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OPEN OCEAN AND COASTAL NEW PARTICLE FORMATION FROM SULPHURIC ACID AND AMINES AROUND THE ANTARCTIC PENINSULA

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28 **ABSTRACT**

29

30 New particle formation is globally one of the major sources of aerosol particles and cloud
31 condensation nuclei. Since primary emissions contribute weakly to particle concentrations,
32 secondary new particle formation processes are likely key in determining Antarctic aerosol number
33 concentrations. However, our knowledge of new particle formation and its mechanisms in the
34 Antarctica is very limited. Here, we study summertime open ocean and coastal new particle
35 formation in the Antarctic Peninsula region based on both ship and station measurements. The rates
36 of particle formation relative to sulphuric acid concentration as well as the sulphuric acid
37 dimer:monomer ratios were similar to those seen for sulphuric acid-dimethylamine-water
38 nucleation. Numerous sulphuric acid-amine peaks were identified during new particle formation
39 events, evidencing that alkylamines were the bases that facilitated sulphuric acid nucleation. Most
40 new particle formation events occurred in air masses arriving from the ice-covered Weddell Sea and
41 its marginal ice zone, which are a significant source of volatile sulphur and alkylamines. This
42 nucleation mechanism is more efficient than the ion-induced sulphuric acid-ammonia pathway
43 previously observed in Antarctica, and one that can occur rapidly under neutral conditions. This
44 hitherto overlooked pathway to biologically-driven aerosol formation should be considered for
45 estimating aerosol and cloud condensation nuclei numbers in ocean – sea ice – aerosols – climate
46 feedback models.

47

48 **Keywords:** New particle formation; Antarctic; nucleation; sulphuric acid; alkylamines

49 **MAIN**

50

51 The Antarctic Peninsula has shown some of the largest increases in near-surface air temperature
52 measured globally across the last 50 years¹, despite a pause to this increase within the last two
53 decades². Climate models struggle to accurately predict the temperature of the Antarctic Peninsula³,
54 and this is due in part to uncertainties in both meteorology⁴ and the gas and aerosol processes
55 governing radiative forcing. One of the largest areas of uncertainty in the latter is the direct and
56 indirect radiative forcing due to aerosols and clouds⁵. Model studies suggest that natural aerosols
57 contribute disproportionately to uncertainty in indirect forcing⁶. Unlike the Arctic, where
58 anthropogenic contributions to aerosol loadings are considerable, the Antarctic is remote from
59 major emission sources, and particles of natural origin dominate the aerosol population⁷. In such a
60 pristine environment, new particle formation (NPF) makes a major contribution both to the
61 condensation nuclei (CN) count, and more critically to the number of cloud condensation nuclei
62 (CCN), hence influencing both the direct and the indirect radiative forcing. NPF processes in
63 Antarctica have been associated with marine air masses⁸ and high fluxes of the trace gas
64 dimethylsulphide (DMS). Indeed, early studies of Antarctic submicron particles found their
65 composition dominated by sulphate (SO₄²⁻), largely accompanied by ammonium⁹. Later studies
66 have found a contribution of low molecular weight alkylamines to aerosol mass, arising from air
67 masses passing over areas of melting sea ice¹⁰. Measurements of amines in seawater further suggest
68 high alkylamine content in or near sea ice, and on-line analysis of Antarctic aerosols show that a
69 significant fraction of aerosol phase alkylamines are secondary in origin, rather than primary¹¹.
70 Recent evidence points towards NPF events originating from sympagic biogenic precursors at the
71 sea ice marginal zone, and Antarctic plateau¹², while long term particle size distribution
72 measurements in the Antarctic Peninsula has linked NPF frequency and faster growth rates of
73 nascent aerosols to upwind emissions of DMS by pelagic phytoplankton⁸. DMS is a biogenic
74 volatile organosulphur compound that in the atmosphere oxidises to both H₂SO₄ and
75 methanesulphonic acid (CH₃SO₃H, MSA). The most efficient pathways for these begin with a H-

76 abstraction, or an addition respectively¹³. H₂SO₄ is thought to be responsible for most nucleation
77 observed in the atmosphere¹⁴. MSA can also form new particles in the presence of bases¹⁵ and has
78 been shown to accelerate nucleation of H₂SO₄ and dimethylamine (DMA) with which it forms
79 stable clusters in the H₂SO₄-MSA-DMA system¹⁶.

80
81 Recent advances in instrumentation have provided new insight into the fundamental steps of NPF in
82 remote boreal forest¹⁷, coastal¹⁸, pristine polar^{18,19}, and urban environments²⁰. This is backed up by
83 a host of chamber experiments that have revealed the role of ammonia²¹ and amines^{22,23} in
84 accelerating H₂SO₄-H₂O nucleation, and the influence of galactic cosmic rays (GCR), temperature,
85 and humidity²¹⁻²⁴. While there have been a number of studies of NPF in Antarctica^{7,25,26}, only one
86 study¹⁹ has investigated the particle nucleation process at a fundamental level. They reported ion-
87 induced H₂SO₄-NH₃-H₂O nucleation, similar to that observed in laboratory experiments where GCR
88 were seen to significantly enhance the nucleation rates²¹, but dissimilar to H₂SO₄-DMA-H₂O
89 nucleation where GCR were less influential²². Here we present evidence for a parallel process in
90 particle nucleation involving H₂SO₄ and small alkylamines that can proceed rapidly under charged
91 or neutral conditions. The study involved air sampling both on coastal land and over the open
92 ocean.

