1 **Comparison of the Mixing State of Long-Range Transported**

2 **Asian and African Mineral Dust**

3 Elizabeth Fitzgerald^a, Andrew P. Ault^{a,1}, Melanie Zauscher^b, Olga L. Mayol-Bracero^c,
4 and Kimberly A. Prather^{a,d*}

5
6 ^a Department of Chemistry and Biochemistry, University of California, San Diego, La
7 Jolla, CA 92093 USA

8 ^b Department of Mechanical and Aerospace Engineering, University of California, San
9 Diego, La Jolla, CA 92093 USA

10 ^c Institute for Tropical Ecosystem Studies, University of Puerto Rico, San Juan, PR
11 00931 USA

12 ^d Scripps Institution of Oceanography, University of California, San Diego, La Jolla,
13 CA 92093 USA

14 *kprather@ucsd.edu, 858-822-5312, fax 858-534-7042

15 ¹current address: Department of Chemistry, University of Michigan, Ann Arbor, MI,
16 48109 USA

17 18 **Abstract**

19 Mineral dust from arid regions represents the second largest global source of aerosols
20 to the atmosphere. Dust strongly impacts the radiative balance of the earth's atmosphere by
21 directly scattering solar radiation and acting as nuclei for the formation of liquid droplets and
22 ice nuclei within clouds. The climate effects of mineral dust aerosols are poorly understood,
23 however, due to their complex chemical and physical properties, which continuously evolve
24 during atmospheric transport. This work focuses on characterizing atmospheric mineral dust
25 from the two largest global dust sources: the Sahara Desert in Africa and the Gobi and
26 Taklamakan Deserts in Asia. Measurements of individual aerosol particle size and chemical
27 mixing state were made at El Yunque National Forest, Puerto Rico, downwind of the Sahara
28 Desert, and Gosan, South Korea, downwind of the Gobi and Taklamakan Deserts. In general,

the chemical characterization of the individual dust particles detected at these two sites reflected the dominant mineralogy of the source regions; aluminosilicate-rich dust was more common at El Yunque (~91% of El Yunque dust particles vs. ~69% of Gosan dust particles) and calcium-rich dust was more common at Gosan (~22% of Gosan dust particles vs. ~2% of El Yunque dust particles). Furthermore, dust particles from Africa and Asia were subjected to different transport conditions and atmospheric processing; African dust showed evidence of cloud processing, while Asian dust was modified via heterogeneous chemistry and direct condensation of secondary species. A larger fraction of dust detected at El Yunque contained the cloud-processing marker oxalate ion compared to dust detected at Gosan (~20% vs ~9%). Additionally, nearly 100% of dust detected at Gosan contained nitrate, showing it was aged via heterogeneous reactions with nitric acid, compared to only ~60% of African dust. Information on the distinct differences in the chemical composition of mineral dust particles, as well as the mechanisms and extent of atmospheric processing, is critical for assessing its impacts on the earth's radiative budget through scattering, absorption, and nucleating cloud droplets and ice crystals.

Keywords: mineral dust; Sahara Desert; Gobi Desert; atmospheric processing

1 Introduction

With annual global emissions of up to 3000 Tg yr⁻¹, mineral dust represents almost half of annual global aerosol emissions (Forster et al., 2007). Once in the atmosphere, mineral dust particles influence global climate directly by scattering and absorbing solar radiation (Myhre and Stordal, 2001). They also act as cloud condensation nuclei (CCN) (Koehler et al., 2009) and ice nuclei (IN) (DeMott et al., 2003), changing the reflectivity and lifetime of clouds (Albrecht, 1989; Twomey, 1977). Additionally, mineral dust particles are known to

52 readily react with trace atmospheric gases such as HNO_3 and SO_2 (Sullivan et al., 2007),
53 changing their scattering and absorption properties (Kandler et al., 2011), their CCN and IN
54 activity (Sullivan et al., 2009), and altering atmospheric trace gas composition (de Reus et al.,
55 2005). In spite of its importance to global climate, mineral dust aerosol is still poorly
56 represented in models, due mainly to a lack of knowledge of the physico-chemical properties
57 of mineral dust aerosol, and how these properties change during transport (Formenti et al.,
58 2011). Many climate models treat mineral dust aerosol as a single entity in terms of its
59 radiative properties (Sokolik and Toon, 1999) and hygroscopicity (Han et al., 2011), when in
60 reality it is a complex mixture, consisting of individual particles with many different, source-
61 dependent, mineralogies (Formenti et al., 2011).

62 The two largest sources of mineral dust to the atmosphere are Africa (Sahara Desert)
63 and Asia (Gobi and Taklamakan Deserts). These two regions account for up to 800 Tg yr^{-1}
64 and 460 Tg yr^{-1} of atmospheric mineral dust, respectively (Laurent et al., 2008; Laurent et al.,
65 2006). The mineralogy of dust emitted from these two regions differs, with African dust being
66 enriched in aluminosilicates, whereas dust from the Loess Plateau in Western China is rich in
67 carbonate minerals (calcite and dolomite) (Formenti et al., 2011). The reactivity of dust from
68 these regions is expected to be different based on these differences in mineralogy (Krueger et
69 al., 2004). Furthermore, differences in water uptake have been linked to mineralogy, which
70 ultimately affect the CCN and IN activity of these dust particles (Connolly et al., 2009;
71 Koehler et al., 2009).

