ACCOUNTS of chemical research

pubs.acs.org/accounts Article

Re-examining Dust Chemical Aging and Its Impacts on Earth's Climate

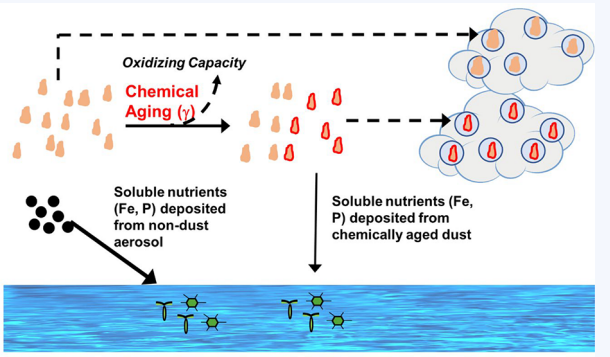
Published as part of the Accounts of Chemical Research special issue "New Frontiers in Chemistry−Climate Interactions".

Cassandra J. Gaston*

Cite This: https://dx.doi.org/10.1021/acs.accounts.0c00102 Read Online

ACCESS | Metrics & More | Article Recommendations

CONSPECTUS: The impact of atmospheric particulate matter (i.e., aerosols) on Earth's radiative balance has been and continues to be the leading source of uncertainty with respect to predictions of future temperature increases due to climate change. Mineral dust particles transported from deserts and semiarid regions across the globe are a dominant contributor to the aerosol burden. Dust has many and diverse effects on Earth's climate: it directly scatters and/or absorbs incoming sunlight; it reacts with trace gases leading to impacts on the oxidizing capacity of the atmosphere that affect both the lifetime of the greenhouse gas methane in addition to concentrations of tropospheric ozone—a greenhouse gas and criteria air pollutant; it influences the production as well as the lifetime and radiative properties of clouds; and it deposits nutrients to aquatic and terrestrial ecosystems that can stimulate primary production and facilitate the sequestration of atmospheric carbon dioxide (CO_2). This Account will focus on the last three effects. The ability of dust to affect clouds and biogeochemical cycles hinges upon the chemical nature of dust particles—in particular, whether the compounds found in dust particles are water-soluble. The solubility of nutrients found in dust is particularly critical for determining the impact of atmospheric deposition on ocean productivity. The traditional viewpoint is that dust is inherently insoluble but reactive toward trace acidic gases, a process herein referred to as chemical aging. These reactions are thought to affect the oxidizing capacity of the atmosphere while effectively transforming the chemical composition of dust by increasing its solubility. Consequently, chemical aging is hypothesized to substantially increase the impact of dust on cloud droplet formation and marine biogeochemical cycles.



This Account presents recent advances in our understanding of the mechanisms that determine how efficiently dust undergoes chemical aging and what the consequences of these processes are for the different effects of dust on Earth's climate. This Account will re-examine the traditional viewpoint that dust chemical aging strongly impacts marine biogeochemical cycles as well as the ability of dust to nucleate cloud droplets. Laboratory studies on environmental samples are combined with chemical analysis of field samples collected at dust transport receptor sites to better understand chemical aging mechanisms and determine the impact of dust on tropospheric oxidants, clouds, and biogeochemical cycles. Our results highlight the important role that dust mineralogy plays in both the nucleation of clouds as well as the kinetics responsible for the chemical aging of dust. This Account will present cases where dust contains inherently soluble minerals and does not require chemical aging in order to efficiently nucleate clouds in the atmosphere. Lastly, this Account illustrates the critical role that nondust aerosols, namely, wildfire and combustion emissions, play as a supplier of soluble nutrients important for biogeochemical cycles, particularly in marine environments. This Account will discuss these findings and highlight future research directions and recommendations to better understand dust−climate interactions and the emerging role of biomass burning aerosol in marine biogeochemical cycles.

INTRODUCTION

Mineral dust is lofted into the atmosphere from arid and semiarid regions, most notably from Northern Africa, and then undergoes long-range transport across the globe.[1−3] Once in the atmosphere, dust affects Earth's temperature both directly, by absorbing and scattering incoming solar radiation, and indirectly, by its impacts on clouds.[4,5] Dust is also thought to

Received: March 3, 2020

https://dx.doi.org/10.1021/acs.accounts.0c00102
Acc. Chem. Res. XXXX, XXX, XXX−XXX

be the main contributor of nutrients, including iron (Fe) and phosphorus (P), that stimulate biological activity in terrestrial and aquatic ecosystems. In turn, this increase in primary productivity sequesters atmospheric carbon dioxide (CO_2) into the ocean and land, thereby linking atmospheric deposition to Earth's climate.[6] Further, dust is reactive with trace atmospheric gases, and these reactions impact budgets and lifetimes of greenhouse gases, aerosols, and criteria air pollutants.[7,8]

The chemical composition of dust plays a dominant role in controlling its climatic properties. A key consideration is whether the compounds found in dust particles are water-soluble. This property determines how efficiently dust can take up water and, then, in turn, directly scatter light and nucleate cloud droplets in the atmosphere.[9] Mineral dust particles are thought to be inherently insoluble and, therefore, poor at taking up water and inefficient as cloud condensation nuclei (CCN).[4,9] However, field measurements have suggested that some dust particles can serve as efficient CCN due to the presence of trace amounts of soluble, hygroscopic minerals, suggesting an important role for dust mineralogy in this process.[10] The solubility of Fe- and P-containing minerals found in dust affects the impact of dust on both ecosystem health and the sequestration of atmospheric CO_2.[6] For aquatic ecosystems, the solubility of Fe and P in dust is especially critical because dust has a residence time in the surface water on the order of weeks;[11] therefore, nutrients must quickly dissolve in the water and stimulate phytoplankton before the dust sinks below the surface water. The solubility of various elements and compounds is thought to depend in part on the dust mineralogy, which varies for different dust source regions.[12] For example, the Bodélé Depression in Africa is thought to be key for biogeochemical cycles not just because of the magnitude of dust transport from this source[13] but also because of its unique mineralogy.[14,15]

Chemical reactions that occur between dust particles and trace gases are thought to completely transform the solubility of dust particles[4,9] and potentially exert a larger role on the composition of dust than mineralogy. These heterogeneous and multiphase reactions are herein referred to as chemical aging. The efficiency of these reactions, typically referred to by their reactive uptake coefficient (denoted by γ), determines how much chemical aging can occur during transport. In addition to mineralogy, dust also contains organic matter and biological material[16] that can affect the efficiency of the chemical aging process. Chemical aging affects trace gas concentrations that determine the oxidizing capacity of the atmosphere, which, consequently, impacts the formation of secondary organic aerosol (SOA), the lifetime of the greenhouse gas methane, and the production of tropospheric ozone, a greenhouse gas and criteria air pollutant.[17] Chemical aging is also thought to increase the solubility of dust particles, thereby dramatically enhancing their water uptake properties and transforming dust from poor CCN to efficient CCN.[4,9] A classic example is the way the chemical aging of dust converts the slightly soluble mineral calcite (calcium carbonate) to the highly hygroscopic calcium nitrate, which is a more efficient CCN.[18,19] In contrast, several studies have shown that chemical aging can reduce the ice nucleating ability of dust.[20,21] Chemical aging can also induce an acid-driven dissolution of insoluble minerals containing Fe and P, thereby increasing the solubility of these nutrients.[22−24]

