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Open ocean and coastal new particle formation from sulfuric acid and amines around the Antarctic Peninsula

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2	OPEN OCEAN AND COASTAL NEW PARTICLE
3	FORMATION FROM SULPHURIC ACID AND AMINES
4	AROUND THE ANTARCTIC PENINSULA
5	
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27	

28 ABSTRACT

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

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

- 49 **MAIN**
- 50

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

abstraction, or an addition respectively¹³. H_2SO_4 is thought to be responsible for most nucleation observed in the atmosphere¹⁴. MSA can also form new particles in the presence of bases¹⁵ and has been shown to accelerate nucleation of H_2SO_4 and dimethylamine (DMA) with which it forms stable clusters in the H_2SO_4 -MSA-DMA system¹⁶.

80

Recent advances in instrumentation have provided new insight into the fundamental steps of NPF in 81 remote boreal forest¹⁷, coastal¹⁸, pristine polar^{18,19}, and urban environments²⁰. This is backed up by 82 a host of chamber experiments that have revealed the role of ammonia²¹ and amines^{22,23} in 83 accelerating H₂SO₄-H₂O nucleation, and the influence of galactic cosmic rays (GCR), temperature, 84 and humidity $^{21-24}$. While there have been a number of studies of NPF in Antarctica^{7,25,26}, only one 85 study¹⁹ has investigated the particle nucleation process at a fundamental level. They reported ion-86 induced H₂SO₄-NH₃-H₂O nucleation, similar to that observed in laboratory experiments where GCR 87 were seen to significantly enhance the nucleation rates²¹, but dissimilar to H₂SO₄-DMA-H₂O 88 nucleation where GCR were less influential²². Here we present evidence for a parallel process in 89 particle nucleation involving H₂SO₄ and small alkylamines that can proceed rapidly under charged 90 or neutral conditions. The study involved air sampling both on coastal land and over the open 91 ocean. 92

93 **RESULTS**

94

95 Characteristics of new particle formation events

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

contribution of background to these signals is not established. We therefore did not derive 103 concentrations from these amine signals, simply reporting ion count rates. However, the instrument 104 was run in pristine Southern Ocean and Antarctic air for several weeks, and we found no evidence 105 106 of amine contamination from the instrument, tubing, or sheath air. While not correcting background signals could introduce uncertainty to the reported signals, it should not affect our conclusions. 107 108 Trimethylamine was not measured in the gas phase but could be present in measured sulphuric acidamine clusters. Clustering between (HNO₃)₁₋₂NO₃⁻ and NH₃ is significantly weaker than that with 109 DMA and hence the sensitivity to NH₃ was likely lower, and the mixing ratio of NH₃ was much 110 higher than that of amines. However, alkylamines have been shown to enhance formation rates at 111 modest mixing ratios^{22,23} in the range of a few pptv, which are sufficient to substitute NH₃ in 112 H₂SO₄-NH₃ clusters²⁸. Minima of amine signals at midday were driven by either clustering with 113 elevated sulphuric acid, which clusters at roughly a 1:1 ratio if mixing ratios are sufficient²⁹, uptake 114 onto particle surfaces, or photolysis³⁰. These amines have a characteristic source from the iced 115 western Weddell Sea region in this data, with the top 90th percentile of C₂ and C₄ amine signals 116 occurring under air masses arising from this iced region. Daily peak H₂SO₄ concentrations were on 117 average above a factor of 2 higher on event days, driven by enhanced solar radiation. Although 118 elevated temperatures can inhibit particle formation rates by promoting rapid cluster evaporation, 119 peak temperatures were markedly similar between days (Figure 1c). The growth rates of new 120 particles calculated from SMPS data (GR_{4.5-10}) varied between 0.41 - 0.58 nm h⁻¹, similar to other 121 reports of Antarctic pure sulphuric acid-driven growth¹⁹, but lower than measured in other Antarctic 122 environments^{25,26,31}, although many of these measurements do not extend below 10 nm. The 123 measured growth rates are similar to those calculated from both the condensation of H_2SO_4 vapour, 124 125 and the condensation of H₂SO₄, MSA and HIO₃ vapour (Extended Data Figure 2). At these rates, growth to CCN size is a process taking place on the order of days. Although we were not able to 126 quantify the contribution of the NPFs to CCN in the studied region, it is likely these new particles 127 128 eventually grow and contribute to CCN concentration downwind.