93 **RESULTS**

94 95 *Characteristics of new particle formation events*

96 NPF events, defined using the criteria of Dal Maso et al. (2005)²⁷, were observed at the research
97 station on Livingston Island on 4 of 29 measurement days (13.8 %, conditions for each event in
98 Extended Data Table 1). Events began concurrently with the rise in H₂SO₄ concentrations, growing
99 to 10 - 20 nm (Figure 1a, 1b). C₂ and C₄ amines were measured in the gas phase clustered with the
100 nitrate dimer and trimer (Extended Data Figure 1). They showed high signals relative to
101 methylamine and ammonia, although this difference may be enhanced by sensitivities which have
102 not yet been quantified for individual bases. No blanks were determined *in situ*, and thus the

103 contribution of background to these signals is not established. We therefore did not derive
104 concentrations from these amine signals, simply reporting ion count rates. However, the instrument
105 was run in pristine Southern Ocean and Antarctic air for several weeks, and we found no evidence
106 of amine contamination from the instrument, tubing, or sheath air. While not correcting background
107 signals could introduce uncertainty to the reported signals, it should not affect our conclusions.
108 Trimethylamine was not measured in the gas phase but could be present in measured sulphuric acid-
109 amine clusters. Clustering between $(\text{HNO}_3)_{1-2}\text{NO}_3^-$ and NH_3 is significantly weaker than that with
110 DMA and hence the sensitivity to NH_3 was likely lower, and the mixing ratio of NH_3 was much
111 higher than that of amines. However, alkylamines have been shown to enhance formation rates at
112 modest mixing ratios^{22,23} in the range of a few pptv, which are sufficient to substitute NH_3 in
113 $\text{H}_2\text{SO}_4\text{-NH}_3$ clusters²⁸. Minima of amine signals at midday were driven by either clustering with
114 elevated sulphuric acid, which clusters at roughly a 1:1 ratio if mixing ratios are sufficient²⁹, uptake
115 onto particle surfaces, or photolysis³⁰. These amines have a characteristic source from the iced
116 western Weddell Sea region in this data, with the top 90th percentile of C_2 and C_4 amine signals
117 occurring under air masses arising from this iced region. Daily peak H_2SO_4 concentrations were on
118 average above a factor of 2 higher on event days, driven by enhanced solar radiation. Although
119 elevated temperatures can inhibit particle formation rates by promoting rapid cluster evaporation,
120 peak temperatures were markedly similar between days (Figure 1c). The growth rates of new
121 particles calculated from SMPS data ($\text{GR}_{4.5-10}$) varied between $0.41 - 0.58 \text{ nm h}^{-1}$, similar to other
122 reports of Antarctic pure sulphuric acid-driven growth¹⁹, but lower than measured in other Antarctic
123 environments^{25,26,31}, although many of these measurements do not extend below 10 nm. The
124 measured growth rates are similar to those calculated from both the condensation of H_2SO_4 vapour,
125 and the condensation of H_2SO_4 , MSA and HIO_3 vapour (Extended Data Figure 2). At these rates,
126 growth to CCN size is a process taking place on the order of days. Although we were not able to
127 quantify the contribution of the NPFs to CCN in the studied region, it is likely these new particles
128 eventually grow and contribute to CCN concentration downwind.

129 MSA concentrations are similar between NPF event and non-event days (Extended Data Figure 3);
130 other sulphur acids (SO_3^- and SO_5^-) were measured, and followed similar trends to MSA, both
131 distinct from H_2SO_4 . The diurnal patterns of MSA were less pronounced and the mean
132 concentrations on event and non-event days were markedly similar, despite enhanced
133 photochemistry. MSA has been shown to form particles in flow reactors at ppbv concentrations¹⁵,
134 with the number of formed particles increasing at lower temperatures. In our data, however,
135 maximum MSA concentrations did not result in NPF events if concurrent with the absence of
136 H_2SO_4 , indicating that MSA alone could not form particles at an appreciable rate compared to
137 H_2SO_4 . A modelling study³² showed a significant increase in global particle number counts when
138 MSA participated in ternary nucleation in the same manner as H_2SO_4 ; however, our results suggest
139 this was not the case. Rather, MSA could have doubled the rates of particle formation from H_2SO_4
140 and amines at the ambient temperatures encountered¹⁶ or influenced the particle size distribution by
141 condensation on newly formed particles³².

142
143 Iodic acid (HIO_3) was slightly elevated on NPF days, though HIO_3 concentrations were around an
144 order of magnitude lower than those of H_2SO_4 and MSA. Organic compounds were comprised both
145 of small ($\leq \text{C}_4$) dicarboxylic acids and larger oxygenated organics with the formula $\text{C}_{5-6}\text{H}_{6-10}\text{O}_{4-7}\text{N}_{0-1}$.
146 Concentrations of both were slightly lower on NPF days. Positive matrix factorisation analyses
147 show that these oxygenated organic molecules had the same oceanic sources as DMS-derived acids.
148 Some dicarboxylic acids were seen to have a local origin from the research station (Extended Data
149 Figure 4). These organic molecules are too volatile to contribute to nucleation or early-stage
150 growth, with $\text{Log}_{10}\text{C}^*(273\text{ K})$ values between $3 \cdot 10^2$ and $10^6 \mu\text{g m}^{-3}$, and classing these molecules as
151 intermediate volatility organic compounds³³. High isoprene mixing ratios can, however, act as OH
152 sinks resulting in suppressed NPF³⁴, with resultant oxygenated C_5 species likely incapable of
153 efficiently participating in particle formation or early stage growth^{33,34}; thus, slight mean elevations
154 of oxygenated organics across non-event days may indicate the role of their precursors as OH

155 scavengers. Across the whole range of particle sizes NPF events increased particle numbers from a
156 median background of 229 cm^{-3} to 1625 cm^{-3} .

