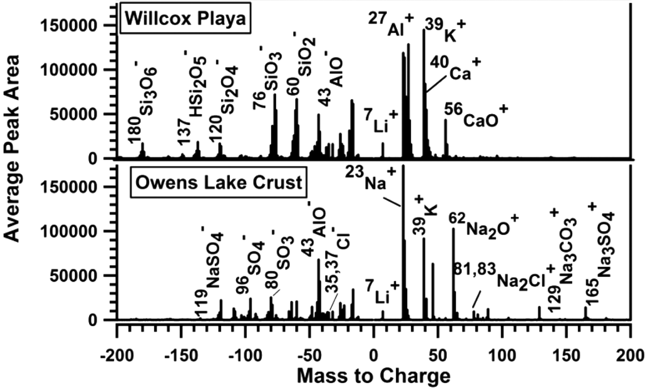

Figure 2. A-ATOFMS spectra of dust particles with the lowest κ (Willcox Playa, top panel) and the highest κ (Owens Lake Crust, bottom panel).

In contrast to the "low hygroscopicity" samples, aerosols generated from the Owens Lake Crust sample produced several ion peaks consistent with soluble sodium carbonates, sodium chloride (halite), and sodium sulfates. These ion peaks include $^{62}Na_2O^+$, which is likely due to the fragmentation of Na_2CO_3 forming $^{62}Na_2O^+$ and $CO_2(g)$, similar to the ions observed for calcite, and further supported by the observation of $^{129}Na_3CO_3^+$ in this sample. The saline-rich, erodible soil from Owens (dry) Lake, especially when collected from the surface containing efflorescent salts, has been found to contain several minerals rich in sodium carbonates, including natron ($Na_2CO_3{\cdot}10H_2O$), thermonatrite ($Na_2CO_3{\cdot}H_2O$), and trona ($Na_3HCO_3CO_3{\cdot}2H_2O$).[31,49−51] The Owens Lake Crust sample produced additional ion peaks indicative of soluble material, including chloride ($^{35,37}Cl^-$, $^{81,83}Na_2Cl^+$), likely due to the presence of halite (NaCl), and sulfate ($^{80}SO_3^-$, $^{96}SO_4^-$). Several sulfate ion peaks present in the Owens Lake Crust sample were associated with sodium (e.g., $^{119}NaSO_4^-$, $^{165}Na_3SO_4^+$), likely due to the presence of thenardite (Na_2SO_4) and mirabilite ($Na_2SO_4{\cdot}10H_2O$), which are present when the surface of Owens (dry)

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Lake is covered with an erodible, efflorescent evaporite salt crust.[32,33,51,62,63] Notably, the Owens Lake Dust sample contained $^{23}Na^+$, $^{27}Al^+$, and silicate peaks ($^{60}SiO_2^-$, $^{76}SiO_3^-$, etc.) consistent with previous results that indicated that this sample contained a mixture of surface salts and the underlying aluminosilicate material.[62,63] Further, this sample lacked ion peaks indicative of sodium sulfates and halite, and had low intensity peaks associated with sodium carbonates consistent with this sample representing a cement-like crust rather than an erodible, saline-rich crust. Overall, the Owens Lake Crust sample generated several ion peaks indicative of highly hygroscopic material (e.g., Na_2SO_4, $\kappa \sim 1.04$; NaCl, $\kappa \sim 1.4$; Na_2CO_3, $\kappa \sim 1.29$[31,47]), which explains the order of magnitude difference in κ between the two different samples from Owens (dry) Lake, as well as the high hygroscopicity of the Owens Lake Crust sample in comparison to the other playa samples. The mineralogy of playas, especially Owens (dry) Lake, is known to change rapidly in time due to changes in groundwater availability and salinity, precipitation, temperature, evaporation rates and other factors;[65] thus, it is likely that these changes are reflected in the chemical composition and cloud nucleating properties of playa dust particles.

A comparison of the single-particle composition of playa samples with their respective κ revealed that several key ion markers indicative of playa dust mineralogy can be used to infer hygroscopicity. Comparisons were made between values of κ and absolute ion peak areas indicative of the hygroscopic compounds halite ($^{81}Na_2Cl^+$) and sulfates ($^{96}SO_4^-$) (Figure 3). The ratio of m/z −81 (halite) to m/z −76 and −77 (silicates) showed a strong correlation with κ ($R^2 = 0.90$, Figure 3a), as did sulfate ($R^2 = 0.74$, Figure 3b). Because the Owens Lake Crust sample had significantly higher sulfate and halite ion peak areas than the other samples, the relationships shown in Figure 3a and b do not include this sample. Analysis of the relationship between κ, sulfate, and the halite/silicate ratio with the Owens Lake Crust sample included yields a tight correlation between κ and the chemical markers associated with hygroscopic material (e.g., $R^2 = 0.99$). We note that the correlation between hygroscopicity and sulfate decreases when the Owens Lake Crust is not considered due to the fact that most of the sulfate associated with this sample was likely in the form of mirabilite, which is much more hygroscopic (e.g., $\kappa \sim 1.04$ for Na_2SO_4[31]) than other sulfate-containing minerals such as gypsum ($\kappa \sim 0.01$ for $CaSO_4$[46,47]), which is not observed at Owens (dry) Lake and not geochemically expected given the composition of its sediments and groundwater.[50] Overall, the hygroscopic properties of playa sediment and dust particles were found to depend on the mineralogy of each sample highlighting the important role that chemical composition plays in the cloud nucleating properties of dust particles.