72 In addition to differences in reactivity based on chemical composition, dust plumes
73 from Africa and Asia often exist in very different air masses as they are transported away from
74 their respective sources (Formenti et al., 2011). In the summer, African dust is lofted above
75 the marine boundary layer as it is transported over the Atlantic Ocean, depositing in the

76 Caribbean with little to no mixing with other air masses (Karyampudi et al., 1999). Asian dust
77 is transported over China and the ocean on its way to Japan and other off-shore islands (Bauer
78 et al., 2013; Carmichael et al., 1997). Asian continental outflow often contains pollution
79 particles as well as anthropogenic gases, like SO₂ and NO_x, which change the composition of
80 mineral dust particles via coagulation and heterogeneous reactions (Chen et al., 1997). As a
81 result, dust measured in Asian continental outflow is often mixed with organic carbon, soot,
82 anthropogenic sulfate, and sea salt (Chen et al., 1997). Understanding the mixing state of
83 African and Asian dust particles with secondary species such as chloride, nitrate, and sulfate,
84 is crucial to understanding the way that dust particles will impact climate, especially as
85 atmospheric dust loadings are expected to increase in a warming climate (Forster et al., 2007).

86 Single-particle mass spectrometric measurements of atmospheric mineral dust, using
87 an aerosol time-of-flight mass spectrometer (ATOFMS), provide unique insights into the
88 chemical composition and mineralogy (Sullivan et al., 2007), optical properties (Moffet and
89 Prather, 2005, 2009), and secondary reactions of dust during transport (Sullivan et al., 2007).
90 Additionally, transported African and Asian dust has been detected by ATOFMS in rainwater
91 over the Western United States, indicating the importance of dust to cloud formation and
92 precipitation processes on a global scale (Ault et al., 2011; Creamean et al., 2013). This study
93 represents the first comparison of the chemical mixing state of transported African and Asian
94 mineral dust using ATOFMS. Distinct differences in mineralogy and atmospheric processing
95 between the two dust source regions were observed, which will determine the direct and
96 indirect forcing of these mineral dust particles. The implications for climate are discussed.

97 **2 Materials and Methods**

98 **2.1 Sampling sites and instrumentation**

99 Ambient aerosol size and chemistry were measured in real-time at Gosan, Jeju Island,
100 S. Korea, and Pico del Este (PE), El Yunque National Forest, Puerto Rico. Aerosol size
101 distribution and mass (PM₁₀ and PM_{2.5}, respectively) were measured at both sampling sites.
102 Gosan sampling was conducted from April 12, 2007 – May 15, 2007 as part of the Pacific
103 Dust Experiment (PACDEX). The Supersite at Gosan is ideally located for sampling the
104 continental outflow of dust after 1-2 days of transport from the Asian mainland (Bauer et al.,
105 2013; Carmichael et al., 1997). Pico del Este sampling was conducted from July 23, 2010 –
106 August 11, 2010 as part of the Puerto Rican African Dust and Clouds Study (PRADACS).
107 Though transport times from the Sahara Desert to the Caribbean are relatively long (>1 week),
108 the lack of anthropogenic sources of air pollution between Africa and Puerto Rico makes the
109 site at Pico del Este ideally situated for sampling background marine aerosol and dust that has
110 undergone minimal chemical processing (Allan et al., 2008; Trapp et al., 2010).

111 **2.2 Aerosol Time-of-Flight Mass Spectrometry**

112 Real-time measurements of aerosol size and chemical composition were made at both
113 the PACDEX and PRADACS sites using an ATOFMS. ATOFMS determines the size and
114 chemical composition of individual aerosol particles from 0.2 – 3 μm (Gard et al., 1997).
115 Particles enter the ATOFMS through a converging-nozzle inlet, and are accelerated to their
116 size-dependent terminal velocities. Scattering signals from two continuous-wave lasers (532
117 nm), located a fixed distance apart, are used to calculate the aerodynamic diameter of the
118 particles based on their terminal velocity. The speed of the particles is also used to time the
119 firing of a Q-switched laser (Nd:YAG, 266 nm), which desorbs and ionizes species from

120 individual particles. The resulting ions are analyzed by a dual-polarity reflectron time-of-
121 flight mass spectrometer.

122 **2.3 Single Particle Data Analysis**

123 Particle size and mass spectral information were imported into MatLab 6.5.1 (The
124 Mathworks Inc.) and analyzed using YAADA 1.2 (www.yaada.org). During PACDEX, a
125 total of 2,984,937 particles were sized and chemically analyzed; during PRADACS, 89,568
126 particles were sized and chemically analyzed. Peak intensities from the mass spectra of
127 individual particles were clustered using an Adaptive Resonance Theory (ART-2a) based
128 neural network algorithm (Song et al., 1999). Particle types were identified using mass
129 spectral markers in the positive ion mass spectra, while negative ion mass spectra give
130 information about particle age (Noble and Prather, 1996). Dust particles were identified by
131 the presence of minerals and crustal markers, including $^{23}\text{Na}^+$, $^{27}\text{Al}^+$, $^{39}\text{K}^+$, $^{40}\text{Ca}^+$, $^{54/56}\text{Fe}^+$, $^{48}\text{Ti}^+$,
132 and $^{76}\text{SiO}^-$, and sorted into different dust types based on the most prominent peaks in the
133 positive ion mass spectra. Additionally, dust types were queried for the absolute areas of mass
134 spectral markers, which exceeded a certain threshold, to further explore the internal mixing of
135 dust particles. Peak identifications in this paper correspond to the most probable ion at a given
136 mass/charge (m/z).