157

158 Two NPF events were observed during the cruise aboard the RV Hesperides, one occurring in close
159 proximity to the research station and the other one just slightly south (Extended Data Figure 5).

160 Here, NPF also occurred under significant elevations of H_2SO_4 and amines, most notably C_4 amines
161 (Extended Data Figure 6). C_2 and C_4 amines were the only bases measurable aboard the cruise, with
162 no significant signal of NH_3 . Events occurred under depletions of both MSA and HIO_3 , and
163 unchanged concentrations of oxygenated organics compared to non-event periods.

164

165 Our observed elevation of H_2SO_4 relative to MSA and HIO_3 (Figure 1, Extended Data Figure 3), as
166 well as the absence of organics that would qualify as ultralow volatility organic
167 compounds (ULVOC), capable of forming new particles in the absence of other acids, suggest that
168 H_2SO_4 was the main driver of NPF in the entire dataset, both at the station and on board the ship.
169 The presence of C_2 and C_4 amines at such high signal relative to NH_3 and methylamine imply the
170 former two may be of greater importance in stabilising H_2SO_4 clusters.

171

172 *New particle formation from sulphuric acid and amines*

173 Figure 2a shows particle formation rates plotted against H_2SO_4 monomer concentration.
174 Measurements are compared to the results of the CLOUD consortium experiments in the
175 presence/absence of galactic cosmic rays (GCR)^{21,22,29}. Particle formation rates of up to $13 \text{ cm}^{-3} \text{ s}^{-1}$
176 occurred at over an order of magnitude lower H_2SO_4 concentration than would be expected for
177 $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$ nucleation at 278 K, and formation rates were greater than those previously
178 observed in Antarctica at higher H_2SO_4 concentrations¹⁹. The upper bound of the measurement
179 uncertainty on $J_{1.7}$ still falls short of the rates seen in the CLOUD chamber for $\text{H}_2\text{SO}_4\text{-DMA-H}_2\text{O}$
180 nucleation on some days, where high mixing ratios of DMA were utilised. The lower bound of our

181 uncertainty on $J_{1.7}$ is still more efficient than the CLOUD $\text{H}_2\text{SO}_4\text{-NH}_3\text{-H}_2\text{O}$ system. Temperatures
182 and relative humidity values during our measurements were 274.8 ± 1.7 K and 70 ± 1.3 %,
183 respectively. These differ from those of the CLOUD experiments, but cluster stabilities and
184 nucleation rates have been shown to be mostly stable across this range of conditions for H_2SO_4 and
185 amines^{22,23,35}.

186

187 The H_2SO_4 dimer concentration in the CI-APi-ToF is elevated relative to the monomer by the
188 presence of stabilising bases (H_2SO_4 clusters often lose base upon charging by nitrate ions²²). Figure
189 2b shows measured H_2SO_4 dimer against H_2SO_4 monomer concentrations. Also plotted are the ratios
190 seen in the CLOUD chamber for $\text{H}_2\text{SO}_4\text{-DMA-H}_2\text{O}$ nucleation experiments²² as well as the estimated
191 H_2SO_4 dimer formed purely from ion induced clustering (IIC) of H_2SO_4 monomer in the NO_3^-
192 chemical ionisation inlet^{20,22}. The positioning of the H_2SO_4 dimer:monomer ratio above the lower IIC
193 limit indicates that there was a secondary stabilising species present in the system, and likely H_2O as
194 a ternary species. This ratio sits below that measured for the ternary $\text{H}_2\text{SO}_4\text{-DMA-H}_2\text{O}$ system, but
195 is similar to that seen for $\text{DMA-H}_2\text{SO}_4$ nucleation in Shanghai²⁰. Compared to the latter study, though,
196 we measured at markedly lower condensation sinks ($10^{-3} - 10^{-4} \text{ s}^{-1}$), to which this ratio is highly
197 sensitive. It is therefore likely that amine concentrations were limiting, or the bases involved were
198 less efficient at stabilising sulphuric acid clusters than DMA, such as methylamine, ethylamine in the
199 case of C_2 amines, or diethylamine in the case of C_4 amines³⁶. While no blank measurements for
200 background amine contamination were taken, the concentration of higher order amine clusters (i.e.,
201 $(\text{C}_2\text{H}_7\text{N})_2\text{H}_2\text{SO}_4\text{HSO}_4^-$) produced purely by clustering in the CI inlet after introduction either in the
202 sampling tube or sheath flow, would be insufficient to produce signal above LOD^{29,37}, even at peak
203 ambient H_2SO_4 concentrations (see methods). The signals attributable to our measured amine-
204 $\text{H}_2\text{SO}_4\text{HSO}_4^-$ clusters are similar to that of our sulphuric acid dimer, far above the instrumental LOD.