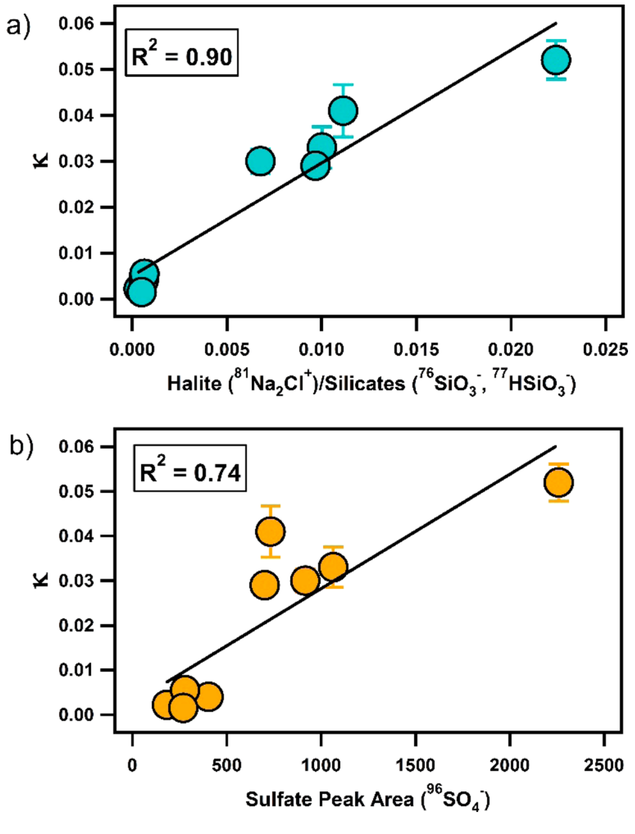

Figure 3. Comparison of κ with the average A-ATOFMS (a) sulfate peak area ($^{96}SO_4^-$), and (b) the halite ($^{81}Na_2Cl^+$)/silicates ($^{76}SiO_3^-$ + $^{77}HSiO_3^-$) ratio. Data from the Owens Lake Crust sample is not included.

Bulk Mineralogy Measurements and Predictions of Hygroscopicity. To further probe the water uptake properties of the playa dust samples, IC was performed to quantify water-soluble ions, ISORROPIA-II was used to model the salts present, and values of $\kappa_{predict}$ were predicted for each sample. Table S3 shows the soluble ion concentrations for each sample. Carbonate, which was not quantified by IC, is suggested to be an important component of the playa dusts, consistent with previous studies[49−51] and with the observed single-particle mineralogy (see Figure 2). Several samples contained unbalanced Ca^{2+} and Na^+, which we attributed to calcite ($CaCO_3$) and Na_2CO_3, respectively.

Table 1 shows the soluble volume fractions and predicted values of $\kappa_{predict}$ for each sample; Figure 4 shows a comparison of κ and $\kappa_{predict}$ for each sample and a 1:1 line for reference. Notably, most of the playa sediment/dust samples are well-predicted by their soluble mass fractions, including the Owens Lake Crust sample (i.e., $\kappa = 0.818 \pm 0.094$ while $\kappa_{predict} = 0.688$) and most of the "low hygroscopicity" samples. However, there are a few notable exceptions. κ was severely under-predicted for the sediment sample taken from TX Salt Flat Basin Site S3 ($\kappa = 0.052 \pm 0.004$ and $\kappa_{predict} = 0.001$), which produced a soluble mass fraction of only 2.7%. Particle-induced X-ray emission

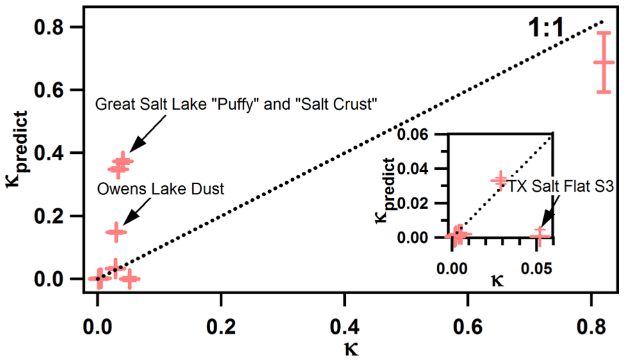

Figure 4. Comparison of the measured (apparent) κ and the calculated κ from minerals predicted using ISORROPIA-II ($\kappa_{predict}$). A 1:1 line is shown for comparison. Inset is the same figure zoomed in on the under-predicted TX Salt Flat Basin S3 sample.