137 **3 Results and Discussion**

138 **3.1 Chemical and physical properties of dust particles**

139 Particles from the PACDEX and PRADACS studies were first divided into 3 general
140 classes: combustion, sea spray, and dust. Combustion particles are typically composed of
141 elemental or organic carbon particles, and are the result of fossil fuel combustion (Toner et al.,

2008). Biomass burning particles were also included in the combustion class (Qin and Prather, 2006). Sea spray particles were identified by the presence of sodium and sodium-chloride clusters (Prather et al., 2013). As mentioned previously, dust particles were identified by the presence of crustal elements. The contribution of each of these three main particle types to overall particle chemistry is shown in Figure 1. The particles analyzed during PACDEX are nearly equally distributed amongst these three categories, indicating approximately equal contributions from each of the three particles sources. As combustion particles are typically markers for anthropogenic emissions, it can be concluded that there was a relatively strong anthropogenic influence on particle chemistry at Gosan. This has been confirmed by model comparisons with single particle data from the site (Bauer et al., 2013). In contrast, only ~4% of particles were classified as combustion during PRADACS, showing very little anthropogenic influence. The remaining ~96% of particles are from dust and sea spray, with dust being the dominant source over sea spray (~56% dust vs. ~40% sea spray).

Dust clusters of individual particle mass spectra were further categorized into 7 subtypes of dust based on the most prominent peaks in the positive ion mass spectra; these dust subtypes are aluminosilicates, K-aluminosilicates, Na-aluminosilicates, hematite, calcite, Dust-EC, and Ti-rich dust. The names of the aluminosilicate classes are meant to relate to general classes of minerals with similar chemical compositions, for example, the K-aluminosilicates type could include a number of K-containing mineral types such as illite or K-feldspar. Similarly, the Na-aluminosilicates class includes montmorillinite, Na-plagioclase, and other sodium-containing silicate minerals. Additionally, the calcite dust particles detected in both of these studies are actually reacted calcite particles, which contain chloride and nitrate. They are referred to as calcite because they are rich in calcium, and calcite is the most likely source mineral. Finally, most dust particles contained markers from more than one dust

166 type, indicating that individual dust particles are internal mixtures of several minerals and not
167 composed of only one type of mineral. Internal mixtures of minerals on individual dust
168 particles has been previously shown for offline samples using electron microscopy and
169 element mapping (Ault et al., 2012). More information on classification, as well as
170 representative mass spectra for the seven types of dust, can be found in the Supplemental
171 section.

172 The contributions from each type of dust to each study are shown in Figure 2. Figure
173 2a shows the chemical composition for all dust particles in each study; Figures 2b and 2c
174 show size-resolved chemical composition of atmospheric dust. For both PRADACS and
175 PACDEX, the most common type of dust was K-aluminosilicates, comprising approximately
176 half of all observed dust particles, but the chemical composition of the remaining 50% of dust
177 particles differ significantly between the two studies (Figure 2a); the Asian dust detected
178 during PACDEX is more chemically diverse than the African dust detected during
179 PRADACS, possibly reflecting the more diverse source regions and transport trajectories
180 identified during the PACDEX campaign (Bauer et al., 2013). These different dust source
181 regions and transport trajectories, as well as their resulting chemical differences, are discussed
182 in more detail in the Supplemental section. Almost 90% of African dust particles were
183 classified as either K- or Na-aluminosilicates. The remaining dust (~10%) from PRADACS is
184 mostly aluminosilicate-rich and hematite. Many field studies have shown that African dust is
185 comprised primarily of aluminum- and silicon-rich minerals, like quartz and illite, consistent
186 with our measurements of transported African dust (Dall'Osto et al., 2010; Thomas and
187 Gautier, 2009). Asian dust had a much lower contribution from the Na-aluminosilicates, and
188 significantly more calcite and aluminosilicate dust. Additionally, clear differences can be
189 seen, not only between the sub- and supermicron dust particles within each study, but also

190 between dust particles in the same size range between the two studies (Figures 2b and 2c). As
191 expected, African dust from PRADACS is enriched in aluminosilicate types in both the sub-
192 and supermicron size ranges, however submicron dust contains more hematite and dust-EC
193 than dust in the supermicron size range. Asian dust from PACDEX is also enriched in
194 hematite in the submicron size range; the supermicron dust contains more calcite and
195 aluminosilicate dust compared to both the submicron PACDEX dust and the supermicron
196 PRADACS dust. The differences in chemical composition between the two studies reflect the
197 differences in chemical composition of the source regions; Saharan dust is rich in
198 aluminosilicates and clays, and Asian dust is calcite-rich (Formenti et al., 2011; Hatch and
199 Grassian, 2008).

200 **3.2 Chemical processing of transported dust particles**

201 To further investigate the differences in the aging processes of Asian and African
202 dust, particles were queried for the presence and intensity of certain secondary markers.
203 These markers were chloride ($^{35}\text{Cl}^-$), nitrate ($^{46}\text{NO}_2^-$), sulfate ($^{97}\text{HSO}_4^-$), oxalate ($^{89}\text{HC}_2\text{O}_4^-$) and
204 nitric acid ($^{125}\text{H}(\text{NO}_3)_2^-$). Chloride, nitrate, and sulfate are typical secondary markers seen on
205 processed mineral dust aerosol (Sullivan et al., 2007); oxalate is a marker for cloud processing
206 (Yu et al., 2004), and the presence of nitric acid on particles indicates a high degree of
207 chemical processing (Pratt and Prather, 2009).

208 Figure 3 shows the total fraction of dust particles which were enriched in each of these
209 five species, as well as the types of dust that make up these fractions. As shown in Figure 3, it
210 is evident that the transported Asian dust detected during PACDEX had undergone more
211 atmospheric processing than the transported African dust detected during PRADACS; larger
212 fractions of Asian dust were mixed with sulfate and nitric acid, and nearly all Asian dust

213 contained significant amounts of nitrate, which indicates that Asian dust became highly aged
214 after several days of transport. In contrast, a larger fraction of African dust particles were
215 mixed with chloride and oxalate, which implies that African dust was cloud-processed.
216 Oxalate is a marker for cloud processing, and chloride on dust particles was likely from in-
217 cloud mixing of dust and sea spray (Ma et al., 2004).