205

206 Figure 2c shows the mass defect plots before, and during a nucleation event on 2019-02-28. Clusters
207 of sulphuric acid and amines with up to three sulphuric acid molecules, and two sulphuric acid
208 molecules with two bases were visible in the CI-APi-ToF spectra. A large range of sulphuric acid-
209 amine peaks were present (time series, diurnals and relative signals in Extended Data Figure 7, peak
210 fits in Extended Data Figure 8, species listed in Extended Data Table 2), alongside other sulphur
211 containing ions, MSA, SO_3^- , SO_5^- , and the H_2SO_4 -MSA cluster. The amines that were clustered with
212 the sulphuric acid dimer ranged from a single C_2 amine through to 2 amines with a combined carbon
213 number of 8. The largest of these peaks have sulphuric acid/bisulphate:amine ratios of 2:2, likely
214 containing multiple methylamine, C_2 and C_4 amines (possibly dimethyl and diethylamine)²³. These
215 clusters of equal ratio of sulphuric acid to base tend to have extremely low evaporation rates^{29,37}, with
216 the $(\text{H}_2\text{SO}_4)_2(\text{DMA})_2$ cluster having evaporation rates on the order of 10^{-6} s^{-1} ³⁷, and these will grow
217 by stepwise collisional addition until they reach detectable size by particle counting instruments.
218 Signals for clusters with a single amine molecule are lower, as their evaporation rates are higher^{23,37}.
219 A peak for the H_2SO_4 -MSA cluster is also observed, which likely has an enhancing effect on
220 nucleation rate¹⁶.

221

222 Taking all of this into account, we suggest that the nucleation events we observed around the Antarctic
223 Peninsula were driven by H_2SO_4 -amine clusters of C_{1-4} amines, with H_2O as a ternary stabilising
224 species. The role of ions cannot be ruled out, but is seen to be minimal when nucleation involves a
225 strong alkylamine base²². Similarly, MSA likely has a synergistic effect on particle formation rates¹⁶.
226 These results add to prior evidence for H_2SO_4 - NH_3 - H_2O nucleation on the coast of mainland
227 Antarctica¹⁹, where no alkylamines were detected in the clusters and formation rates were in
228 agreement with previous chamber work for H_2SO_4 - NH_3 - H_2O nucleation.

229

230

231

232 *Links to air mass trajectories*

233 Ninety-six-hour HYSPLIT air-mass back trajectories ending up in our measurement locations were
234 clustered based upon their Euclidian distance (Figure 3a). The NPF events were most associated
235 with cluster 2 (Figure 3b), i.e., air blowing from the eastern coast of the Antarctic Peninsula and the
236 Weddell Sea. These same air masses, which blew over the largest fraction of sea-ice covered ocean
237 (Figure 3c), carried the highest signals of H₂SO₄ (Figure 3d) and C₂ and C₄ amines (Figure 3e). The
238 marginal ice zone and adjacent open ocean of the Weddell Sea have already been reported to be a
239 source of DMS and alkylamine emissions from the microbiota of sea ice and plankton^{10,11}, and thus
240 we suggest that these regions were the principal providers of the strong acid and base components
241 needed for NPF.

242

243 **DISCUSSION**

244

245 We show that NPF events around the northern Antarctic Peninsula occurred in association with
246 elevated H₂SO₄ concentrations as a necessary condition (Figure 1). Elevated concentrations of other
247 acids and oxygenated organics, such as MSA, typically co-occurred with high H₂SO₄ during NPF
248 events due to midday photochemistry, but by themselves without the latter they did not lead to
249 measurable particle formation and growth (Extended Data Figures 3 & 6). Therefore, our results
250 confirm previous observations of the essential role of H₂SO₄ in NPF in the Antarctic region¹⁹. Here
251 we show that particle formation occurs at a rate similar to that seen in chamber experiments of
252 H₂SO₄-DMA-H₂O particle formation, with markedly similar measured sulphuric acid
253 dimer:monomer ratios, indicating sulphuric acid clusters stabilised by a strong ternary stabilising
254 species (Figure 2a, 2b). C₁-C₄ amines are evidenced as this stabilising species by the appearance of
255 H₂SO₄-amine clusters in the mass spectra, which have a daytime maximum at the period of
256 maximum particle formation rate. Previous measurements in coastal mainland Antarctica at Aboa,
257 2000 km southeast of our sampling location, provide evidence of nucleation proceeding via
258 clustering of H₂SO₄-NH₃-H₂O¹⁹. Here we provide evidence for H₂SO₄-amine-H₂O nucleation as a

259 dominant process in the Antarctic Peninsula. It is likely that the amines are from regions of sea ice
260 in Antarctic Peninsula – western Weddell Sea region. Sympagic waters in this region have been
261 shown to be rich in methyl, dimethyl and trimethylamines and their precursors¹¹, and aerosol
262 originating from iced regions have shown a near 5-fold enhancement in amine concentration¹⁰.
263 Enhanced amine concentrations arising from these regions in our own data may similarly arise from
264 the degradation of nitrogen containing osmolytes³⁸⁻³⁹ produced by phytoplankton and other marine
265 biota⁴⁰. Diatoms, which are found numerously in the marginal sea ice zones of the nearby Antarctic
266 Amundsen Sea have been identified as a noteworthy source of protein-like components in
267 aerosols⁴¹, these protein-like components being positively correlated with organic nitrogen in
268 aerosols¹⁰. This mechanism will likely to be important in regions where there are substantial amine
269 emissions, such as in the regions where sympagic conditions are similar to those of the Weddell Sea
270 region. Figure 3a shows that sea ice extent around coastal Antarctica is substantial, suggesting that
271 this process may be important in a large area close to these iced regions. Long-term reports of NPF
272 from a station only ~100 km northeast show markedly similar formation rates to our own, and an 11
273 % elevation to CCN counts following NPF, indicating the potential significance of this mechanism
274 for aerosol-cloud interaction³¹. The presence of a H₂SO₄-MSA cluster in the mass spectrum
275 suggests that concurrent MSA, as well as HIO₃ and oxygenated organics, dependent upon their
276 abundance and volatility, may be involved in the stabilisation of clusters, and subsequent particle
277 growth.