While chemical aging is hypothesized to strongly modulate dust−cloud−climate interactions in addition to aerosol biogeochemical cycles, our understanding of these processes is limited. First, the chemical mechanisms responsible for dust chemical aging and the implications for the oxidizing capacity of the atmosphere are poorly understood. Second, it is unclear whether extensive chemical aging is always required for dust to nucleate cloud droplets. Third, it is unclear how extensively dust undergoes chemical aging during long-range transport. And last, it has been suggested that the importance of chemically aged dust for marine biogeochemical cycles may be overstated for some environments. Notably, nondust aerosols contain chemical forms of Fe and P that are intrinsically more soluble than mineral forms of these nutrients,[25] and therefore, the atmospheric deposition of these nondust aerosols may be more important than dust for biogeochemical cycles for some ecosystems. In this Account, I will examine three issues: the mechanisms of dust chemical aging and its potential impact on the oxidizing capacity of the atmosphere, the importance of the chemical aging process for the water uptake properties of dust, and the relative importance of chemically aged dust for biogeochemical cycles. To address these issues, I will highlight recent advances from our work using both laboratory experiments and ambient measurements at our long-term research stations in the Caribbean and South America. I will also discuss the implications of our work and recommendations for future research directions.

RESULTS AND DISCUSSION

How Does the Mineralogy of Dust Influence Its Ability to Undergo Chemical Aging and Affect the Oxidizing Capacity of the Atmosphere?

In order to understand the impact of dust chemical aging on climate, we must first understand how efficiently dust is processed by heterogeneous reactions (i.e., gas-particle reactions). Laboratory studies have been performed on proxies of mineral dust, including individual minerals and Arizona Test Dust (ATD),[26,27] in addition to soil samples used to generate dust aerosols. The reactant gas that has been primarily studied is dinitrogen pentoxide (N_2O_5). It is considered a benchmark gas for heterogeneous reactions,[28] and we will therefore focus our discussion of the mechanisms for dust chemical aging on N_2O_5, though other reactant gases certainly contribute to this process.

The reactive uptake of N_2O_5 typically proceeds by a hydrolysis mechanism leading to the production of two molecules of nitric acid (HNO_3) per molecule of N_2O_5 reacted. This pathway is considered a terminal loss mechanism for nitrogen oxides ($NO_x \equiv NO + NO_2$), thereby reducing the oxidizing capacity of the atmosphere.[29] Laboratory experiments that characterize this heterogeneous reaction are typically conducted at different relative humidities (RHs), which controls the aerosol liquid water content and the efficiency of the N_2O_5 hydrolysis mechanism.[30,31] The measurable parameter in these studies is the reactive uptake coefficient, $\gamma(N_2O_5)$, that denotes the amount of reactant gas that irreversibly reacts with the particles. Reactive uptake experiments on inorganic aerosols have shown an increase in $\gamma(N_2O_5)$ with increasing RH.[30,31] However, a review by Tang et al.[26] showed a puzzling result that an increase in RH can have a positive, neutral, or negative effect on the $\gamma(N_2O_5)$ for mineral dust aerosol and proxy minerals. We also tested the impact of RH on the reactive uptake of N_2O_5 to dust emitted from dried out saline lake beds, also known as playas. Playas have unique mineralogy that is a blend of clays, carbonates (such as calcite), and evaporites, which are salts derived from saline groundwater or dissolved minerals in surface

https://dx.doi.org/10.1021/acs.accounts.0c00102
Acc. Chem. Res. XXXX, XXX, XXX−XXX

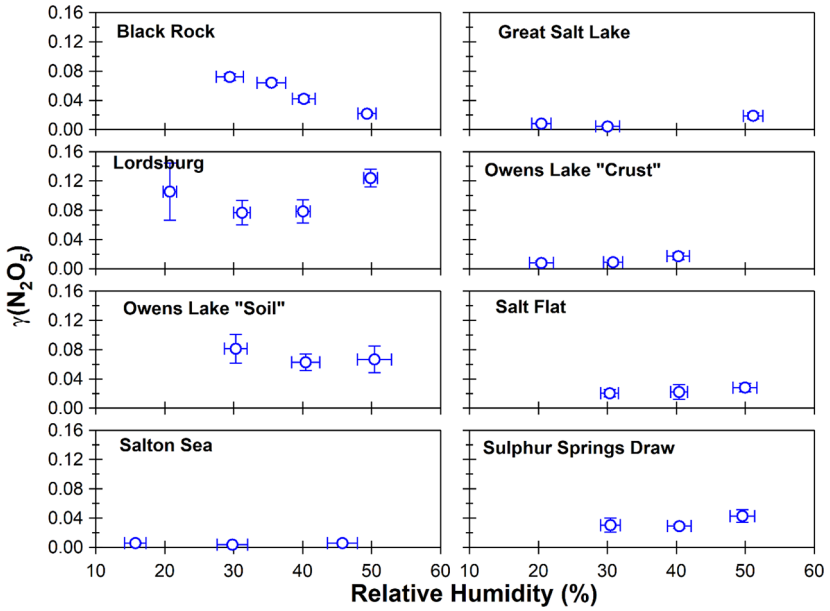


Figure 1. Reactive uptake coefficient of N_2O_5 ($\gamma(N_2O_5)$) measured as a function of relative humidity for eight different dust samples. Error bars represent one standard deviation. Reproduced from ref 34. Copyright 2019 American Chemical Society.

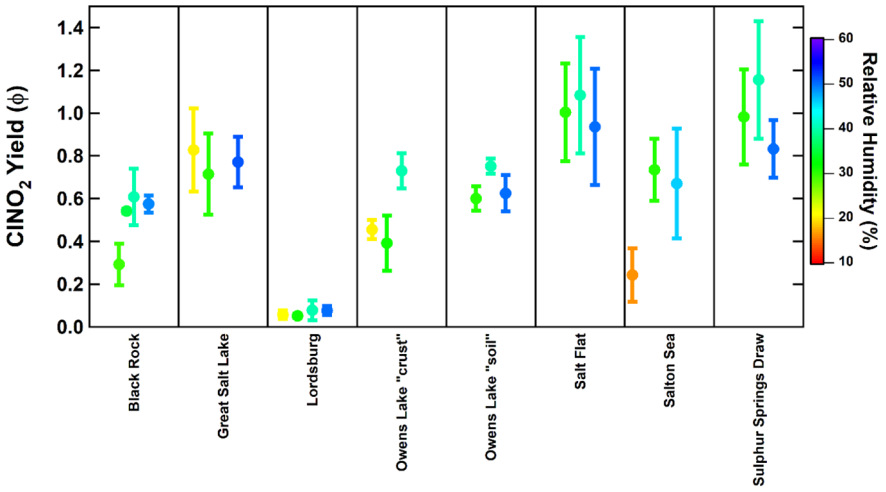


Figure 2. $ClNO_2$ yields measured as a function of relative humidity (colored dots) for eight different dust samples. Error bars represent one standard deviation. Reproduced from ref 34. Copyright 2019 American Chemical Society.