218 These trends in dust particle reactivity can be explained by looking at the general
219 transport trajectories for Asian and African dust, which are discussed in more detail in the
220 Supplemental section. Dust from the Gobi and Taklamakan Deserts is transported over the
221 Asian continent where it is often mixed with pollution plumes containing high levels of SO₂
222 NO_x, and NO_y, which increase the amount of sulfate, nitrate, and nitric acid on the particles
223 via heterogeneous reactions (Ooki and Uematsu, 2005; Sullivan et al., 2007). However, dust
224 from the Sahara desert is transported over the Atlantic Ocean, and typically has little to no
225 exposure to pollution plumes before being measured at PE (Allan et al., 2008). The sampling
226 site at PE is located in a tropical montane cloud forest, and thus air masses are often subject to
227 in-cloud processing, resulting in increased levels of oxalate and chloride on African dust, as
228 previously mentioned. It can therefore be concluded that the main mechanism of aging for
229 dust particles emitted from the Gobi and Taklamakan Deserts was heterogeneous reactions
230 with anthropogenic gas phase pollutants as the air masses were transported over the Asian
231 Continent. For dust emitted from the Sahara Desert and lofted over the Atlantic Ocean, the
232 main aging mechanism was in-cloud processing at the sampling site.

233 **3.2.1 Atmospheric Aging and Mineralogy**

234 Despite varying transport conditions experienced by Asian and African dust particles,
235 the chemistry of the mineral dust particles plays a large role in determining how they will

236 react in the atmosphere. Laboratory studies and field measurements have shown that sulfate
237 formation is more efficient on aluminosilicate-rich dust particles, and that nitrate formation is
238 favored on calcium-rich particles (Shi et al., 2008; Sullivan et al., 2007), findings which are
239 supported by our ambient measurements. Figure 4 shows the enrichment of nitrate and sulfate
240 by dust type. This figure illustrates which dust types contained sulfate or nitrate relative to the
241 number of particles of each type, in contrast to Figure 3, which shows secondary species
242 enrichment over all dust particles. Figure 3 shows that, in general, higher fractions of Asian
243 dust contain sulfate and nitrate, consistent with the fact that it has the opportunity to become
244 more processed by mixing with pollution plumes. However, regardless of differences in
245 transport conditions and aging processes, the types of dust particles that are most enriched in
246 sulfate and nitrate are consistent between the two studies. Aluminosilicate dust and dust-EC
247 particles are the most enriched in sulfate in both studies. Internal mixtures of dust and EC
248 particles are the result of cloud processing, which is also a source of particulate sulfate. This
249 indicates that cloud processing is an effective mechanism by which dust particles may acquire
250 sulfate, regardless of the presence or absence of anthropogenic SO₂ in the initial air mass.
251 Comparison studies between source African dust particles detected and African dust particles
252 transported across the continent and to Europe, show an accumulation of sulfate on the
253 transported African dust particles (Dall'Osto et al., 2010). Furthermore, the internal mixture of
254 EC and dust will change the optical properties of the aerosol, potentially making it even more
255 absorbing. Additionally, sulfate is known to form preferentially on aluminosilicate dust
256 (Formenti et al., 2011); our results show this trend to hold true for both aging mechanisms
257 encountered during the two studies.

258 Additionally, several types of dust showed an enrichment in nitrate in both studies;
259 these types were calcite, hematite, and titanium. This study is the first using ATOFMS to

260 show that calcite particles from Africa are nearly as processed as those from Asia after long-
261 range transport. Despite the higher levels of pollutant gases in Asian outflow compared to
262 over the Atlantic Ocean, significant fractions of calcite particles contained nitrate in both
263 studies (~65% for PRADACS vs ~80% for PACDEX). As calcium nitrate is a much better
264 CCN than fresh calcite (Laskin et al., 2005), this finding has significant implications for the
265 ability of these dust particles to act as CCN on a global scale. In both studies, hematite was
266 also enriched in nitrate, which has important implications for the transport of soluble iron
267 species to remote oceans (Jickells et al., 2005). Hematite dust often contained titanium, and
268 the uptake and oxidation of nitrogen oxides on irradiated TiO_2 has been suggested as a source
269 of renoxification during the daytime (de Reus et al., 2005). Our results show that, regardless
270 of source region or transport conditions, calcite, hematite, and titanium-containing dust reacts
271 readily with nitrogen oxides to form nitrate-containing particles, which could contribute to
272 global CCN concentrations, soluble iron species, and renoxification, especially in remote and
273 clean regions.

274 Though certain minerals (calcite, aluminosilicates, etc.) were seen to react similarly in
275 the atmosphere despite differences in transport conditions, the extent to which these reactions
276 take place is dependent on the composition of the air mass and the availability of trace gas
277 species for reaction. Figure 5 shows the average hourly ATOFMS peak area for nitrate (m/z -
278 46) on all particles plotted against the fraction of particles that were classified as dust for the
279 same hour. For PACDEX, there is a weak correlation between dust fraction and nitrate peak
280 area ($r^2 = 0.367$); as the fraction of dust in the plume increases, so does the amount of nitrate
281 on particles as a whole. This seems to indicate that Asian dust continues to take up nitrate as
282 it is transported away from the source to the sampling location; because of the high
283 availability of NO_x and NO_y in Asian outflow, particles transported in the outflow contain

284 more nitrate than particles transported in low-NO_x/NO_y conditions (like those observed during
285 the PRADACS study). Particles detected during the PRADACS study show no correlation
286 between the fraction of dust particles and the amount of nitrate on the particles ($r^2 = 0.0227$).
287 Not only was there a lower amount of NO_x/NO_y available for reaction, but the majority of dust
288 particles measured during PRADACS were not comprised of minerals which react readily
289 with nitrogen oxides. Most PRADACS dust was K and Na aluminosilicates which tend to
290 form sulfates, whereas PACDEX dust contained larger fractions of Ti-rich dust, hematite, and
291 calcite, known to react with nitrogen oxides to form nitrate.