(PIXE) and X-ray diffraction (XRD) conducted on this sample revealed the dominance of calcium, sulfur, and magnesium due to high mass fractions of gypsum and dolomite ($CaMg(CO_3)_2$), aluminum and silicon due to the presence of aluminosilicates, and smaller contributions from halite.[66] Overall, this analysis suggests that the bulk composition of this sample contains only a small amount of soluble material, which is inconsistent with our measured value of κ. Chemical heterogeneities as a function of particle size have been noted for playa dusts[63] and likely explain our under-predictions of κ. This is due to smaller particles, measured during our water uptake studies, containing a higher fraction of soluble material than the larger particles that dominate the mass of the sample analyzed by bulk techniques (IC and PIXE). Alternatively, chemical distinctions between the particle core and surface could also explain our observations. While the bulk data provided by the IC is not sensitive to chemical distinctions between the core and surface of particles, the single-particle data could be more sensitive to the particle surface, especially because a slightly lower laser fluence was used for this study, which favors ablation of surface material.[67,68] The TX Salt Flat sample does show a strong signal at $^{81}Na_2Cl^+$ compared to most of the other playa dusts suggestive of halite, which could be concentrated at the particle surface. The common observation that playas contain aluminosilicate grains that become coated or frosted with salts after the brine water has dried out is also consistent with this hypothesis.[69−72]

In contrast to the TX Salt Flat Basin Site S3 sample, $\kappa_{predict}$ for the Owens Lake Dust sample and both Great Salt Lake samples are overpredicted. Notably, excess Na^+, assumed to be in the form of Na_2CO_3, accounts for a large fraction (8.6%) of the total mass analyzed for the Owens Lake Dust sample. The single-particle data from this sample shows a signal at $^{62}Na_2O^+$ that is less intense than the signal present for the crust sample. When the excess Na^+ in the Owens Lake Dust sample is ignored, $\kappa_{predict}$ (0.038) matches κ (0.030), which suggests that a different compound could explain the excess Na^+. Na-containing compounds known to be present at Owens (dry) Lake include natron ($Na_2CO_3 \cdot 10H_2O$), trona ($Na_2CO_3NaHCO_3 \cdot 2H_2O$), pirssonite ($Na_2Ca(CO_3)_2 \cdot 2H_2O$), and burkeite ($2Na_2SO_4Na_2CO_3$).[49,50] The higher molecular weights of these compounds favor a lower intrinsic κ which would lower $\kappa_{predict}$. Indeed, substitution of Na_2CO_3 for these compounds does lower $\kappa_{predict}$ to 0.110 for trona, pirssonite, and burkeite and $\kappa_{predict}$ to 0.061 for natron, which likely explains the overprediction of $\kappa_{predict}$, in part. The Great Salt Lake samples are overpredicted by an order of magnitude. The most reasonable explanation for this observation is the presence of hydrates with higher molecular weights and lower values of κ.

Overall, comparisons between the hygroscopic, bulk chemical, and single-particle chemical properties of playa dust particles provide insight into the water uptake properties and mineralogy of dust particles. Further investigation into "κ-closure" for dust particles using bulk methods is clearly warranted. The results presented herein highlight that single-particle methods show promise for linking dust mineralogy with their water uptake properties by providing detailed information regarding the mineralogy of the different samples. Further analysis probing differences between the mineralogy of the particle surface and core using single-particle techniques should be explored.

Atmospheric Implications. The results presented herein highlight the widespread in hygroscopicity observed for playa dust particles, which ranged from more hygroscopic than ammonium sulfate ($\kappa \sim 0.818$) to nearly nonhygroscopic ($\kappa \sim 0.002$). The wide range in hygroscopicity was directly linked with variations in the mineralogy of the dust samples. Typically values of κ are reported as a singular value that represents the average of multiple aerosol populations. The wide range in κ shown herein suggests that a single, average value of κ for dusts, even from the same type of source (e.g., playas), is not sufficient to capture the diverse hygroscopicity that dust aerosols exhibit. Activation by the adsorption of water was also explored in this work. The adsorption parameters that best fit the data were $A_{FHH} = 2.20 \pm 0.60$ and $B_{FHH} = 1.24 \pm 0.14$ in close agreement with values reported for unprocessed mineral dust samples.[55]

Despite the low hygroscopicity of some of the playa dust/sediment samples, it should be pointed out that even "low hygroscopicity" playa dusts that are rich in aluminosilicates could induce the formation of ice crystals in the atmosphere.[7−9] Further, the dust from the Lordsburg and Willcox playas have been detected in precipitation collected in the southwestern United States highlighting the potential significance of playa dusts as contributors to precipitation.[73,74] Notably, more than half of the samples measured in this study were defined as "highly hygroscopic" or "slightly hygroscopic" demonstrating that playas can emit fine dust particles that do not require chemical aging in order to efficiently seed cloud droplets. This finding indicates that the commonly held assumption that all dust is nonhygroscopic should be re-examined. The Owens (dry) Lake Basin is a fugitive dust source created when water was diverted away from Owens Lake starting in 1913.[33] Because dust from this dried lake bed can be highly hygroscopic, this basin serves as a potential example of how humans can modify clouds and climate. It is anticipated that continued anthropogenic activities, including agricultural practices, diversion of water away from lakes, and other land use practices, combined with desiccation due to climate change will increase the spatial extent of playas and exacerbate dust emissions from dried lake beds.[2,75] Our findings indicate that increased playa dust emissions could significantly impact the formation of cloud droplets in the atmosphere.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b04487.