waters.[32,33] Our results from Mitroo et al.[34] replicate the positive, neutral, and negative trends in $\gamma(N_2O_5)$ with increasing RH seen in Tang et al.[26] (see Figure 1). This was surprising because, unlike dust from other source regions that are dominated by clays, playas contain both mineral clays and high levels of evaporite salts, the latter of which should produce a strong, positive trend with increasing RH.[30,31] Our results suggest that although playas contain well-studied, inorganic salts that show positive trends in $\gamma(N_2O_5)$ with RH, other minerals or compounds in dust particles may increase or decrease $\gamma(N_2O_5)$ as a function of RH.[34] For the Salton Sea sample shown in Figure 1, organic material present on the dust was hypothesized to suppress the reactive uptake of N_2O_5.[34,35] For the remaining samples, previous work on mineral proxies can help shed light on our findings. The reactivity of the clay mineral Illite with N_2O_5 shows a *decrease* as RH increases.[36] This finding is significant because clays are the most abundant class of minerals found in all dust particles.[8] The proposed mechanism for this finding is that hydroxyl groups on the surface of clays are more reactive with N_2O_5 than water, leading to very efficient uptake of N_2O_5 on dust at low RH (i.e., $\gamma(N_2O_5) > 0.03$). As RH increases, a layer of adsorbed water forms on the surface of the dust and N_2O_5 reacts with water rather than the clay surface, leading to a decrease in $\gamma(N_2O_5)$ to a value of ~0.03.[37] Indeed, our work on aerosolized playa dusts confirms that clays can outcompete water for N_2O_5, particularly at low RH, and likely explain the decreasing trend in $\gamma(N_2O_5)$ with an increase in RH observed for several playa dust samples seen in Figure 1.[34]

Our findings further suggest that in addition to affecting $\gamma(N_2O_5)$, dust mineralogy can also affect the production of other gaseous compounds generated from heterogeneous reactions. Reactions between N_2O_5 and particulate chloride lead to the production of one molecule of nitryl chloride ($ClNO_2$) and only one molecule of HNO_3 per molecule of N_2O_5 reacted. This is in comparison to the two molecules of HNO_3 produced from the hydrolysis mechanism. The production of $ClNO_2$ is significant

https://dx.doi.org/10.1021/acs.accounts.0c00102
Acc. Chem. Res. XXXX, XXX, XXX−XXX

for both air quality and climate. $ClNO_2$ is photolyzed and regenerates one molecule of NO_x and generates atomic chlorine radicals that react with volatile organic compounds (VOCs) leading to the production of secondary organic aerosol (SOA) that affects climate and degrades urban air quality.[38] Chlorine radicals also increase the oxidizing capacity of the atmosphere by reacting with and altering the lifetime of methane, a greenhouse gas, and facilitating the production of ground-level ozone, a criteria air pollutant and greenhouse gas.[17] This reaction pathway also potentially affects the degree of acidity that dust can achieve. Figure 2 taken from Mitroo et al.[34] shows the first laboratory measured yields of $ClNO_2$ from playa dust samples. Our results show that saline dust particles can generate high yields of $ClNO_2$,[34] which has implications for tropospheric ozone and urban air quality. Although our work focused on playa dusts, reactions between dust and N_2O_5 leading to $ClNO_2$ production should not be limited to just playa dusts. This reaction should also be prominent after dust has undergone long-range transport in the marine boundary layer and coagulated with sea spray aerosol and/or reacted heterogeneously with hydrochloric acid (HCl).[39]

It is clear from these results that dust mineralogy strongly affects the efficiency of heterogeneous reactions with implications both for particle acidity as well as the yield of other gaseous products that affect air quality and the oxidizing capacity of the atmosphere, such as $ClNO_2$. Our work suggests that additional studies, particularly on environmental samples, are needed to further clarify the role of different minerals on γ in order to better predict how much chemical aging dust can undergo during atmospheric transport.

Is Chemical Aging Always Important for Dust–Cloud Interactions?

Fine dust particles are generally thought to be nonhygroscopic and poor CCN unless they have undergone extensive chemical aging.[9] The water uptake ability of aerosols is typically denoted by the single hygroscopicity parameter, κ, which delineates the aerosol hygroscopicity or the effect of a particle's chemical composition on its ability to take up water and nucleate cloud droplets.[40] Values of κ range from 0, which represents insoluble but wettable particles, up to 1.4 for highly water-soluble salts, such as sodium chloride (NaCl). Due to its assumed insoluble nature, dust is thought to have $\kappa = 0$.[41] Indeed, several common minerals such as clays and calcite (i.e., calcium carbonate ($CaCO_3$)) have been shown to be poorly hygroscopic.[18,42] Further, small increases in soluble material have been shown to dramatically increase κ,[43] and chemical aging would presumably lead to this increase in soluble material. However, there are two major assumptions that need to be examined: (1) all multiphase and heterogeneous reactions will equally increase the hygroscopicity of dust and (2) the dust makeup is an unimportant consideration because dust is poorly hygroscopic no matter the source. The assumption that dust aging leads to increased hygroscopicity in all cases fails to take into account the critical role of chemical composition in increasing κ.

The first assumption has been challenged by recent laboratory and field studies. Work by Sullivan et al.[18] shows that reactions between the dust mineral calcite and different reactant gases have different outcomes. For instance, the reaction between calcite and HNO_3, leading to the formation of calcium nitrate, dramatically increases the hygroscopicity of dust, while reactions with either sulfuric acid (H_2SO_4) or oxalic acid have little to no impact on κ.[19,44] This finding is corroborated by experiments using particles collected in the field showing substantial water uptake for calcium nitrate particles and limited uptake for calcium sulfate.[26,44]

Our work challenges the second assumption. We tested the hygroscopicity of dusts generated in the laboratory from playa soil and sediment samples using a dry generation system coupled to instrumentation capable of measuring κ. Our values of κ are shown in Figure 3;[32] the red line denotes the $\kappa = 0$ line, the expected value of κ for dust that has not undergone chemical aging.[45] The figure is broken up by varying degrees of hygroscopicity. We performed ion chromatography measurements and showed that none of the dust samples contained detectable levels of nitrate or ammonium, confirming that none of the samples had been impacted by atmospheric aging. Despite the lack of chemical aging, most of our samples had values of κ that were moderately hygroscopic (e.g., $0.01 \leq \kappa \leq 0.1$) and one sample was even more hygroscopic than ammonium sulfate, which is considered a classic example of a hygroscopic aerosol that is efficient as a CCN.[40] Chemical analysis with single-particle mass spectrometry and ion chromatography revealed the presence of sodium carbonates, sodium sulfates, and halite (i.e., sodium chloride), minerals that are intrinsically very hygroscopic (e.g., $\kappa > 1$).[32] Indeed, strong correlations were found between κ and several chemical compounds detected by single-particle mass spectrometry, namely, sulfate, which was primarily detected in the form of sodium sulfate (Figure 4a), and halite (Figure 4b). The few samples that had low hygroscopicity lacked these salts and were rich in aluminosilicates, it is likely that these poorly hygroscopic samples could serve as efficient ice nuclei in the atmosphere. Our results shown in Figure 4 demonstrate the important role of minor salts intrinsically found in these samples for determining the water uptake properties of dust.[32] Another important finding was that single-particle techniques were better predictors of trends between trace salts and κ than bulk chemical analysis.[32] We attributed this finding to the important role of the dust particle surface for determining the water uptake properties of our samples. Overall, these findings demonstrate that chemical aging is not necessary to explain dust-cloud-climate interactions under all conditions.