278

279 Our results reveal the complexity of aerosol processes in Antarctica. NPF occurs frequently when
280 air masses blow over regions of extended sea ice marginal zone, these air masses contain elevated
281 concentrations of alkylamines and H₂SO₄, confirming that emissions from marine plankton and sea
282 ice melt play crucial roles in the creation of particles critical to regulation of the Antarctic climate.
283 The novel mechanism observed here represents a highly efficient particle formation pathway, with
284 the amine driven nucleation occurring at formation rates 1,000 times faster than that of ammonia at

285 278 K, even in the presence of ionising radiation, and with stabilization of H₂SO₄ clusters by amines
286 proceeding at near the kinetic limit with negligible evaporation. Due to its high potential as an
287 aerosol source, this mechanism should be incorporated in modelling efforts towards CCN number
288 estimations and aerosol-cloud interaction studies. Currently, *chlorophyll-a* data are not available
289 over iced regions. Therefore, it is not possible to directly link the *chlorophyll-a* over the iced
290 regions with amine data in this study. Further observations are needed to confirm the spatial and
291 temporal variations in alkylamine emissions and their role in NPF in and around Antarctica, as well
292 as to understand their formation mechanism in sympagic waters. Our results are demonstrative of
293 the need of mechanistic understanding on ocean-atmosphere interactions in the pristine polar
294 environments, and more broadly, of the aerosol processes likely to have had major roles in the pre-
295 industrial climate.

296

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- 398

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413

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415

416 **FIGURE CAPTIONS**

417

418 **Figure 1: Mean diurnal cycles on NPF and non-NPF days.** Plots show the mean data of NPF
419 days (left column) and mean data of non-NPF days (right column). Shaded regions show 95%
420 confidence intervals on the mean, and do not represent systematic measurement errors. Panels show
421 (a) SMPS contour plots with $J_{1.7}$ values overlaid, nucleation rates peaking at 11:00, (b) sulphuric
422 acid and amines. Sulphuric acid reported as concentration in molecules cm^{-3} , and amines reported as
423 ions s^{-1} . Amine signals were not corrected for background (see text for discussion). Here, sulphuric
424 acid also peaks at 11:00, and (c), global radiation and temperature.

425

426 **Figure 2: Evidence for sulphuric acid-amine nucleation.** (a) Particle formation rate as a function
427 of H_2SO_4 monomer concentration, and (b) H_2SO_4 dimer as a function of H_2SO_4 monomer
428 concentration. Green circles show ambient Antarctic data where 1 data point corresponds to a single
429 NPF event, orange squares show the CLOUD data from experiments of H_2SO_4 -DMA- H_2O
430 nucleation²², purple diamonds show CLOUD data from experiments of H_2SO_4 - H_2O nucleation, pink
431 triangles show CLOUD data from experiments of H_2SO_4 - NH_3 - H_2O nucleation²⁶, and the dashed
432 line shows theoretical concentration of H_2SO_4 dimer produced due to ion induced clustering in the
433 CI-APi-ToF ionisation inlet²⁴. All chamber data is recorded at 278 K and 38% RH under GCR
434 conditions, except H_2SO_4 -DMA- H_2O data, which includes both GCR and neutral data. Error bars
435 represent systematic uncertainties on data. Panels (c & d) show the mass defect plot before and
436 during the beginning of an NPF event on 05-03-2019. The size of the datapoints is proportional to
437 the common logarithm of signal intensity. Mass defect is defined as the deviation of the mass of a
438 species from the nearest integer mass.

439

440 **Figure 3: Association between sea ice extent and new particle formation.** (a) Clustered 96 hour
441 back trajectories for station measurements, lighter traces showing the unclustered trajectories, (b)
442 The association of each back trajectory cluster with regions of sea ice, (c) the percentage of NPF
443 events associated with each of these back trajectory clusters, and (d, e) box plots displaying the
444 median (centre line), interquartile range (IQR, box) and $1.5 \cdot \text{IQR}$ (whiskers), as well as any outliers
445 (points). These show concentrations and signals per cluster for H_2SO_4 , and C_2 & C_4 alkylamines, as
446 measured by the CI-APi-ToF.

447

448

449

450 **METHODS**

451

452 **Field site.** Ship measurements took place between 2019-01-25 and 2019-02-04 aboard the RV

453 Hesperides. The cruise began at the South Shetland Islands (around -63° latitude), sailing down to -

454 68° latitude across several days to Adelaide Island, and then back through to the South Shetland

455 Islands. Frequent ship plume related particle events were seen, and these have been filtered out

456 based on the size distributions and particle concentrations seen. Ground measurements took place

457 between 2019-02-12 and 2019-03-13 at the Spanish research station, Juan Carlos I (-62.66, -60.39).

458 The station is located directly on the coast on the south of Livingston Island in the South Shetland

459 Islands. All measurements were taken approximately 100 meters from the main station at a height

460 of 1 meter, with occasional pollution seen in the SMPS spectra from vehicles, generators, or waste

461 incineration. These spectra have been filtered from the dataset. The same instruments were

462 deployed both on the cruise and aboard the ship.