> A description of the dry generation setup and IC systems, results of the experiments using salt standards, a description of the adsorption model used in this work, a table of densities and values of κ for compounds detected in dust samples, photos taken of the Great Salt Lake, Lordsburg Playa, and Willcox Playa soil samples, average spectra for each playa dust sample, and tables containing bulk composition measurements from the IC are included (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Huneeus, N.; Schulz, M.; Balkanski, Y.; Griesfeller, J.; Prospero, J.; Kinne, S.; Bauer, S.; Boucher, O.; Chin, M.; Dentener, F.; Diehl, T.; Easter, R.; Fillmore, D.; Ghan, S.; Ginoux, P.; Grini, A.; Horowitz, L.; Koch, D.; Krol, M. C.; Landing, W.; Liu, X.; Mahowald, N.; Miller, R.; Morcrette, J. J.; Myhre, G.; Penner, J.; Perlwitz, J.; Stier, P.; Takemura, T.; Zender, C. S. Global dust model intercomparison in AeroCom phase I. *Atmos. Chem. Phys.* **2011**, *11* (15), 7781−7816.

(2) Gill, T. E. Eolian sediments generated by anthropogenic disturbance of playas: Human impacts on the geomorphic system and geomorphic impacts on the human system. *Geomorphology* **1996**, *17*, 207−228.

(3) Prospero, J. M.; Ginoux, P.; Torres, O.; Nicholson, S. E.; Gill, T. E. Environmental characterization of global sources of atmospheric soil dust identified with the Nimbus 7 Total Ozone Mapping Spectrometer (TOMS) absorbing aerosol product. *Rev. Geophys.* **2002**, *40* (1), DOI:10.1029/2000RG000095.

(4) Ridgwell, A. J. Dust in the Earth system: the biogeochemical linking of land, air and sea. *Philos. Trans. R. Soc., A* **2002**, *360*, 2905−2924.

(5) Myhre, G.; Shindell, D.; Bréon, F.-M.; Collins, W.; Fuglestvedt, J.; Huang, J.; Koch, D.; Lamarque, J.-F.; Lee, D.; Mendoza, B.; Nakajima, T.; Robock, A.; Stephens, G.; Takemura, T.; Zhang, H. Anthropogenic and Natural Radiative Forcing. In *Climate Change 2013: The Physical Science Basis Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*; Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P. M., Eds.; Cambridge University Press: Cambridge, 2013.

(6) Usher, C. R.; Michel, A. E.; Grassian, V. H. Reactions on mineral dust. *Chem. Rev.* **2003**, *103* (12), 4883−4939.

(7) DeMott, P. J.; Sassen, K.; Poellot, M. R.; Baumgardner, D.; Rogers, D. C.; Brooks, S. D.; Prenni, A. J.; Kreidenweis, S. M. African dust aerosols as atmospheric ice nuclei. *Geophys. Res. Lett.* **2003**, *30* (14), 1732.

(8) Pratt, K. A.; DeMott, P. J.; French, J. R.; Wang, Z.; Westphal, D. L.; Heymsfield, A. J.; Twohy, C. H.; Prenni, A. J.; Prather, K. A. In situ detection of biological particles in cloud ice-crystals. *Nat. Geosci.* **2009**, *2* (6), 397−400.

(9) Twohy, C. H. Measurements of Saharan Dust in Convective Clouds over the Tropical Eastern Atlantic Ocean. *J. Atmos. Sci.* **2015**, *72* (1), 75−81.

(10) Cziczo, D. J.; Murphy, D. M.; Hudson, P. K.; Thomson, D. S. Single particle measurements of the chemical composition of cirrus ice residue during CRYSTAL-FACE. *J. Geophys. Res., Atmos.* **2004**, *109* (D4), DOI: n/a10.1029/2003JD004032.

(11) Rosenfeld, D.; Rudich, Y.; Lahav, R. Desert dust suppressing precipitation: A possible desertification feedback loop. *Proc. Natl. Acad. Sci. U. S. A.* **2001**, *98* (11), 5975−5980.

(12) Levin, Z.; Teller, A.; Ganor, E.; Yin, Y. On the interactions of mineral dust, sea-salt particles, and clouds: A measurement and modeling study from the Mediterranean Israeli Dust Experiment campaign. *J. Geophys. Res.* **2005**, *110* (D20), DOI:10.1029/2005JD005810.