MSA concentrations are similar between NPF event and non-event days (Extended Data Figure 3); 129 other sulphur acids (SO₃⁻ and SO₅⁻) were measured, and followed similar trends to MSA, both 130 distinct from H₂SO₄. The diurnal patterns of MSA were less pronounced and the mean 131 132 concentrations on event and non-event days were markedly similar, despite enhanced photochemistry. MSA has been shown to form particles in flow reactors at ppbv concentrations¹⁵, 133 with the number of formed particles increasing at lower temperatures. In our data, however, 134 maximum MSA concentrations did not result in NPF events if concurrent with the absence of 135 H₂SO₄, indicating that MSA alone could not form particles at an appreciable rate compared to 136 H₂SO₄. A modelling study³² showed a significant increase in global particle number counts when 137 MSA participated in ternary nucleation in the same manner as H₂SO₄; however, our results suggest 138 this was not the case. Rather, MSA could have doubled the rates of particle formation from H₂SO₄ 139 and amines at the ambient temperatures encountered¹⁶ or influenced the particle size distribution by 140 condensation on newly formed particles 32 . 141

142

Iodic acid (HIO₃) was slightly elevated on NPF days, though HIO₃ concentrations were around an 143 order of magnitude lower than those of H₂SO₄ and MSA. Organic compounds were comprised both 144 of small ($\leq C_4$) dicarboxylic acids and larger oxygenated organics with the formula $C_{5-6}H_{6-10}O_{4-7}N_{0-1}$ 145 1. Concentrations of both were slightly lower on NPF days. Positive matrix factorisation analyses 146 show that these oxygenated organic molecules had the same oceanic sources as DMS-derived acids. 147 Some dicarboxylic acids were seen to have a local origin from the research station (Extended Data 148 Figure 4). These organic molecules are too volatile to contribute to nucleation or early-stage 149 growth, with $Log_{10}C^*(273 \text{ K})$ values between $3 \cdot 10^2$ and $10^6 \,\mu\text{g m}^{-3}$, and classing these molecules as 150 intermediate volatility organic compounds³³. High isoprene mixing ratios can, however, act as OH⁻ 151 sinks resulting in supressed NPF³⁴, with resultant oxygenated C₅ species likely incapable of 152 efficiently participating in particle formation or early stage growth^{33,34}; thus, slight mean elevations 153 of oxygenated organics across non-event days may indicate the role of their precursors as OH⁻ 154

scavengers. Across the whole range of particle sizes NPF events increased particle numbers from a 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 ₂ SO 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 ₂ SO ₄ clusters.

171

172 New particle formation from sulphuric acid and amines

Figure 2a shows particle formation rates plotted against H₂SO₄ monomer concentration. 173 Measurements are compared to the results of the CLOUD consortium experiments in the 174 presence/absence of galactic cosmic rays (GCR)^{21,22,29}. Particle formation rates of up to 13 cm⁻³ s⁻¹ 175 occurred at over an order of magnitude lower H₂SO₄ concentration than would be expected for 176 H₂SO₄-NH₃-H₂O nucleation at 278 K, and formation rates were greater than those previously 177 observed in Antarctica at higher H₂SO₄ concentrations¹⁹. The upper bound of the measurement 178 uncertainty on J_{1.7} still falls short of the rates seen in the CLOUD chamber for H₂SO₄-DMA-H₂O 179 nucleation on some days, where high mixing ratios of DMA were utilised. The lower bound of our 180

uncertainty on J_{1.7} is still more efficient than the CLOUD H₂SO₄-NH₃-H₂O system. Temperatures and relative humidity values during our measurements were 274.8 \pm 1.7 K and 70 \pm 1.3 %, respectively. These differ from those of the CLOUD experiments, but cluster stabilities and nucleation rates have been shown to be mostly stable across this range of conditions for H₂SO₄ and amines^{22,23,35}.