463 **Instrumental setup.** The Aerodyne Nitrate Chemical Ionisation Atmospheric Pressure Interface

464 Time of Flight Mass Spectrometer (CI-API-ToF) was used to make measurements of neutral

465 oxidised organic compounds, strong acids (HIO₃, H₂SO₄ etc.), and their molecular clusters at high

466 time resolution with high resolving power. The ionization system charges molecules by adduct

467 formation, such as in the case of organic compounds with two or more hydrogen bond donor

468 groups, or proton transfer in the case of strong acids like H₂SO₄. Hydroxyl or hydroperoxyl

469 functionalities are both common hydrogen bond donating groups. The front end consists of a

470 chemical ionisation system where a 15 LPM sample flow is drawn in through the 1 metre length 1”

471 OD stainless steel tubing opening. A secondary flow is run parallel and concentric to this sample

472 flow, rendering the reaction chamber effectively wall-less. We used pristine, unfiltered Antarctic

473 ambient air for this flow. A 3 SCCM flow of a carrier gas (N₂) is passed over a reservoir of liquid

474 HNO₃, entraining vapour which is subsequently ionised to NO₃⁻ via an X-ray source. Ions are then

475 guided into the sample flow. The nitrate ions will then charge molecules either by clustering or

476 proton transfer. The mixed flows travelling at 15 LPM enter the critical orifice at the front end of

477 the instrument at 0.8 LPM and are guided through a series of differentially pumped chambers before
478 reaching the ToF analyser. Two of these chambers contain quadrupoles which focus the ion beam
479 and can be used to select greater sensitivity for certain mass ranges, and the voltages across each
480 individual chamber can be tuned to maximise sensitivity and resolution for ions of interest. All data
481 analysis was carried out in the Tofware package (Tofwerk AG, Switzerland) in Igor Pro 7
482 (Wavemetrics Inc., USA). Normalization was performed using signals for NO_3^- , H_2ONO_3^- ,
483 $\text{HNO}_3\text{NO}_3^-$, and $(\text{HNO}_3)_2\text{NO}_3^-$, corresponding to the ionised nitric acid monomer, nitric acid
484 monomer-water cluster, nitric acid dimer and nitric acid trimer, respectively. Signals were
485 normalised by the sum of all these ions except for the amine signals, which were normalised by the
486 nitrate trimer⁴². Our data have been treated with a calibration coefficient of 10^{10} cm^{-3} , based upon
487 an earlier calibration⁴³, and presented with a systematic uncertainty of +50%/-33%, in line with
488 other publications. No calibration was applied to the amine data, as calibrations and sensitivities are
489 not currently well constrained. Similarly, CI-APi-ToF data taken aboard the cruise showed a
490 sensitivity issue and as no in-situ calibration was applied, only ion signals are reported for these
491 measurements. Peak fits and correlations of amines and ammonia in its two measured forms
492 (clustered with the nitrate dimer and trimer) are plotted in Extended Data Figure 1. No blanks were
493 performed *in situ*. However, we calculate the concentrations of sulphuric acid-amine clusters that
494 would form through clustering during the 200 ms residence time in the inlet as significantly below
495 the instrumental LOD with $3 \cdot 10^7 \text{ cm}^{-3}$ DMA (applying the calibration coefficient of ref. 42 to our
496 own data) and $7 \cdot 10^6 \text{ cm}^{-3}$ H_2SO_4 (peak hourly concentration on averaged NPF days, Fig. 1a), and
497 collision coefficients between sulphuric acid, DMA and their clusters in the range $4\text{-}6 \cdot 10^{-15} \text{ m}^3 \text{ s}^{-1}$
498 ^{29,37}. Our laboratory blanks run with 30 lpm CP grade N_2 as sheath and inlet flows produce C_2 & C_4
499 amine signals at slightly below, and a factor of 3 above the mean for our Antarctic campaign
500 respectively, hence we can eliminate our N_2 carrier flow as an amine source, as these N_2 flows are
501 orders of magnitude greater than that used for the Antarctic sampling campaign. Further, if the
502 sampling apparatus were a major amine source, we would have seen a steady decline in amine

503 concentrations as pristine Antarctic air was flown over it across the course of several weeks, and it
 504 volatilised from the apparatus, as these low molecular weight amines are semivolatile in nature. The
 505 instrument was run for several weeks in remote Southern Ocean air before collection of data used to
 506 produce most figures (i.e., Figure 1), hence giving plenty of time to self-cleanse.

507 A Nano Scanning Mobility Particle Sizer (NanoSMPS) instrument measured particle size
 508 distributions at five minute time resolution. The NanoSMPS consists of the 3082 EC, 3085 Nano
 509 DMA, and 3776 CPC (TSI, USA). This measures the size ranges 10-157 nm, and 4.5-65 nm at two
 510 periods on the station, and 10-157 nm aboard the ship. A condensation particle counter (CPC 3775,
 511 TSI, USA) was also run in parallel collecting total particle count ≥ 4 nm.

512 ***Formation rates***

513 The formation rate of new particles at size d_p is calculated as follows:

$$514 \quad J_{d_p} = \frac{dN_{d_p}}{dt} + CoagS_{d_p} \cdot N_{d_p} + \frac{GR}{\Delta d_p} \cdot N_{d_p} \quad (2)$$

515 Where the first term on the right-hand side comprises the rate at which particles enter the size d_p ,
 516 and the latter two terms represent losses from this size by coagulation and growth, respectively. See
 517 ref. 44 for more information on calculation of coagulation sinks, growth rates, and formation rates.