(13) Yin, Y.; Wurzler, S.; Levin, Z.; Reisin, T. G. Interactions of mineral dust particles and clouds: Effects on precipitation and cloud optical properties. *J. Geophys. Res.* **2002**, *107* (D23), DOI:AAC 19-110.1029/2001JD001544.

(14) Rudich, Y.; Khersonsky, O.; Rosenfeld, D. Treating clouds with a grain of salt. *Geophys. Res. Lett.* **2002**, *29* (22), DOI:17-110.1029/2002GL016055.

(15) Pruppacher, H. R.; Klett, J. D. *Microphysics of Clouds and Precipitation*; 2nd ed: Springer; 1996.

(16) McFiggans, G.; Artaxo, P.; Baltensperger, U.; Coe, H.; Facchini, M. C.; Feingold, G.; Fuzzi, S.; Gysel, M.; Laaksonen, A.; Lohmann, U.; Mentel, T. F.; Murphy, D. M.; O'Dowd, C. D.; Snider, J. R.; Weingartner, E. The effect of physical and chemical aerosol properties on warm cloud droplet activation. *Atmos. Chem. Phys.* **2006**, *6*, 2593−2649.

(17) Quinn, P. K.; Bates, T. S.; Coffman, D. J. Covert, D. S. Influence of particle size and chemistry on the cloud nucleating properties of aerosols. *Atmos. Chem. Phys.* **2008**, *8* (4), 1029−1042.

(18) Fan, S. M.; Horowitz, L. W.; Levy, H.; Moxim, W. J. Impact of air pollution on wet deposition of mineral dust aerosols. *Geophys. Res. Lett.* **2004**, *31* (2), DOI:10.1029/2003GL018501.

(19) Gong, S. L.; Barrie, L. A.; Blanchet, J. P.; von Salzen, K.; Lohmann, U.; Lesins, G.; Spacek, L.; Zhang, L. M.; Girard, E.; Lin, H.; Leaitch, R.; Leighton, H.; Chylek, P.; Huang, P. Canadian Aerosol Module: A size-segregated simulation of atmospheric aerosol processes for climate and air quality models - 1. Module development. *J. Geophys. Res.* **2003**, *108* (D1), DOI: 10.1029/2001JD002002.

(20) Andreae, M. O.; Rosenfeld, D. Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of cloud-active aerosols. *Earth-Sci. Rev.* **2008**, *89* (1−2), 13−41.

(21) Twohy, C. H.; Kreidenweis, S. M.; Eidhammer, T.; Browell, E. V.; Heymsfield, A. J.; Bansemer, A. R.; Anderson, B. E.; Chen, G.; Ismail, S.; DeMott, P. J.; Van den Heever, S. C. Saharan dust particles nucleate droplets in eastern Atlantic clouds. *Geophys. Res. Lett.* **2009**, *36*, (1), DOI:10.1029/2008GL035846.

(22) Karydis, V. A.; Kumar, P.; Barahona, D.; Sokolik, I. N.; Nenes, A. On the effect of dust particles on global cloud condensation nuclei and cloud droplet number. *J. Geophys. Res.* **2011**, *116* (D23), DOI:n/a10.1029/2011JD016283.

(23) Petters, M. D.; Kreidenweis, S. M. A single parameter representation of hygroscopic growth and cloud condensation nucleus activity. *Atmos. Chem. Phys.* **2007**, *7* (8), 1961−1971.

(24) Gibson, E. R.; Hudson, P. K.; Grassian, V. H. Aerosol chemistry and climate: Laboratory studies of the carbonate component of mineral dust and its reaction products. *Geophys. Res. Lett.* **2006**, *33* (13), DOI: 10.1029/2006GL026386.

(25) Herich, H.; Tritscher, T.; Wiacek, A.; Gysel, M.; Weingartner, E.; Lohmann, U.; Baltensperger, U.; Cziczo, D. J. Water uptake of clay and desert dust aerosol particles at sub- and supersaturated water vapor conditions. *Phys. Chem. Chem. Phys.* **2009**, *11* (36), 7804−7809.

(26) Schuttlefield, J. D.; Cox, D.; Grassian, V. H. An investigation of water uptake on clays minerals using ATR-FTIR spectroscopy coupled

with quartz crystal microbalance measurements. *J. Geophys. Res.* **2007**, *112* (D21), DOI: 10.1029/2007JD008973.

(27) Sullivan, R. C.; Moore, M. J. K.; Petters, M. D.; Kreidenweis, S. M.; Roberts, G. C.; Prather, K. A. Effect of chemical mixing state on the hygroscopicity and cloud nucleation properties of calcium mineral dust particles. *Atmos. Chem. Phys.* **2009**, *9*, 3303−3316.

(28) Koehler, K. A.; Kreidenweis, S. M.; DeMott, P. J.; Petters, M. D.; Prenni, A. J.; Carrico, C. M. Hygroscopicity and cloud droplet activation of mineral dust aerosol. *Geophys. Res. Lett.* **2009**, *36* (8), DOI:10.1029/2009GL037348.