292 Our findings indicate that even though dust particle chemistry influences how mineral
293 particles will react in the atmosphere (calcite tends to take up nitrate, aluminosilicates will
294 take up sulfate), transport conditions also play a role in determine the reactivity of dust
295 particles in the atmosphere. Figure 5 shows that dust in high-NO_x/NO_y conditions (like Asian
296 continental outflow), will continue to take up nitrate, resulting in more aged particles.
297 Because of their highly aged nature, we would expect these mineral dust particle to be good
298 CCN. Additionally, the uptake of nitric acid on dust particles does not destroy particles'
299 ability to act as IN, and in some cases can even enhance this ability (Sullivan et al., 2010a).

300 **4 Conclusions**

301 As mineral dust represents a large fraction of the global aerosol burden, an accurate
302 representation of dust in climate models is crucial for determining its impact on climate.
303 However, in models, dust is often treated as chemically homogeneous, with a single refractive
304 index, hygroscopicity, and reactivity (Han et al., 2011; Shi et al., 2008). This work shows that
305 the chemical mixing state of dust particles is important in determining the behavior of dust in
306 the atmosphere in terms of its reactivity and effect on atmospheric composition. Dust from

307 different source regions is chemically distinct, and both the initial chemistry and transport
308 conditions affect dust reactivity. Dust particles from the Gobi Desert detected at Gosan, South
309 Korea, during PACDEX, were subjected to different atmospheric processing conditions than
310 Saharan dust detected in Puerto Rico, during PRADACS; Asian dust was mixed with pollution
311 and underwent atmospheric aging by heterogeneous chemistry, while dust from Africa was
312 cloud processed. These processing mechanisms result in dust particles from Asia which are
313 richer in nitrate, and dust particles from Africa which are richer in sulfate and oxalate.

314 Despite differences in transport, certain types of dust were observed to react similarly
315 in both studies. During both PACDEX and PRADACS, aluminosilicate dust was enriched in
316 sulfate, in agreement with results from previous field and laboratory studies (Shi et al., 2008;
317 Sullivan et al., 2007). The fraction of PRADACS aluminosilicate particles that were enriched
318 in sulfate was nearly identical to the fraction from PACDEX, despite the fact that much of the
319 dust detected at Gosan was transported over the Asian continent and became mixed with
320 pollution. This finding has implications for the IN activity of these dust particles, as fresh
321 aluminosilicate dust makes an effective IN (DeMott et al., 2003), however, sulfate uptake has
322 been shown to inhibit IN ability for some minerals (Cziczo et al., 2009; Sullivan et al., 2010b).
323 The detection of unprocessed aluminosilicate dust in Puerto Rico indicates that these dust
324 particles may still be a significant source of atmospheric IN despite undergoing long-range
325 transport. Similarly, certain types of dust reacted with nitrogen oxides. Calcite, hematite, and
326 Ti-rich dust detected at Puerto Rico and Jeju Island were enriched in nitrate showing that, in
327 spite of different transport conditions, dust particles with similar chemical compositions will
328 react similarly.

329 However, it was also determined that transport conditions influence dust particle
330 reactivity. A correlation between particle nitrate and the fraction of particles classified as dust

331 was observed for PACDEX, but not for PRADACS. This indicates that, in high nitrogen
332 oxide conditions (like pollution plumes), dust particles will take up large amounts of nitrate
333 and become highly aged. Though calcite particles observed during PRADACS did take up
334 nitrate, the amount of nitrate per particle was smaller and the particles were less aged. Due to
335 this reactivity, dust particles that travel over Asia would be expected to be much better CCN
336 than those that travel over the Atlantic Ocean.

337 These findings show that it is not possible to represent mineral dust aerosol in climate
338 models using one hygroscopicity value; the hygroscopicity of dust depends on particle
339 mineralogy and on the transport conditions of the dust air mass. The highly aged dust
340 particles detected during PACDEX would be expected to be better CCN than the fresher dust
341 particles detected during PRADACS. However, because the uptake of secondary species
342 (sulfate in particular) is thought to impair particle IN ability, African dust would be a larger
343 source of IN. The ability of dust particles to nucleate clouds is an important parameter that
344 affects the direct and indirect climate effects of dust aerosol, and these properties depend
345 strongly on particle chemistry as well as atmospheric aging, two parameters which are not
346 currently well represented in models.

347 **Acknowledgments**

348 For PACDEX, the authors would like to acknowledge the financial support of the
349 Atmospheric Brown Cloud project funded by the United Nations Environmental Programme
350 and the National Oceanic and Atmospheric Administration (NOAA). Andrew Ault is grateful
351 for a Department of Energy Global Change Education Program (GCEP) Graduate Research
352 Environmental Fellowship (GREF). We thank S.C. Yoon at Seoul National University and his
353 group for their hospitality and assistance during the PACDEX campaign, as well as V.

354 Ramanathan and Aihua Zhu from The Scripps Institution of Oceanography for their assistance
 355 during the campaign. Funding for the PRADACS project was provided by NSF AGS grant
 356 #0936879. Elizabeth Fitzgerald would like to acknowledge the San Diego Fellowship
 357 Foundation for financial support. Melanie Zauscher was funded by U.S. Environmental
 358 Protection Agency PM Center Grant (R832415). The authors would also like to thank Prof.
 359 Olga L. Mayol-Bracero and her research group, especially Carlos J. Valle Díaz and Félix
 360 Zurcher, for all their help, support, and hospitality during the PRADACS campaign.