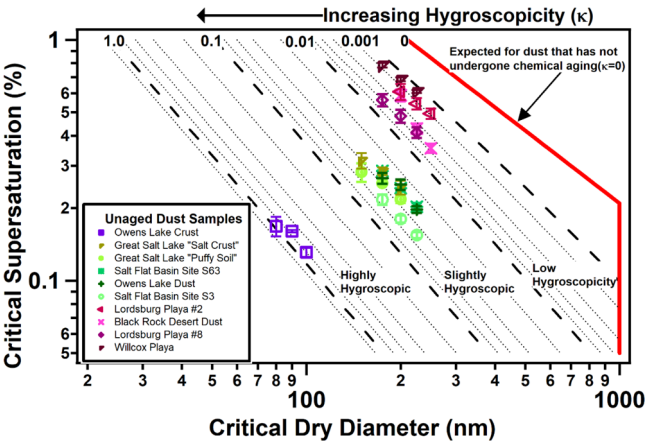


Figure 3. Hygroscopicity depicted as the hygroscopicity parameter κ measured for 10 different dust samples that have not undergone chemical aging in the atmosphere. Error bars represent one standard deviation. The $\kappa = 0$ line is depicted in red and denotes the expected value of κ for dust that has not undergone chemical aging. Reproduced from ref 32. Copyright 2017 American Chemical Society.

https://dx.doi.org/10.1021/acs.accounts.0c00102
Acc. Chem. Res. XXXX, XXX, XXX−XXX

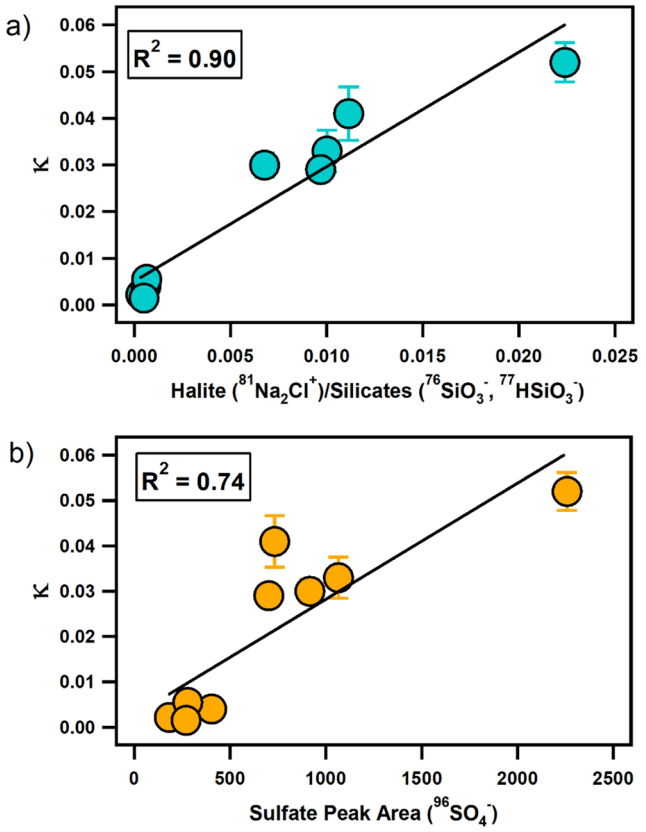


Figure 4. Comparison of the hygroscopicity parameter κ with (a) the average ion peak area of sulfate ($^{96}SO_4^-$) and (b) the halite ($^{81}Na_2Cl^+$)/silicates ($^{76}SiO_3^-$ + $^{77}HSiO_3^-$) ratio from single-particle mass spectrometry. Data shown are from aerosols generated from playa sediment samples and have not undergone chemical aging in the atmosphere. Error bars represent one standard deviation. Reproduced from ref 32. Copyright 2017 American Chemical Society.

Our results underscore the important, yet underappreciated role of minor salts in determining the ability of fine dust particles to nucleate cloud droplets in the atmosphere. Indeed, the importance of playas for clouds has also been shown in the field.[46,47] This is not to say that chemical aging is not important, but rather that we need to re-evaluate the common assumption that all dust starts with a single κ value of 0 that dramatically increases with aging. While playa dusts represent a unique case due to the presence of soluble evaporite salts that clearly shape their water uptake properties, it is important to note that other dust sources can contain trace salts that are also important for aerosol hygroscopicity and cloud droplet formation.[10,48] Further, the impact of dust emitted from playas is increasing worldwide due to increased demands for water and increased aridity associated with climate change.[49] Thus, our work has important implications for rethinking present and future dust–cloud–climate interactions on a global scale.

What is the Relative Importance of Chemically Aged Dust for Marine Biogeochemical Cycles?

The solubility of nutrients found in dust is critically important for determining the impact of atmospheric dust deposition on the ocean. While some minerals contain inherently soluble forms of Fe and P,[12,15] several laboratory studies have shown that the solubility of Fe and P in dust can dramatically increase due to chemical aging with strong acids.[22−24] Indeed, field studies show that nutrient solubility is correlated with increased distance from dust sources in Africa in some cases,[50] suggesting that chemical aging can increase the solubility of nutrients associated with dust during long-range transport.

Multiple studies in the field have observed an inverse correlation between dust mass concentrations and soluble nutrients.[50−52] Two mechanisms potentially explain this trend: (1) chemical aging is most efficient on small dust particles, although they make up less of the dust mass[22,53] or (2) biomass burning and combustion aerosols, which contain intrinsically more soluble forms of nutrients, are more important contributors of soluble Fe and P than chemically aged dust.[54,55] The first mechanism highlights the fact that smaller particles have larger surface area-to-volume ratios and longer atmospheric lifetimes and, consequently, will have more time and opportunity to undergo chemical aging.[56] The key question is: which mechanism (i.e., chemically aged small dust particles or biomass burning and combustion aerosols) is most important for supplying soluble nutrients to different ecosystems?

In our recent work, Barkley et al.[57] explored the hypothesis that African dust is the dominant supplier of nutrients to the Amazon Basin and the Tropical Atlantic Ocean that can stimulate primary production. We collected aerosol year-round in Cayenne, French Guiana at a site located upwind of the Amazon Basin on the northeastern coast of the western Tropical Atlantic Ocean.[57,58] We focused our analysis on the seasonality of total and soluble P found in aerosols, as P is expected to be a key limiting nutrient for both ecosystems. As expected, dust was the dominant source of P to our measurement site during peak dust season (i.e., boreal winter and spring);[58] however, on days with high loadings of dust, the solubility was very limited, on the order of 5% (see Figure 5a).[57] As shown in Figure 5a, we also observed an inverse trend between dust mass concentrations and the percentage of soluble P. Using scanning electron microscopy (SEM), we observed both dust and biomass burning aerosol on filters in the winter and spring (see Figure 5b);[57] most of the dust particles lacked indicators of chemical aging (e.g., sulfur as detected by energy dispersive X-ray spectroscopy (EDX)) even after long-range transport. These observations suggest an important role for biomass burning aerosol for explaining the high percentages of soluble P observed on some days even during peak dust season.