(29) Navea, J. G.; Chen, H.; Huang, M.; Carmichael, G. R.; Grassian, V. H. A comparative evaluation of water uptake on several mineral dust sources. *Environ. Chem.* **2010**, *7*, 162−170.

(30) Vlasenko, A.; Sjogren, S.; Weingartner, E.; Gaggeler, H. W.; Ammann, M. Generation of submicron Arizona test dust aerosol: Chemical and hygroscopic properties. *Aerosol Sci. Technol.* **2005**, *39* (5), 452−460.

(31) Koehler, K. A.; Kreidenweis, S. M.; DeMott, P. J.; Prenni, A. J.; Petters, M. D. Potential impact of Owens (dry) Lake dust on warm and cold cloud formation. *J. Geophys. Res.* **2007**, *112* (D12), DOI:10.1029/2007JD008413.

(32) Cahill, T. A.; Gill, T. E.; Reid, J. S.; Gearhart, E. A.; Gillette, D. A. Saltating particles, playa crusts and dust aerosols at Owens (dry) Lake, California. *Earth Surf. Processes Landforms* **1996**, *21*, 621−639.

(33) Gill, T. E.; Gillette, D. A.; Niemeyer, T. C.; Winn, R. T. Elemental geochemistry of wind-erodible playa sediments, Owens Lake, California. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2002**, *189*, 209−213.

(34) Niemeyer, T. C.; Gillette, D. A.; Deluisi, J. J.; Kim, Y. J.; Niemeyer, W. F.; Ley, T.; Gill, T. E.; Ono, D. Optical depth, size distribution, and flux of dust from Owens Lake, California. *Earth Surf. Processes Landforms* **1999**, *24* (5), 463−479.

(35) Rosen, M. R. The importance of groundwater in playas: A review of playa classifications and the sedimentology and hydrology of playas. In *Paleoclimate and Basin Evolution of Playa Systems*; Rosen, M. R., Ed.; Geological Society of America: Boulder, CO, 1994; Special Paper 289.

(36) Pratt, K. A.; Twohy, C. H.; Murphy, S. M.; Moffet, R. C.; Heymsfield, A. J.; Gaston, C. J.; DeMott, P. J.; Field, P. R.; Henn, T. R.; Rogers, D. C.; Gilles, M. K.; Seinfeld, J. H.; Prather, K. A. Observation of playa salts as nuclei in orographic wave clouds. *J. Geophys. Res.* **2010**, *115* (D15), DOI:10.1029/2009JD013606.

(37) Abuduwaili, J.; Gabchenko, M. V.; Junrong, X. Eolian transport of salts–A case study in the area of Lake Ebinur (Xinjiang, Northwest China). *J. Arid Environ.* **2008**, *72*, 1843−1852.

(38) Bullard, J. E.; Harrison, S. P.; Baddock, M. C.; Drake, N.; Gill, T. E.; McTainsh, G.; Sun, Y. Preferential dust sources: A geomorphological classification designed for use in global dust-cycle models. *J. Geophys. Res.* **2011**, *116* (F04); DOI:10.1029/2011JF002061.

(39) Jones, B. F.; Deocampo, D. M. Geochemistry of saline lakes. In *Treastise on Geochemistry*. Holland, H. D., Turekian, K. K., Eds.; Elsevier: New York, 2003; pp 393−424.

(40) Lewis, J. M.; Kaplan, M. L.; Vellore, R.; Rabin, R. M.; Hallett, J.; Cohn, S. A. Dust storm over the Black Rock Desert: Larger-scale dynamic signatures. *J. Geophys. Res.* **2011**, *116* (D06), DOI:10.1029/2010JD014784.

(41) Rivera Rivera, N. I.; Gill, T. E.; Bleiweiss, M. P.; Hand, J. L. Source characteristics of hazardous Chihuahuan Desert dust outbreaks. *Atmos. Environ.* **2010**, *44*, 2457−2468.

(42) Lee, J. A.; Gill, T. E.; Mulligan, K. R.; Dominguez Acosta, M.; Perez, A. E. Land use/land cover and point sources of the 15 December 2003 dust storm in southwestern North America. *Geomorphology* **2009**, *105*, 18−27.

(43) Pratt, K. A.; Mayer, J. E.; Holecek, J. C.; Moffet, R. C.; Sanchez, R. O.; Rebotier, T. P.; Furutani, H.; Gonin, M.; Fuhrer, K.; Su, Y.; Guazzotti, S.; Prather, K. A. Development and characterization of an aircraft aerosol time-of-flight mass spectrometer. *Anal. Chem.* **2009**, *81* (5), 1792−1800.

(44) Roberts, G. C.; Nenes, A. A continuous-flow streamwise thermal-gradient CCN chamber for atmospheric measurements. *Aerosol Sci. Technol.* **2005**, *39* (3), 206−221.

(45) Rose, D.; Gunthe, S. S.; Mikhailov, E.; Frank, G. P.; Dusek, U.; Andreae, M. O.; Poschl, U. Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment. *Atmos. Chem. Phys.* **2008**, *8* (5), 1153−1179.