361

362

363 **References**

- 364 Albrecht, B.A., 1989. Aerosols, cloud microphysics, and fractional cloudiness. *Science* 245,
 365 1227-1230.
- 366 Allan, J.D., Baumgardner, D., Raga, G.B., Mayol-Bracero, O.L., Morales-García, F., García-
 367 García, F., Montero-Martínez, G., Borrmann, S., Schneider, J., Mertes, S., Walter, S., Gysel,
 368 M., Dusek, U., Frank, G.P., Krämer, M., 2008. Clouds and aerosols in Puerto Rico - a new
 369 evaluation. *Atmos. Chem. Phys.* 8, 1293-1309.
- 370 Ault, A.P., Peters, T.M., Sawvel, E.J., Casuccio, G.S., Willis, R.D., Norris, G.A., Grassian,
 371 V.H., 2012. Single-particle SEM-EDX analysis of iron-containing coarse particulate matter in
 372 an urban environment: sources and distribution of iron within Cleveland, Ohio. *Environmental*
 373 *Science & Technology* 46, 4331-4339.
- 374 Ault, A.P., Williams, C.R., White, A.B., Neiman, P.J., Creamean, J.M., Gaston, C.J., Ralph,
 375 F.M., Prather, K.A., 2011. Detection of Asian dust in California orographic precipitation. *J.*
 376 *Geophys. Res.* 116, D16205.
- 377 Bauer, S.E., Ault, A., Prather, K.A., 2013. Evaluation of aerosol mixing state classes in the
 378 GISS modelE-MATRIX climate model using single-particle mass spectrometry
 379 measurements. *Journal of Geophysical Research: Atmospheres* 118, 9834-9844.
- 380 Carmichael, G.R., Hong, M.-S., Ueda, H., Chen, L.-L., Murano, K., Park, J.K., Lee, H., Kim,
 381 Y., Kang, C., Shim, S., 1997. Aerosol composition at Cheju Island, Korea. *J. Geophys. Res.*
 382 102, 6047-6061.
- 383 Chen, L.-L., Carmichael, G.R., Hong, M.-S., Ueda, H., Shim, S., Song, C.H., Kim, Y.P.,
 384 Arimoto, R., Prospero, J., Savoie, D., Murano, K., Park, J.K., Lee, H.-g., Kang, C., 1997.
 385 Influence of continental outflow events on the aerosol composition at Cheju Island, South
 386 Korea. *J. Geophys. Res.* 102, 28551-28574.

387 Connolly, P.J., Möhler, O., Field, P.R., Saathoff, H., Burgess, R., Choularton, T., Gallagher,
 388 M., 2009. Studies of heterogeneous freezing by three different desert dust samples. *Atmos.*
 389 *Chem. Phys.* 9, 2805-2824.
 390 Creamean, J.M., Suski, K.J., Rosenfeld, D., Cazorla, A., DeMott, P.J., Sullivan, R.C., White,
 391 A.B., Ralph, F.M., Minnis, P., Comstock, J.M., Tomlinson, J.M., Prather, K.A., 2013. Dust
 392 and Biological Aerosols from the Sahara and Asia Influence Precipitation in the Western U.S.
 393 *Science* 339, 1572-1578.
 394 Cziczo, D.J., Froyd, K.D., Gallavardin, S.J., Moehler, O., Benz, S., Saathoff, H., Murphy,
 395 D.M., 2009. Deactivation of ice nuclei due to atmospherically relevant surface coatings.
 396 *Environ. Res. Lett.* 4.
 397 Dall'Osto, M., Harrison, R.M., Highwood, E.J., O'Dowd, C., Ceburnis, D., Querol, X.,
 398 Achterberg, E.P., 2010. Variation of the mixing state of Saharan dust particles with
 399 atmospheric transport. *Atmospheric Environment* 44, 3135-3146.
 400 de Reus, M., Fischer, H., Sander, R., Gros, V., Kormann, R., Salisbury, G., Van Dingenen, R.,
 401 Williams, J., Zöllner, M., Lelieveld, J., 2005. Observations and model calculations of trace gas
 402 scavenging in a dense Saharan dust plume during MINATROC. *Atmos. Chem. Phys.* 5, 1787-
 403 1803.
 404 DeMott, P.J., Sassen, K., Poellot, M.R., Baumgardner, D., Rogers, D.C., Brooks, S.D., Prenni,
 405 A.J., Kreidenweis, S.M., 2003. African dust aerosols as atmospheric ice nuclei. *Geophys. Res.*
 406 *Lett.* 30, 1732.
 407 Formenti, P., Schütz, L., Balkanski, Y., Desboeufs, K., Ebert, M., Kandler, K., Petzold, A.,
 408 Scheuven, D., Weinbruch, S., Zhang, D., 2011. Recent progress in understanding physical
 409 and chemical properties of African and Asian mineral dust. *Atmos. Chem. Phys.* 11, 8231-
 410 8256.
 411 Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D.W., Haywood, J.,
 412 Lean, J., Lowe, D.C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M., Dorlan, R.V.,
 413 2007. Changes in atmospheric constituents and in radiative forcing, in: Solomon, S., Qin, D.,
 414 Manning, M., Chen, Z., Marquis, M., Averyt, K.B., Tignor, M., Miller, H.L. (Eds.), *Climate*
 415 *Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth*
 416 *Assessment Report of the Intergovernmental Panel on Climate Change.* Cambridge University
 417 Press, Cambridge, United Kingdom and New York, NY, USA, pp. 129-234.
 418 Gard, E., Mayer, J.E., Morrical, B.D., Dienes, T., Fergenson, D.P., Prather, K.A., 1997. Real-
 419 time analysis of individual atmospheric aerosol particles: Design and performance of a
 420 portable ATOFMS. *Analytical Chemistry* 69, 4083-4091.
 421 Han, X., Zhang, M., Han, Z., Xin, J., Liu, X., 2011. Simulation of aerosol direct radiative
 422 forcing with RAMS-CMAQ in East Asia. *Atmospheric Environment* 45, 6576-6592.
 423 Hatch, C.D., Grassian, V.H., 2008. 10th Anniversary Review: Applications of analytical
 424 techniques in laboratory studies of the chemical and climatic impacts of mineral dust aerosol
 425 in the Earth's atmosphere. *Journal of Environmental Monitoring* 10, 919-934.
 426 Jickells, T.D., An, Z.S., Andersen, K.K., Baker, A.R., Bergametti, G., Brooks, N., Cao, J.J.,
 427 Boyd, P.W., Duce, R.A., Hunter, K.A., Kawahata, H., Kubilay, N., laRoche, J., Liss, P.S.,
 428 Mahowald, N., Prospero, J.M., Ridgwell, A.J., Tegen, I., Torres, R., 2005. Global Iron
 429 Connections Between Desert Dust, Ocean Biogeochemistry, and Climate. *Science* 308, 67-71.
 430 Kandler, K., Lieke, K., Benker, N., Emmel, C., KÜpper, M., MÜller-Ebert, D., Ebert, M.,
 431 Scheuven, D., Schladitz, A., SchÜtz, L., Weinbruch, S., 2011. Electron microscopy of
 432 particles collected at Praia, Cape Verde, during the Saharan Mineral Dust Experiment: particle
 433 chemistry, shape, mixing state and complex refractive index. *Tellus B* 63, 475-496.