186

The H₂SO₄ dimer concentration in the CI-APi-ToF is elevated relative to the monomer by the 187 presence of stabilising bases (H₂SO₄ clusters often lose base upon charging by nitrate ions²²). Figure 188 2b shows measured H₂SO₄ dimer against H₂SO₄ monomer concentrations. Also plotted are the ratios 189 seen in the CLOUD chamber for H₂SO₄-DMA-H₂O nucleation experiments²² as well as the estimated 190 H₂SO₄ dimer formed purely from ion induced clustering (IIC) of H₂SO₄ monomer in the NO₃⁻ 191 chemical ionisation inlet^{20,22}. The positioning of the H₂SO₄ dimer:monomer ratio above the lower IIC 192 limit indicates that there was a secondary stabilising species present in the system, and likely H₂O as 193 a ternary species. This ratio sits below that measured for the ternary H₂SO₄–DMA–H₂O system, but 194 is similar to that seen for DMA-H₂SO₄ nucleation in Shanghai²⁰. Compared to the latter study, though, 195 we measured at markedly lower condensation sinks $(10^{-3} - 10^{-4} \text{ s}^{-1})$, to which this ratio is highly 196 sensitive. It is therefore likely that amine concentrations were limiting, or the bases involved were 197 less efficient at stabilising sulphuric acid clusters than DMA, such as methylamine, ethylamine in the 198 case of C₂ amines, or diethylamine in the case of C₄ amines³⁶. While no blank measurements for 199 background amine contamination were taken, the concentration of higher order amine clusters (i.e., 200 (C₂H₇N)₂H₂SO₄HSO₄⁻) produced purely by clustering in the CI inlet after introduction either in the 201 sampling tube or sheath flow, would be insufficient to produce signal above $LOD^{29,37}$, even at peak 202 ambient H₂SO₄ concentrations (see methods). The signals attributable to our measured amine-203 H₂SO₄HSO₄⁻ clusters are similar to that of our sulphuric acid dimer, far above the instrumental LOD. 204 205

Figure 2c shows the mass defect plots before, and during a nucleation event on 2019-02-28. Clusters 206 of sulphuric acid and amines with up to three sulphuric acid molecules, and two sulphuric acid 207 molecules with two bases were visible in the CI-APi-ToF spectra. A large range of sulphuric acid-208 209 amine peaks were present (time series, diurnals and relative signals in Extended Data Figure 7, peak fits in Extended Data Figure 8, species listed in Extended Data Table 2), alongside other sulphur 210 containing ions, MSA, SO₃⁻, SO₅⁻, and the H₂SO₄-MSA cluster. The amines that were clustered with 211 the sulphuric acid dimer ranged from a single C_2 amine through to 2 amines with a combined carbon 212 number of 8. The largest of these peaks have sulphuric acid/bisulphate:amine ratios of 2:2, likely 213 containing multiple methylamine, C_2 and C_4 amines (possibly dimethyl and diethylamine)²³. These 214 clusters of equal ratio of sulphuric acid to base tend to have extremely low evaporation rates^{29,37}, with 215 the $(H_2SO_4)_2(DMA)_2$ cluster having evaporation rates on the order of 10^{-6} s⁻¹ ³⁷, and these will grow 216 by stepwise collisional addition until they reach detectable size by particle counting instruments. 217 Signals for clusters with a single amine molecule are lower, as their evaporation rates are higher^{23,37}. 218 A peak for the H₂SO₄-MSA cluster is also observed, which likely has an enhancing effect on 219 nucleation rate¹⁶. 220

221

Taking all of this into account, we suggest that the nucleation events we observed around the Antarctic Peninsula were driven by H₂SO₄-amine clusters of C₁₋₄ amines, with H₂O as a ternary stabilising species. The role of ions cannot be ruled out, but is seen to be minimal when nucleation involves a strong alkylamine base²². Similarly, MSA likely has a synergistic effect on particle formation rates¹⁶. These results add to prior evidence for H₂SO₄-NH₃-H₂O nucleation on the coast of mainland Antarctica¹⁹, where no alkylamines were detected in the clusters and formation rates were in agreement with previous chamber work for H₂SO₄-NH₃-H₂O nucleation.

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230

232 Links to air mass trajectories

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

242

243 **DISCUSSION**

244

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

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

278

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

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

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- 398

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413

414 **Competing financial interests**: The authors declare no conflict of interests.

416 FIGURE CAPTIONS

417

418 **Figure 1: Mean diurnal cycles on NPF and non-NPF days**. Plots show the mean data of NPF