Barkley et al.[57] measured unexpectedly high concentrations of very soluble P during nondust season in fall. As shown in Figure 5c, by that time of year, mass concentrations of African dust had fallen by an order of magnitude, yet P mass concentrations were at most a factor of 2 lower in the fall than in the winter and spring, and soluble P levels were much higher in the fall. Indeed, dust mass concentrations observed in the fall could only explain 17% of the total P observed. SEM analysis of our filters revealed the dominant presence of soot particles, likely from biomass burning in the fall (see Figure 5d) further suggesting the importance of biomass burning aerosol for explaining our elevated soluble P concentrations in the fall. Using remote sensing data from Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO), we determined the vertical profile and source of aerosol transported to our site in Cayenne and found contributions of biomass burning from southern Africa in the fall. On days when CALIPSO did not observe African biomass burning transport to Cayenne, soluble P measurements were below the limit of quantification (LOQ) in our samples, as denoted by green asterisks in Figure 5a and c, confirming the important contribution of African biomass burning to soluble P concentrations at our South American

https://dx.doi.org/10.1021/acs.accounts.0c00102
Acc. Chem. Res. XXXX, XXX, XXX−XXX

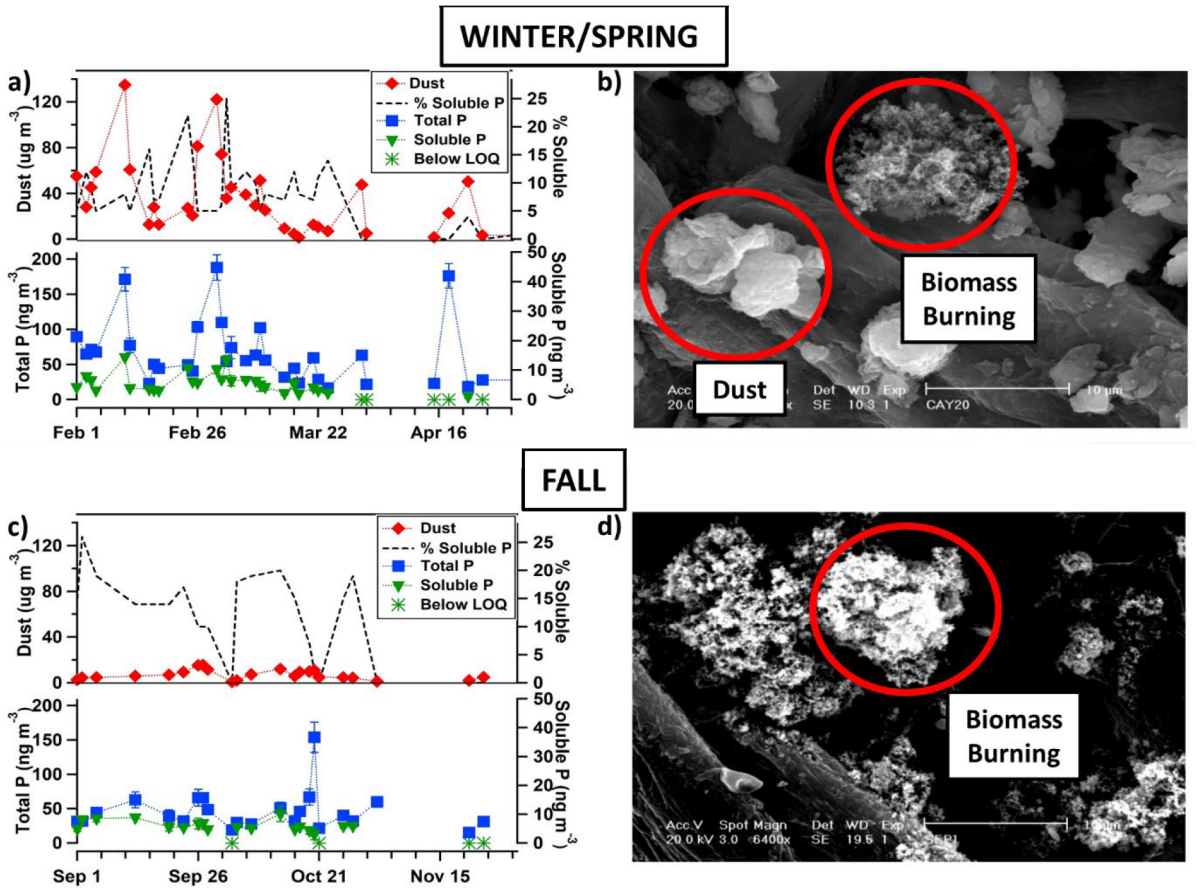


Figure 5. Seasonal dust mass concentrations (red line with diamonds), total phosphorus (P) (blue line with squares), and soluble P mass concentrations (green line with upside down triangles), and the percentage of soluble P (dashed black line) are shown for (a) winter and spring and (c) fall. Soluble P data that is below the limit of quantification (LOQ) is denoted with asterisks. Images from SEM data taken from filters from (b) winter and spring and (d) fall are also shown. Adapted with permission from ref 57. Copyright 2019 Proceedings of the National Academy of Sciences.

site.[57] Using an atmospheric transport model, we estimated that African biomass burning is an important source of soluble, bioavailable P year-round that is estimated to contribute up to 20−60% of the deposited soluble P to the Tropical Atlantic Ocean.[57] Importantly, Barkley et al.[57] show that African biomass burning has importance beyond tropical ecosystems and contributes up to 20−70% of soluble P deposition to parts of the higher latitude oceans in the southern hemisphere, primarily in the summer and fall.

Overall, our work suggests that the relative importance of dust compared to biomass burning aerosol for biogeochemical cycles needs to be assessed for different ecosystems. In principle, dust should be the dominant contributor of soluble nutrients, even if its intrinsic solubility is limited, simply due to the sheer magnitude of dust transport and its P and Fe content. In some environments, chemically aged dust can indeed provide the majority of the soluble nutrients.[22,59] However, our recent work and work from others has found that biomass burning aerosol is a more important source of soluble nutrients than dust.[55,57] The impact of atmospheric deposition on biogeochemical cycles and Earth's climate is an emerging topic, and it is clear that current parameterizations of biogeochemical cycles need to include biomass burning and combustion aerosols in addition to dust to accurately represent the impact of atmospheric deposition on carbon sequestration.