(46) Padro, L. T.; Tkacik, D.; Lathem, T.; Hennigan, C. J.; Sullivan, A. P.; Weber, R. J.; Huey, L. G.; Nenes, A. Investigation of cloud condensation nuclei properties and droplet growth kinetics of the water-soluble aerosol fraction in Mexico City. *J. Geophys. Res.* **2010**, *115* (D09), DOI:10.1029/2009JD013195.

(47) Kumar, P.; Sokolik, I. N.; Nenes, A. Cloud condensation nuclei activity and droplet activation kinetics of wet processed regional dust samples and minerals. *Atmos. Chem. Phys.* **2011**, *11* (16), 8661−8676.

(48) Fountoukis, C.; Nenes, A. ISORROPIA II: A computationally efficient thermodynamic equilibrium model for K^+-Ca^{2+}-Mg^{2+}-NH_4^+-Na^+-SO_4^{2-}-NO_3^--Cl^--H_2O aerosols. *Atmos. Chem. Phys.* **2007**, *7*, 4639−4659.

(49) Brown, N.; Lamos, P.; Scarr, I. Present-day features related to the deposition of trona at Owens Lake, California, and a comparison with the trona deposits of the Green River Basin. *Nevada Bureau of Mines and Geology Special Publication* **2003**, *33*, 36−40.

(50) Levy, D. B.; Schramke, J. A.; Esposito, K. J.; Erickson, T. A.; Moore, J. C. The shallow ground water chemistry of arsenic, fluorine, and major elements: Eastern Owens Lake, California. *Appl. Geochem.* **1999**, *14*, 53−65.

(51) Reheis, M. C. Dust deposition downwind of Owens (dry) Lake, 1991−1994: Preliminary findings. *J. Geophys. Res.* **1997**, *102* (D22), 25999−26008.

(52) Carrico, C. M.; Petters, M. D.; Kreidenweis, S. M.; Sullivan, A. P.; McMeeking, G. R.; Levin, E. J. T.; Engling, G.; Malm, W. C.; Collett, J. L. Water uptake and chemical composition of fresh aerosols generated in open burning of biomass. *Atmos. Chem. Phys.* **2010**, *10* (11), 5165−5178.

(53) Kumar, P.; Nenes, A.; Sokolik, I. N. Importance of adsorption for CCN activity and hygroscopic properties of mineral dust aerosol. *Geophys. Res. Lett.* **2009**, *36* (24), DOI:10.1029/2009GL040827.

(54) Kumar, P.; Sokolik, I. N.; Nenes, A. Parameterization of cloud droplet formation for global and regional models: Including adsorption activation from insoluble CCN. *Atmos. Chem. Phys.* **2009**, *9*, 2517−2532.

(55) Kumar, P.; Sokolik, I. N.; Nenes, A. Measurements of cloud condensation nuclei activity and droplet activation kinetics of fresh unprocessed regional dust samples and minerals. *Atmos. Chem. Phys.* **2011**, *11*, 3527−3541.

(56) Sorjamaa, R.; Laaksonen, A. The effect of H_2O adsorption on cloud drop activation of insoluble particles: a theoretical framework. *Atmos. Chem. Phys.* **2007**, *7* (24), 6175−6180.

(57) Gibson, E. R.; Gierlus, K. M.; Hudson, P. K.; Grassian, V. H. Generation of internally mixed insoluble and soluble aerosol particles to investigate the impact of atmospheric aging and heterogeneous processing on the CCN activity of mineral dust aerosol. *Aerosol Sci. Technol.* **2007**, *41* (10), 914−924.

(58) Lathem, T.; Beyersdorf, A. J.; Thornhill, K. L.; Winstead, E. L.; Cubison, M. J.; Hecobian, A.; Jimenez, J. L.; Weber, R. J.; Anderson, B. E.; Nenes, A. Analysis of CCN activity of Arctic aerosol and Canadian biomass burning during summer 2008. *Atmos. Chem. Phys.* **2013**, *13*, 2735−2756.

(59) Pringle, K. J.; Tost, H.; Pozzer, A.; Poschl, U.; Lelieveld, J. Global distribution of the effective aerosol hygroscopicity parameter for CCN activation. *Atmos. Chem. Phys.* **2010**, *10*, 5241−5255.