518 From our $J_{4.5}$ values, we calculated $J_{1.7}$ using the equation of Korhonen et al., (2014)⁴⁵.

$$519 \quad J_{1.7}(t) = J_{x(\Delta t+t)} \cdot \exp\left(\frac{CoagS_{d_{p1.7}}}{GR_{1.7}} \cdot d_{p1.7} \cdot \gamma\right) \quad (3)$$

520 where $J_{1.7}$ is the formation rate to be calculated at 1.7 nm, $CoagS_{d_{p1.7}}$ is the coagulation sink at that
 521 size, $GR_{1.7}$ is the growth rate between 1.7 nm and 4.5 nm calculated from condensation of H_2SO_4 ,
 522 MSA and HIO_3 , J_x is the original particle formation rate, and Δt is determined using a time-delay
 523 method using sulphuric acid. γ is a factor defined as

$$524 \quad \gamma = \frac{1}{m-n+1} \left[\left(\frac{d_{pX}}{d_{p1.7}} \right)^{m-n+1} - 1 \right] \quad (4)$$

525 Where m is a coefficient describing the slope of coagulation sink with diameter, dependent upon the
526 background particle population

$$527 \quad m = \frac{\log(\text{CoagS}_{d_{px}}/\text{CoagS}_{d_{p1.7}})}{\log(d_{px}/d_{p1.7})} \quad (5)$$

528 and n is dependent upon the slope of the growth rate (GR) with diameter

$$529 \quad n = \frac{\log(\text{GR}_{d_{px}}/\text{GR}_{d_{p1.7}})}{\log(d_{px}/d_{p1.7})} \quad (6)$$

530 Systematic uncertainties on our calculated values of $J_{1.7}$ include a factor of +100% / -50% on the
531 calculated growth rates, a factor of $\pm 25\%$ on d_p of the NanoSMPS, and $\pm 50\%$ on the established
532 losses due to condensation sink.

533
534 ***Growth rate***

535 The growth rate of new particles is defined as

$$536 \quad GR = \frac{ddp}{dt} \quad (7)$$

537 Two methods to determine the GR of particles were employed here. The first was growth rates
538 determined from the lognormal distribution function method outlined in ref. 44, wherein a
539 lognormal distribution function was fitted to the new mode of particles. The increase to the
540 geometric mean of the diameter of this mode over time, once corrected for coagulation effects,
541 gives the condensational growth rate, this gave $GR_{4.5-10}$. Secondly, as equation 3 requires growth
542 rates from the critical diameter upwards (here presumed 1.7 nm, but is typically estimated 1.5 ± 0.4
543 nm), we calculated theoretical growth rates due to both H_2SO_4 condensation, and condensation of
544 H_2SO_4 , MSA, and HIO_3 through the method of Nieminen et al., 2010⁴⁶. At our measured relative
545 humidity, sulphuric acid favours binding to 3 H_2O molecules⁴⁷. As amine concentrations are likely
546 limited, we presume no mass from amines in the condensing species. For simplicity, the properties
547 of MSA regarding density and hydration were presumed the same as H_2SO_4 , whereas HIO_3 was
548 presumed the same, with enhanced density¹⁸, with this we produce both $GR_{1.7-4.5}$, and $GR_{4.5-10}$.

549 Calculated rates per day are shown in Extended Data Figure 2. Measured growth of particles in the
550 range 4.5-10 nm is within error for both sets of calculations. The efficiency of condensation of
551 MSA and HIO₃ onto particles of sizes 1.7 through 4.5 nm has not been studied in detail, however,
552 they are non-negligible, and so here we presume they condense with the same efficiency as H₂SO₄
553 and utilise these GR_{1.7-4.5} values in our calculation of J_{1.7}. This may lead to a possible
554 underestimation in J_{1.7}. GRs from both size ranges were then input into our formation rate
555 calculations. Calculated growth rates are presented with errors of +100%/-50%⁴⁶, and growth rates
556 fitted to SMPS data given an error of ±50% (±25% from fitting, ±25% from instrument errors⁴⁸).

557

558 ***Condensation sink***

559 The condensation sink (CS) represents the rate at which a vapour phase molecule will collide with
560 pre-existing particle surface, and was calculated from the size distribution data as follows⁴⁴:

$$561 \quad CS = 2\pi D \sum_{d_p} \beta_{m,d_p} d_p N_{d_p}, \quad (8)$$

562 where D is the diffusion coefficient of the diffusing vapour (assumed H₂SO₄), β_m is a transition
563 regime correction, d_p is particle diameter, and N_{d_p} is the number of particles at diameter d_p.

564

565 ***Back trajectories and sea ice extent***

566 The NOAA HYSPLIT model was used to calculate 4 day back-trajectories for air masses arriving at
567 the sampling sites. Each back-trajectory data point was assigned to sea ice concentration percentage
568 on a 12.5 km grid from microwave satellite data, providing a sea ice concentration from 0 – 100%
569 (5% width)⁴⁹. These air masses were then clustered using an angle-based distance matrix to produce
570 the 5 back trajectory clusters.

571

572 ***Positive matrix factorisation***

573 Positive matrix factorisation (PMF) was applied to our Nitrate CI-APi-ToF data to identify
574 contaminants. Analyses were performed using the PMF2 algorithm in robust mode using a data

575 matrix of 304 high resolution peaks across 1 week of data at 10 minute time resolution (1000 data
576 points). The error matrix was generated according to Poisson counting statistics as follows⁵⁰

$$577 \quad \sigma_{ij} = \sqrt{I/t_s} \quad (9)$$

578 Where I is the ion signal and t_s is the time for integration. After an initial run, an 8 factor solution
579 was chosen. To produce a final 8 factor solution, those species with large scaled residuals (21 of our
580 peaks) had their uncertainties scaled by a factor of 10, and the uncertainties of the rest of the data
581 matrix was scaled by a factor of 1.06, producing a Q/Qexp value of 1.004.