434 Karyampudi, V.M., Palm, S.P., Reagen, J.A., Fang, H., Grant, W.B., Hoff, R.M., Moulin, C.,
 435 Pierce, H.F., Torres, O., Browell, E.V., Melfi, S.H., 1999. Validation of the Saharan Dust
 436 Plume Conceptual Model Using Lidar, Meteosat, and ECMWF Data. *Bulletin of the American*
 437 *Meteorological Society* 80, 1045-1075.
 438 Koehler, K.A., Kreidenweis, S.M., DeMott, P.J., Petters, M.D., Prenni, A.J., Carrico, C.M.,
 439 2009. Hygroscopicity and cloud droplet activation of mineral dust aerosol. *Geophys. Res.*
 440 *Lett.* 36, L08805.
 441 Krueger, B.J., Grassian, V.H., Cowin, J.P., Laskin, A., 2004. Heterogeneous chemistry of
 442 individual mineral dust particles from different dust source regions: the importance of particle
 443 mineralogy. *Atmospheric Environment* 38, 6253-6261.
 444 Laskin, A., Iedema, M.J., Ichkovich, A., Graber, E.R., Taraniuk, I., Rudich, Y., 2005. Direct
 445 observation of completely processed calcium carbonate dust particles. *Faraday Discussions*
 446 130, 453-468.
 447 Laurent, B., Marticorena, B., Bergametti, G., Léon, J.F., Mahowald, N.M., 2008. Modeling
 448 mineral dust emissions from the Sahara desert using new surface properties and soil database.
 449 *J. Geophys. Res.* 113, D14218.
 450 Laurent, B., Marticorena, B., Bergametti, G., Mei, F., 2006. Modeling mineral dust emissions
 451 from Chinese and Mongolian deserts. *Global and Planetary Change* 52, 121-141.
 452 Ma, C.-J., Tohno, S., Kasahara, M., Hayakawa, S., 2004. Properties of the size-resolved and
 453 individual cloud droplets collected in western Japan during the Asian dust storm event.
 454 *Atmospheric Environment* 38, 4519-4529.
 455 Moffet, R.C., Prather, K.A., 2005. Extending ATOFMS measurements to include refractive
 456 index and density. *Analytical Chemistry* 77, 6535-6541.
 457 Moffet, R.C., Prather, K.A., 2009. In-situ measurements of the mixing state and optical
 458 properties of soot with implications for radiative forcing estimates. *Proceedings of the*
 459 *National Academy of Sciences* 106, 11872-11877.
 460 Myhre, G., Stordal, F., 2001. Global sensitivity experiments of the radiative forcing due to
 461 mineral aerosols. *J. Geophys. Res.* 106, 18193-18204.
 462 Noble, C.A., Prather, K.A., 1996. Real-time measurement of correlated size and composition
 463 profiles of individual atmospheric aerosol particles. *Environmental Science & Technology*
 464 30, 2667-2680.
 465 Ooki, A., Uematsu, M., 2005. Chemical interactions between mineral dust particles and acid
 466 gases during Asian dust events. *J. Geophys. Res.* 110, D03201.
 467 Prather, K.A., Bertram, T.H., Grassian, V.H., Deane, G.B., Stokes, M.D., DeMott, P.J.,
 468 Aluwihare, L.I., Palenik, B.P., Azam, F., Seinfeld, J.H., Moffet, R.C., Molina, M.J., Cappa,
 469 C.D., Geiger, F.M., Roberts, G.C., Russell, L.M., Ault, A.P., Baltrusaitis, J., Collins, D.B.,
 470 Corrigan, C.E., Cuadra-Rodriguez, L.A., Ebben, C.J., Forestieri, S.D., Guasco, T.L., Hersey,
 471 S.P., Kim, M.J., Lambert, W.F., Modini, R.L., Mui, W., Pedler, B.E., Ruppel, M.J., Ryder,
 472 O.S., Schoepp, N.G., Sullivan, R.C., Zhao, D., 2013. Bringing the ocean into the laboratory to
 473 probe the chemical complexity of sea spray aerosol. *Proceedings of the National Academy of*
 474 *Sciences* 110, 7550-7555.
 475 Pratt, K.A., Prather, K.A., 2009. Real-Time, Single-Particle Volatility, Size, and Chemical
 476 Composition Measurements of Aged Urban Aerosols. *Environmental Science & Technology*
 477 43, 8276-8282.
 478 Qin, X.Y., Prather, K.A., 2006. Impact of biomass emissions on particle chemistry during the
 479 California Regional Particulate Air Quality Study. *Int. J. Mass Spectrom.* 258, 142-150.