(60) Jimenez, J. L.; Canagaratna, M. R.; Donahue, N. M.; Prevot, A. S. H.; Zhang, Q.; Kroll, J. H.; DeCarlo, P. F.; Allan, J. D.; Coe, H.; Ng, N. L.; Aiken, A. C.; Docherty, K. S.; Ulbrich, I. M.; Grieshop, A. P.; Robinson, A. L.; Duplissy, J.; Smith, J. D.; Wilson, K. R.; Lanz, V. A.; Hueglin, C.; Sun, Y. L.; Tian, J.; Laaksonen, A.; Raatikainen, T.;

Rautiainen, J.; Vaattovaara, P.; Ehn, M.; Kulmala, M.; Tomlinson, J. M.; Collins, D. R.; Cubison, M. J.; Dunlea, E. J.; Huffman, J. A.; Onasch, T. B.; Alfarra, M. R.; Williams, P. I.; Bower, K.; Kondo, Y.; Schneider, J.; Drewnick, F.; Borrmann, S.; Weimer, S.; Demerjian, K.; Salcedo, D.; Cottrell, L.; Griffin, R.; Takami, A.; Miyoshi, T.; Hatakeyama, S.; Shimono, A.; Sun, J. Y.; Zhang, Y. M.; Dzepina, K.; Kimmel, J. R.; Sueper, D.; Jayne, J. T.; Herndon, S. C.; Trimborn, A. M.; Williams, L. R.; Wood, E. C.; Middlebrook, A. M.; Kolb, C. E.; Baltensperger, U.; Worsnop, D. R. Evolution of organic aerosols in the atmosphere. *Science* **2009**, *326* (5959), 1525−1529.

(61) Reheis, M. C. Dust deposition downwind of Owens (dry) Lake, 1991−1994: Preliminary findings. *J. Geophys. Res.* **1997**, *102* (D22), 25999−26008.

(62) Rojo, L.; Barnes, M. A.; Gill, T. E. Intercomparison of PIXE and ICP-AES analyses of aeolian dust from Owens (dry) Lake, California. *Geostand. Geoanal. Res.* **2012**, *36* (1), 83−102.

(63) Rojo, L.; Gill, T. E.; Gillette, D. A. Particle size/composition relationships of wind-eroding sediments, Owens (dry) Lake, California, USA. *X-Ray Spectrom.* **2008**, *37*, 111−115.

(64) Sullivan, R. C.; Moore, M. J. K.; Petters, M. D.; Kreidenweis, S. M.; Roberts, G. C.; Prather, K. A. Timescale for hygroscopic conversion of calcite mineral particles through heterogeneous reaction with nitric acid. *Phys. Chem. Chem. Phys.* **2009**, *11*, 7826−7837.

(65) Reynolds, R. L.; Yount, J. C.; Reheis, M. C.; Goldstein, H.; Chavez, P.; Fulton, R.; Whitney, J.; Fuller, C.; Forester, R. M. Dust emission from wet and dry playas in the Mojave Desert, USA. *Earth Surf. Processes Landforms* **2007**, *32*, 1811−1827.

(66) Perez, A. E. Application of integrated remote sensing and GIS technologies to geoenvironmental issues in far west Texas and southern New Mexico. Ph.D. Dissertation, University of Texas at El Paso, El Paso, TX, 2008.

(67) Ault, A. P.; Guasco, T. L.; Ryder, O. S.; Baltrusaitis, J.; Cuadra-Rodriguez, L. A.; Collins, D. B.; Ruppel, M. J.; Bertram, T. H.; Prather, K. A.; Grassian, V. H. Inside versus outside: Ion redistribution in nitric acid reacted sea spray aerosol particles as determined by single particle analysis. *J. Am. Chem. Soc.* **2013**, *135*, 14528−14531.

(68) Zelenyuk, A.; Yang, J.; Song, C.; Zaveri, R. A.; Imre, D. Depth-profiling" and quantitative characterization of the size, composition, shape, density, and morphology of fine particles with SPLAT, a single-particle mass spectrometer. *J. Phys. Chem. A* **2008**, *112*, 669−677.

(69) Eswaran, H.; Stoops, G.; Abtahi, A. SEM morphologies of halite (NaCl) in soils. *J. Microsc.* **1980**, *120* (3), 343−352.

(70) Goodall, T. M.; North, C. P.; Glennie, K. W. Surface and subsurface sedimentary structures produced by salt crusts. *Sedimentology* **2000**, *47*, 99−118.

(71) Mees, F. Salt mineral distribution patterns in soils of the Otjomongwa pan, Namibia. *Catena* **2003**, *54*, 425−437.

(72) Mees, F.; Singer, A. Surface crusts on soils/sediments of the southern Aral Sea basin, Uzbekistan. *Geoderma* **2006**, *136* (1), 152−159.

(73) Gilbert, J.; Gill, T. E.; Borrok, D.; Frey, B.; Hertel, T.; Lane, M.; Bleiweiss, M.; Lehmann, C.; Gay, D.; Ramana, C. V. Geochemistry and potential playa sources of the January 7, 2008 Southwestern New Mexico "Milky Rain". *Natural Resources and Environmental Issues* **2009**, *15*, 119.

(74) Sorooshian, A.; Shingler, T.; Harpold, A.; Feagles, C. W.; Meixner, T.; Brooks, P. D. Aerosol and precipitation chemistry in the southwestern United States: spatiotemporal trends and interrelationships. *Atmos. Chem. Phys.* **2013**, *13* (15), 7361−7379.

(75) Pelletier, J. D. Sensitivity of playa windblown-dust emissions to climate and anthropogenic change. *J. Arid Environ.* **2006**, *66*, 62−75.