SUMMARY AND OUTLOOK

The work presented in this Account provides an update to our knowledge of the chemical processes responsible for the aging of dust during atmospheric transport and the ramifications of this process for Earth's climate. Our work shows that dust mineralogy determines both the efficiency of reactions responsible for the chemical aging process in addition to the production of gaseous products that impact the oxidizing capacity of the atmosphere.[34] Heterogeneous reactions between dust and N_2O_5 are traditionally thought to reduce the oxidizing capacity of the atmosphere through losses of NO_x that can reduce tropospheric ozone production.[29] However, our work highlights the potential for dusts emitted from sources such as saline playas to increase the oxidizing capacity of the atmosphere through the production of $ClNO_2$, which can degrade urban air quality and affect climate through impacts on concentrations of tropospheric ozone and SOA, and the lifetime of methane.[17,34] Parameterizations of the reactive uptake of N_2O_5 and production of $ClNO_2$ should account for the important role of dust in both processes, particularly in urban regions impacted by playas. This Account also underscores the power of using environmental samples for controlled laboratory experiments. Aerosols generated from environmental samples are more chemically complex and can provide insight into the competing reactions that affect both the efficiency of the aging process (i.e., $\gamma(N_2O_5)$), and the product yield (e.g., $ClNO_2$ in the case of

https://dx.doi.org/10.1021/acs.accounts.0c00102
Acc. Chem. Res. XXXX, XXX, XXX−XXX

playa dusts as our work has shown). It is anticipated that new chemical mechanisms and competing reactions will be discovered by exploring heterogeneous reactions on environmental samples. These new chemical mechanisms will be important for updating current parameterizations of these reactions and will likely have relevance for other ambient aerosol systems beyond dust.

In this Account, several examples were presented that challenge the viewpoint that chemical aging is the only mechanism that can transform insoluble dust particles into a source of efficient CCN and bioavailable nutrients. We have shown that the inherent mineralogy of different dust sources matters for shaping the climatic properties of dust. While we showed that dust emitted from playas does not require atmospheric processing to be highly efficient as CCN, we anticipate that dust from other sources that contain similar trace amounts of soluble minerals will also show similar hygroscopic properties. It is important to point out that our results presented in this Account are not meant to suggest that chemical aging is unimportant in shaping the radiative properties of dust. Rather, these results underscore the importance of both the mineralogy of unaged dust particles as well as the chemical nature of the dust aging process, since not all reactions will result in an increase in the hygroscopicity and CCN activity of dust. The importance of mineralogy and the chemical nature of dust aging highlights the need to re-evaluate the common assumption that all dust starts with a single κ value of 0 that dramatically increases with aging. Further, both dust mineralogy and the chemical nature of dust aging also likely affect the ice nucleating properties of dust; therefore, additional experiments that aim to link both parameters with both the CCN and ice nucleating properties of dust will greatly improve our understanding of how the radiative properties of dust evolve during atmospheric transport.

In the case of soluble nutrients, we find that the importance of dust may be overstated and that biomass burning is a more important supplier of soluble nutrients to some parts of the ocean.[57] There is an emerging body of work, including the work of Barkley et al.[57] highlighted in this Account, underscoring the important role of nondust aerosol sources, namely, biomass burning from wildfires and combustion aerosol, for biogeochemical cycles. It is likely that the relative importance of dust vs wildfires for biogeochemical cycles will vary depending on the receptor site and whether dust undergoes extensive chemical aging. We, therefore, recommend chemical measurements of dust at established and new transport receptor sites, particularly in the Caribbean, the coast of South America, and island sites in the Pacific Ocean, to better constrain the relative importance of dust and biomass burning aerosol as suppliers of soluble nutrients. Remote sensing products, particularly those that can differentiate biomass burning from dust, can also help better understand the importance of dust vs wildfires as sources of soluble nutrients to ocean and land ecosystems. Further exploration of the chemical composition and solubility of organic and inorganic forms of nutrients found in different aerosol sources, the dissolution rate of different forms of aerosolized nutrients in seawater, and the relationship between nutrient solubility and nutrient bioavailability would help clarify the relative importance of dust and wildfires for biogeochemical cycles. The work of Barkley et al.[57] also highlights the need for improved model representation of wildfire long-range transport for understanding the global impact of this source on biogeochemical cycles. In particular, better understanding of wildfire emissions, plume injection height, and the concentration of nutrients found in wildfires emitted from different fuels and different ecosystems would greatly improve the parameterization of this additional aerosol source in biogeochemical models.

AUTHOR INFORMATION

Corresponding Author

Cassandra J. Gaston − *Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Miami, Florida 33149, United States;* orcid.org/0000-0003-1383-8585; Phone: 305-421-4979; Email: cgaston@rsmas.miami.edu

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.accounts.0c00102

Notes

The author declares no competing financial interest.

Biography

Cassandra Gaston is an Assistant Professor of Atmospheric Sciences at the Rosenstiel School of Marine and Atmospheric Science at the University of Miami. Her research interests include physical and chemical measurements of aerosols, aerosol−cloud interactions, air−sea and atmosphere−biosphere interactions, and heterogeneous reactions. She received her undergraduate degree (2005, Biology and Environmental Chemistry) from the University of California, San Diego; Ph.D. (2012, Oceanography) from the Scripps Institution of Oceanography advised by Prof. Kim Prather. She was then a postdoctoral researcher advised by Prof. Joel Thornton at the University of Washington from 2012-2015.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation (NSF) grants AGS-1663740 and AGS-1663726. C.J.G. acknowledges an NSF CAREER award (AGS-1944958). C.J.G. acknowledges the University of Miami Provost Research Award program and the University of Miami Institute of the Americas program. C.J.G. acknowledges and thanks the coauthors and collaborators that contributed to the published work mentioned in this Account. C.J.G. thanks the reviewers of this manuscript for their insightful comments.

REFERENCES

(1) Huneeus, N.; Schulz, M.; Balkanski, Y.; Griesfeller, J.; Prospero, J.; Kinne, S.; Bauer, S.; Boucher, O.; Chin, M.; Dentener, F.; Diehl, T. Global Dust Model Intercomparison in AeroCom Phase I. *Atmos. Chem. Phys.* **2011**, *11*, 7781−7816.

(2) 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*, 2-1−2-31.

(3) Uno, I.; Eguchi, K.; Yumimoto, K.; Takemura, T.; Shimizu, A.; Uematsu, M.; Liu, Z.; Wang, Z.; Hara, Y.; Sugimoto, N. Asian Dust Transported One Full Circuit around Theglobe. *Nat. Geosci.* **2009**, *2*, 557−560.

(4) Andreae, M. O.; Rosenfeld, D. Aerosol-Cloud-Precipitation Interactions. Part 1. The Nature and Sources of Cloud-Active Aerosols. *Earth-Sci. Rev.* **2008**, *89*, 13−41.

(5) Rosenfeld, D.; Rudich, Y.; Lahav, R. Desert Dust Suppressing Precipitation: A Possible Desertification Feedback Loop. *Proc. Natl. Acad. Sci. U. S. A.* **2001**, *98*, 5975−5980.

(6) Mahowald, N. Aerosol Indirect Effect on Biogeochemical Cycles and Climate. *Science* **2011**, *334*, 794−796.