582

583 Extended Data Figure 4 shows the PMF solution for 8 factors. Factors 1 & 2 relate to daytime
584 photochemistry, the latter containing dicarboxylic acids of marine origin, and the former
585 corresponding to daytime oxidation of DMS and VOCs. Due to the mass range selected,
586 deprotonated MSA and H_2SO_4 are not included, but their clusters with NO_3^- , and with other species
587 (MSA- HSO_4^- cluster, HSO_4^- amine clusters etc) are. Contaminant peaks as identified below are
588 absent in these factors, and the dominant wind direction was from the north (the station was located
589 to the south-east) confirming the absence of contaminants in our analysis of nucleation mechanisms,
590 and confirm the role of marine air masses in the production of sulphuric acid, methanesulphonic
591 acid, and oxygenated organics.

592

593 The remaining factors belonged to contaminants from either station activities, or from instrument
594 contamination. Most of these factors comprised of just a few large peaks, and thus we identify
595 several contaminant ions through this method. Contaminants arose partially from a narrow wind
596 sector from the station, with factors 3, 4, & 5 being associated with a narrow south easterly air mass
597 band, containing emissions from the nearby station (~250 m distance). Dicarboxylic acids such as
598 the $\text{C}_4\text{H}_4\text{O}_4\text{-NO}_3^-$ ion, which may be fumaric acid, a food additive, is found in factor 3, and factor 5
599 contains brominated organic compounds at 305 – 311 m/Q. Other contaminants arose from within

600 the instrument, with factors 6, 7 & 8 containing fluorinated organic compounds, arising from the
601 tubing within the instrument.

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627 the Southern Oxidant and Aerosol Study (SOAS) 2013. *ACS Earth Sp. Chem.* **2**, 653–672
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- 629

630 **Data and materials availability:** Data supporting this publication are openly available from the

631 UBIRA eData repository at <https://doi.org/10.25500/edata.bham.00000400>. Daily sea ice

632 concentrations⁴⁹ are available from NSIDC at <https://doi.org/10.7265/N5K072F8>.

633

634 **Code availability:** Code required to produce the figures is available from the authors upon

635 reasonable request.

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639

EXTENDED DATA

Date	H ₂ SO ₄ (10 ⁶ cm ⁻³)	J _{4.5} (cm ⁻³ s ⁻¹)	J _{1.7} (cm ⁻³ s ⁻¹)	GR _{4.5-10SMPs} (nm h ⁻¹)	GR _{4.5-10Acids} (nm h ⁻¹)	GR _{4.5-10H₂SO₄} (nm h ⁻¹)	GR _{1.7-4.5H₂SO₄} (nm h ⁻¹)	Temperature (°C)	Relative humidity (%)
21/02/2019	5.84	0.36	1.64	0.58	0.71	0.33	0.42	1.35	72.2
22/02/2019	3.67	0.10	0.40	0.55	0.75	0.25	0.33	1.32	74.6
28/02/2019	3.04	0.21	1.21	0.41	0.87	0.30	0.39	0.16	55.1
05/03/2019	2.00	0.24	3.07	0.41	0.56	0.22	0.28	3.5	85.2

640
641

Mass to charge ratio (mz ⁻¹)	Assigned formulae	Potential base identity	Acid:Base ratio
79.960	SO ₃ ⁻		1:0
94.983	CH ₃ SO ₃ ⁻		1:0
96.960	HSO ₄ ⁻		1:0
111.947	SO ₅ ⁻		1:0
192.950	H ₂ SO ₄ CH ₃ SO ₃ ⁻		2:0
194.928	H ₂ SO ₄ HSO ₄ ⁻		2:0
239.994	H ₂ SO ₄ HSO ₄ C ₂ H ₇ N ⁻	C ₂ amine	2:1
257.012	H ₂ SO ₄ HSO ₄ (CH ₅ N) ₂ ⁻	Methylamine, methylamine	2:2
268.020	H ₂ SO ₄ HSO ₄ C ₄ H ₁₁ N ⁻	C ₄ amine	2:1
271.031	H ₂ SO ₄ HSO ₄ C ₂ H ₇ NC ₂ H ₅ N ⁻	C ₂ amine, methylamine	2:2
285.044	H ₂ SO ₄ HSO ₄ (C ₂ H ₇ N) ₂ ⁻	2 C ₂ amines/Methylamine + C ₃ amine	2:2
292.905	(H ₂ SO ₄) ₂ HSO ₄ ⁻		3:0
299.048	H ₂ SO ₄ HSO ₄ C ₂ H ₇ NC ₃ H ₉ N ⁻	C ₂ + C ₃ amine, methylamine + C ₄ amine	2:2
313.066	H ₂ SO ₄ HSO ₄ (C ₃ H ₉ N) ₂ ⁻	2 C ₃ amines, C ₂ + C ₄ amine, Methylamine + C ₅ amine	2:2
327.078	H ₂ SO ₄ HSO ₄ C ₃ H ₉ NC ₄ H ₁₁ N ⁻	C ₃ + C ₄ amines, C ₂ + C ₅ amines, Methylamine + C ₆ amine	2:2
341.093	H ₂ SO ₄ HSO ₄ (C ₄ H ₁₁ N) ₂ ⁻	2 C ₄ amines, C ₃ + C ₅ amine, C ₂ + C ₆ amine, methylamine + C ₇ amine	2:2

642
643