480 Shi, Z., Zhang, D., Hayashi, M., Ogata, H., Ji, H., Fujie, W., 2008. Influences of sulfate and
 481 nitrate on the hygroscopic behaviour of coarse dust particles. *Atmospheric Environment* 42,
 482 822-827.
 483 Sokolik, I.N., Toon, O.B., 1999. Incorporation of mineralogical composition into models of
 484 the radiative properties of mineral aerosol from UV to IR wavelengths. *J. Geophys. Res.* 104,
 485 9423-9444.
 486 Song, X.-H., Hopke, P.K., Fergenson, D.P., Prather, K.A., 1999. Classification of Single
 487 Particles Analyzed by ATOFMS Using an Artificial Neural Network, ART-2A. *Analytical*
 488 *Chemistry* 71, 860-865.
 489 Sullivan, R.C., Guazzotti, S.A., Sodeman, D.A., Prather, K.A., 2007. Direct observations of
 490 the atmospheric processing of Asian mineral dust. *Atmos. Chem. Phys.* 7, 1213-1236.
 491 Sullivan, R.C., Miñambres, L., DeMott, P.J., Prenni, A.J., Carrico, C.M., Levin, E.J.T.,
 492 Kreidenweis, S.M., 2010a. Chemical processing does not always impair heterogeneous ice
 493 nucleation of mineral dust particles. *Geophys. Res. Lett.* 37, L24805.
 494 Sullivan, R.C., Moore, M.J.K., Petters, M.D., Kreidenweis, S.M., Roberts, G.C., Prather,
 495 K.A., 2009. Effect of chemical mixing state on the hygroscopicity and cloud nucleation
 496 properties of calcium mineral dust particles. *Atmos. Chem. Phys.* 9, 3303-3316.
 497 Sullivan, R.C., Petters, M.D., DeMott, P.J., Kreidenweis, S.M., Wex, H., Niedermeier, D.,
 498 Hartmann, S., Clauss, T., Stratmann, F., Reitz, P., Schneider, J., Sierau, B., 2010b. Irreversible
 499 loss of ice nucleation active sites in mineral dust particles caused by sulphuric acid
 500 condensation. *Atmos. Chem. Phys.* 10, 11471-11487.
 501 Thomas, M., Gautier, C., 2009. Investigations of the March 2006 African dust storm using
 502 ground-based column-integrated high spectral resolution infrared (8–13 μm) and visible
 503 aerosol optical thickness measurements: 2. Mineral aerosol mixture analyses. *Journal of*
 504 *Geophysical Research: Atmospheres* 114, n/a-n/a.
 505 Toner, S.M., Shields, L.G., Sodeman, D.A., Prather, K.A., 2008. Using mass spectral source
 506 signatures to apportion exhaust particles from gasoline and diesel powered vehicles in a
 507 freeway study using UF-ATOFMS. *Atmospheric Environment* 42, 568-581.
 508 Trapp, J.M., Millero, F.J., Prospero, J.M., 2010. Temporal variability of the elemental
 509 composition of African dust measured in trade wind aerosols at Barbados and Miami. *Marine*
 510 *Chemistry* 120, 71-82.
 511 Twomey, S., 1977. The Influence of Pollution on the Shortwave Albedo of Clouds. *Journal of*
 512 *the Atmospheric Sciences* 34, 1149-1152.
 513 Yu, J.Z., Huang, X.-F., Xu, J., Hu, M., 2004. When aerosol sulfate goes up, so does oxalate:
 514 Implication for the formation mechanisms of oxalate. *Environmental Science & Technology*
 515 39, 128-133.

516

517

518

Figures

Figure 1. Pie charts showing relative composition of ATOFMS particles detected during the PACDEX and PRADACS campaigns. Particles were divided into three general classes: dust, combustion, and sea spray.

528

529 **Figure 2.** Fractional composition of dust particles detected during PRADACS and PACDEX.
 530 Panel (a) depicts overall dust composition. Panels (b) and (c) show the size-resolved
 531 composition of dust particles; panel (b) shows the composition of submicron dust particles,
 532 and panel (c) shows the composition of supermicron dust particles.

533

534

535

536

537

538

539 **Figure 3.** Fraction of ATOFMS dust particles enriched in secondary species by types of dust.
 540 Panel (a) shows dust particles from the PRADACS study, and panel (b) shows dust particles
 541 from the PACDEX study.

542

543

544

545

546 **Figure 4.** Fraction of each dust type that is enriched in nitrate and sulfate for PACDEX (solid
 547 bars) and PRACDACS (hatched bars). For both studies, a large fraction of aluminosilicate
 548 dust and dust-EC contain sulfate, and large fractions of calcite, hematite, and Ti-rich dust
 549 contain nitrate.

550

551

552 **Figure 5.** Average hourly ATOFMS nitrate peak area for all particles versus fraction of
 553 ATOFMS particles classified as dust. Results from PACDEX (dots) show a strong
 554 dependence of nitrate peak area on dust fraction; PRADACS data (triangles) show no such
 555 correlation.

556