(7) Dentener, F. J.; Carmichael, G. R.; Zhang, Y.; Lelieveld, J.; Crutzen, P. J. Role of Mineral Aerosol as a Reactive Surface in the Global Troposphere. *J. Geophys. Res.* **1996**, *101*, 22869−22889.
(8) Usher, C. R.; Michel, A. E.; Grassian, V. H. Reactions on Mineral Dust. *Chem. Rev.* **2003**, *103*, 4883−4939.
(9) 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*, L02104−1.
(10) 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.; et al. Saharan Dust Particles Nucleate Droplets in Eastern Atlantic Clouds. *Geophys. Res. Lett.* **2009**, *36*, L01807.
(11) Jickells, T.; Moore, C. M. The Importance of Atmospheric Deposition for Ocean Productivity. *Annu. Rev. Ecol. Evol. Syst.* **2015**, *46*, 481−501.
(12) Journet, E.; Desboeufs, K. V.; Caquineau, S.; Colin, J. L. Mineralogy as a Critical Factor of Dust Iron Solubility. *Geophys. Res. Lett.* **2008**, *35*, L07805.
(13) Koren, I.; Kaufmann, Y. J.; Washington, R.; Todd, M. C.; Rudich, Y.; Martins, J. V.; Rosenfeld, D. The Bodélé Depression: A Single Spot in the Sahara That Provides Most of the Mineral Dust to the Amazon Forest. *Environ. Res. Lett.* **2006**, *1*, 014005.
(14) Moskowitz, B. M.; Reynolds, R. L.; Goldstein, H. L.; Berquo, T. S.; Kokaly, R. F.; Bristow, C. S. Iron Oxide Minerals in Dust-Source Sediments from the Bodélé Depression, Chad: Implications for Radiative Properties and Fe Bioavailability of Dust Plumes from the Sahara. *Aeolian Res.* **2016**, *22*, 93−106.
(15) Hudson-Edwards, K. A.; Bristow, C. S.; Cibin, G.; Mason, G.; Peacock, C. L. Solid-Phase Phosphorus Speciation in Saharan Bodélé Depression Dusts and Source Sediments. *Chem. Geol.* **2014**, *384*, 16−26.
(16) Gat, D.; Mazar, Y.; Cytryn, E.; Rudich, Y. Origin-Dependent Variations in the Atmospheric Microbiome Community in Eastern Mediterranean Dust Storms. *Environ. Sci. Technol.* **2017**, *51*, 6709−6718.
(17) Simpson, W. R.; Brown, S. S.; Saiz-Lopez, A.; Thornton, J. A.; von Glasow, R. Tropospheric Halogen Chemistry: Sources, Cycling, and Impacts. *Chem. Rev.* **2015**, *115*, 4035−4062.
(18) 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.
(19) Laskin, A.; Iedema, M. J.; Ichkovich, A.; Graber, E. R.; Taraniuk, I.; Rudich, Y. Direct Observation of Completely Processed Calcium Carbonate Dust Particles. *Faraday Discuss.* **2005**, *130*, 453−468.
(20) Cziczo, D. J.; Froyd, K. D.; Gallavardin, S. J.; Moehler, O.; Benz, S.; Saathoff, H.; Murphy, D. M. Deactivation of Ice Nuclei Due to Atmospherically Relevant Surface Coatings. *Environ. Res. Lett.* **2009**, *4*, 044013.
(21) Möhler, O.; Benz, S.; Saathoff, H.; Schnaiter, M.; Wagner, R.; Schneider, J.; Walter, S.; Ebert, V.; Wagner, S. The Effect of Organic Coating on the Heterogeneous Ice Nucleation Efficiency of Mineral Dust Aerosols. *Environ. Res. Lett.* **2008**, *3*, 025007.
(22) Nenes, A.; Krom, M. D.; Mihalopoulos, N.; Van Cappellen, P.; Shi, Z.; Bougiatioti, A.; Zarmpas, P.; Herut, B. Atmospheric Acidification of Mineral Aerosols: A Source of Bioavailable Phosphorus for the Oceans. *Atmos. Chem. Phys.* **2011**, *11*, 6265−6272.
(23) Stockdale, A.; Krom, M. D.; Mortimer, R. J. G.; Benning, L. G.; Carslaw, K. S.; Herbert, R. J.; Shi, Z.; Myriokefalitakis, S.; Kanakidou, M.; Nenes, A. Understanding the Nature of Atmospheric Acid Processing of Mineral Dusts in Supplying Bioavailable Phosphorus to the Oceans. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 14639−14644.
(24) Spokes, L. J.; Jickells, T. D. Factors Controlling the Solubility of Aerosol Trace Metals in the Atmosphere and on Mixing into Seawater. *Aquat. Geochem.* **1996**, *1*, 355−374.
(25) Mahowald, N.; Jickells, T. D.; Baker, A. R.; Artaxo, P.; Benitez-Nelson, C. R.; Bergametti, G.; Bond, T. C.; Chen, Y.; Cohen, D. D.; Herut, B.; Kubilay, N.; et al. Global Distribution of Atmospheric Phosphorus Sources, Concentrations and Deposition Rates, and Anthropogenic Impacts. *Global Biogeochem. Cycles* **2008**, *22*, GB4026.
(26) Tang, M. J.; Cziczo, D. J.; Grassian, V. H. Interactions of Water with Mineral Dust Aerosol: Water Adsorption, Hygroscopicity, Cloud Condensation, and Ice Nucleation. *Chem. Rev.* **2016**, *116*, 4205−4259.
(27) Wagner, C.; Schuster, G.; Crowley, J. N. An Aerosol Flow Tube Study of the Interaction of N_2O_5 with Calcite, Arizona Dust and Quartz. *Atmos. Environ.* **2009**, *43*, 5001−5008.
(28) Abbatt, J. P. D.; Lee, A. K. Y.; Thornton, J. A. Quantifying Trace Gas Uptake to Tropospheric Aerosol: Recent Advances and Remaining Challenges. *Chem. Soc. Rev.* **2012**, *41*, 6555−6581.
(29) Alexander, B.; Hastings, M. G.; Allman, D. J.; Dachs, J.; Thornton, J. A.; Kunasek, S. A. Quantifying Atmospheric Nitrate Formation Pathways Based on a Global Model of the Oxygen Isotopic Composition ($\Delta^{17}O$) of Atmospheric Nitrate. *Atmos. Chem. Phys.* **2009**, *9*, 5043−5056.
(30) Bertram, T. H.; Thornton, J. A. Toward a General Parameterization of N_2O_5 Reactivity on Aqueous Particles: The Competing Effects of Particle Liquid Water, Nitrate and Chloride. *Atmos. Chem. Phys.* **2009**, *9*, 8351−8363.
(31) Thornton, J. A.; Braban, C. F.; Abbatt, J. P. D. N_2O_5 Hydrolysis on Sub-Micron Organic Aerosols: The Effect of Relative Humidity, Particle Phase, and Particle Size. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4593−4603.
(32) Gaston, C. J.; Pratt, K. A.; Suski, K. J.; May, N. W.; Gill, T. E.; Prather, K. A. Laboratory Studies of the Cloud Droplet Activation Properties and Corresponding Chemistry of Saline Playa Dust. *Environ. Sci. Technol.* **2017**, *51*, 1348−1356.
(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) Mitroo, D.; Gill, T. E.; Haas, S.; Pratt, K. A.; Gaston, C. J. $ClNO_2$ Production from N_2O_5 Uptake on Saline Playa Dusts: New Insights into Potential Inland Sources of $ClNO_2$. *Environ. Sci. Technol.* **2019**, *53*, 7442−7452.
(35) Gaston, C. J.; Thornton, J. A.; Ng, N. L. Reactive Uptake of N_2O_5 to Internally Mixed Inorganic and Organic Particles: The Role of Organic Carbon Oxidation State and Inferred Organic Phase Separations. *Atmos. Chem. Phys.* **2014**, *14*, 5693−5707.
(36) Tang, M. J.; Schuster, G.; Crowley, J. N. Heterogeneous Reaction of N_2O_5 with Illite and Arizona Test Dust Particles. *Atmos. Chem. Phys.* **2014**, *14*, 245−254.
(37) Seisel, S.; Borensen, C.; Vogt, R.; Zellner, R. Kinetics and Mechanism of the Uptake of N_2O_5 on Mineral Dust at 298K. *Atmos. Chem. Phys.* **2005**, *5*, 3423−3432.
(38) Wang, L.; Arey, J.; Atkinson, R. Reactions of Chlorine Atoms with a Series of Aromatic Hydrocarbons. *Environ. Sci. Technol.* **2005**, *39*, 5302−5310.
(39) Sullivan, R. C.; Guazzotti, S. A.; Sodeman, D. A.; Tang, Y.; Carmichael, G. R.; Prather, K. A. Mineral Dust is a Sink for Chlorine in the Marine Boundary Layer. *Atmos. Environ.* **2007**, *41*, 7166−7179.
(40) Petters, M. D.; Kreidenweis, S. M. A Single Parameter Representation of Hygroscopic Growth and Cloud Condensation Nucleus Activity. *Atmos. Chem. Phys.* **2007**, *7*, 1961−1971.
(41) 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.
(42) 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*, 7804−7809.
(43) Roberts, G. C.; Artaxo, P.; Zhou, J. C.; Swietlicki, E.; Andreae, M. O. Sensitivity of CCN Spectra on Chemical and Physical Properties of Aerosol: A Case Study from the Amazon Basin. *J. Geophys. Res.* **2002**, *107*, LBA−37.
(44) Guo, L.; Gu, W.; Peng, C.; Wang, W.; Li, Y. J.; Zong, T.; Tang, Y.; Wu, Z.; Lin, Q.; Ge, M.; Zhang, G.; et al. A Comprehensive Study of Hygroscopic Properties of Calcium-and Magnesium-Containing Salts:

https://dx.doi.org/10.1021/acs.accounts.0c00102
Acc. Chem. Res. XXXX, XXX, XXX−XXX

Implication for Hygroscopicity of Mineral Dust and Sea Salt Aerosols. *Atmos. Chem. Phys.* **2019**, *19*, 2115−2133.
(45) Shi, Z.; Zhang, D.; Hayashi, M.; Ogata, H.; Ji, H.; Fujiie, W. Influences of Sulfate and Nitrate on the Hygroscopic Behaviour of Coarse Dust Particles. *Atmos. Environ.* **2008**, *42*, 822−827.
(46) Rudich, Y.; Khersonsky, O.; Rosenfeld, D. Treating Clouds with a Grain of Salt. *Geophys. Res. Lett.* **2002**, *29*, 17-1−17-4.
(47) 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.; Giles, M. K.; et al. Observation of Playa Salts as Nuclei in Orographic Wave Clouds. *J. Geophys. Res.* **2010**, *115*, D15301.
(48) Kelly, J. T.; Chuang, C. C.; Wexler, A. S. Influence of Dust Composition on Cloud Droplet Formation. *Atmos. Environ.* **2007**, *41*, 2904−2916.
(49) Wurtsbaugh, W. A.; Miller, C.; Null, S. E.; DeRose, R. J.; Wilcock, P.; Hahnenberger, M.; Howe, F.; Moore, J. Decline of the World's Saline Lakes. *Nat. Geosci.* **2017**, *10*, 816−821.
(50) Baker, A. R.; French, M.; Linge, K. L. Trends in Aerosol Nutrient Solubility along a West-East Transect of the Saharan Dust Plume. *Geophys. Res. Lett.* **2006**, *33*, L07805.
(51) Buck, C. S.; Landing, W. M.; Resing, J. A.; Lebon, G. T. Aerosol Iron and Aluminum Solubility in the Northwest Pacific Ocean: Results from the 2002 IOC Cruise. *Geochem., Geophys., Geosyst.* **2006**, *7*, Q04M07.
(52) Chen, Y.; Siefert, R. L. Seasonal and Spatial Distributions and Dry Deposition Fluxes of Atmospheric Total and Labile Iron over the Tropical and Subtropical North Atlantic Ocean. *J. Geophys. Res.* **2004**, *109*, D09305−1.
(53) Baker, A. R.; Jickells, T. D. Mineral Particle Size as a Control on Aerosol Iron Solubility. *Geophys. Res. Lett.* **2006**, *33*, L17608.
(54) Sholkovitz, E. R.; Sedwick, P. N.; Church, T. M. Influence of Anthropogenic Combustion Emissions on the Deposition of Soluble Aerosol Iron to the Ocean: Empirical Estimates for Island Sites in the North Atlantic. *Geochim. Cosmochim. Acta* **2009**, *73*, 3981−4003.
(55) Guieu, C.; Bonnet, S.; Wagener, T.; Loye-Pilot, M. D. Biomass Burning as a Source of Dissolved Iron to the Open Ocean? *Geophys. Res. Lett.* **2005**, *32*, L19608.
(56) Mahowald, N. M.; Hamilton, D. S.; Mackey, K. R. M.; Moore, J. K.; Baker, A. R.; Scanza, R. A.; Zhang, Y. Aerosol Trace Metal Leaching and Impacts on Marine Microorganisms. *Nat. Commun.* **2018**, *9*, 2614.
(57) Barkley, A. E.; Prospero, J. M.; Mahowald, N.; Hamilton, D. S.; Popendorf, K. J.; Oehlert, A. M.; Pourmand, A.; Gatineau, A.; Panechou-Pulcherie, K.; Blackwelder, P.; Gaston, C. J. African Biomass Burning is a Substantial Source of Phosphorus Deposition to the Amazon, Tropical Atlantic Ocean, and Southern Ocean. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116*, 16216−16221.
(58) Prospero, J. M.; Collard, F. X.; Molinie, J.; Jeannot, A. Characterizing the Annual Cycle of African Dust Transport to the Caribbean Basin and South America and Its Impact on the Environment and Air Quality. *Global Biogeochem. Cycles* **2014**, *28*, 757−773.
(59) Zamora, L. M.; Prospero, J. M.; Hansell, D. A.; Trapp, J. M. Atmospheric P Deposition to the Subtropical North Atlantic: Sources, Properties, and Relationship to N Deposition. *J. Geophys. Res.* **2013**, *118*, 1546−1562.

https://dx.doi.org/10.1021/acs.accounts.0c00102
Acc. Chem. Res. XXXX, XXX, XXX−XXX