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

Figure 2: Evidence for sulphuric acid-amine nucleation. (a) Particle formation rate as a function 426 of H₂SO₄ monomer concentration, and (b) H₂SO₄ dimer as a function of H₂SO₄ monomer 427 concentration. Green circles show ambient Antarctic data where 1 data point corresponds to a single 428 429 NPF event, orange squares show the CLOUD data from experiments of H₂SO₄-DMA-H₂O nucleation²², purple diamonds show CLOUD data from experiments of H₂SO₄-H₂O nucleation, pink 430 triangles show CLOUD data from experiments of H₂SO₄-NH₃-H₂O nucleation²⁶, and the dashed 431 line shows theoretical concentration of H₂SO₄ dimer produced due to ion induced clustering in the 432 CI-APi-ToF ionisation inlet²⁴. All chamber data is recorded at 278 K and 38% RH under GCR 433 conditions, except H₂SO₄-DMA-H₂O data, which includes both GCR and neutral data. Error bars 434 represent systematic uncertainties on data. Panels (c & d) show the mass defect plot before and 435 during the beginning of an NPF event on 05-03-2019. The size of the datapoints is proportional to 436 the common logarithm of signal intensity. Mass defect is defined as the deviation of the mass of a 437

438 species from the nearest integer mass.

440 **Figure 3: Association between sea ice extent and new particle formation. (a)** Clustered 96 hour

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

events associated with each of these back trajectory clusters, and (\mathbf{d}, \mathbf{e}) box plots displaying the

444 median (centre line), interquartile range (IQR, box) and $1.5 \cdot IQR$ (whiskers), as well as any outliers 445 (points). These show concentrations and signals per cluster for H₂SO₄, and C₂ & C₄ alkylamines, as

446 measured by the CI-APi-ToF.

447

439

448

- 450 **METHODS**
- 451

Field site. Ship measurements took place between 2019-01-25 and 2019-02-04 aboard the RV 452 Hesperides. The cruise began at the South Shetland Islands (around -63° latitude), sailing down to -453 454 68° latitude across several days to Adelaide Island, and then back through to the South Shetland Islands. Frequent ship plume related particle events were seen, and these have been filtered out 455 based on the size distributions and particle concentrations seen. Ground measurements took place 456 between 2019-02-12 and 2019-03-13 at the Spanish research station, Juan Carlos I (-62.66, -60.39). 457 The station is located directly on the coast on the south of Livingston Island in the South Shetland 458 Islands. All measurements were taken approximately 100 meters from the main station at a height 459 of 1 meter, with occasional pollution seen in the SMPS spectra from vehicles, generators, or waste 460 incineration. These spectra have been filtered from the dataset. The same instruments were 461 deployed both on the cruise and aboard the ship. 462

Instrumental setup. The Aerodyne Nitrate Chemical Ionisation Atmospheric Pressure Interface 463 Time of Flight Mass Spectrometer (CI-APi-ToF) was used to make measurements of neutral 464 oxidised organic compounds, strong acids (HIO₃, H₂SO₄ etc.), and their molecular clusters at high 465 time resolution with high resolving power. The ionization system charges molecules by adduct 466 formation, such as in the case of organic compounds with two or more hydrogen bond donor 467 groups, or proton transfer in the case of strong acids like H₂SO₄. Hydroxyl or hydroperoxyl 468 functionalities are both common hydrogen bond donating groups. The front end consists of a 469 chemical ionisation system where a 15 LPM sample flow is drawn in through the 1 metre length 1" 470 OD stainless steel tubing opening. A secondary flow is run parallel and concentric to this sample 471 flow, rendering the reaction chamber effectively wall-less. We used pristine, unfiltered Antarctic 472 ambient air for this flow. A 3 SCCM flow of a carrier gas (N₂) is passed over a reservoir of liquid 473 HNO₃, entraining vapour which is subsequently ionised to NO₃⁻ via an X-ray source. Ions are then 474 guided into the sample flow. The nitrate ions will then charge molecules either by clustering or 475 proton transfer. The mixed flows travelling at 15 LPM enter the critical orifice at the front end of 476

the instrument at 0.8 LPM and are guided through a series of differentially pumped chambers before 477 reaching the ToF analyser. Two of these chambers contain quadrupoles which focus the ion beam 478 and can be used to select greater sensitivity for certain mass ranges, and the voltages across each 479 480 individual chamber can be tuned to maximise sensitivity and resolution for ions of interest. All data analysis was carried out in the Tofware package (Tofwerk AG, Switzerland) in Igor Pro 7 481 (Wavemetrics Inc., USA). Normalization was performed using signals for NO₃⁻, H₂ONO₃⁻, 482 HNO₃NO₃⁻, and (HNO₃)₂NO₃⁻, corresponding to the ionised nitric acid monomer, nitric acid 483 monomer-water cluster, nitric acid dimer and nitric acid trimer, respectively. Signals were 484 normalised by the sum of all these ions except for the amine signals, which were normalised by the 485 nitrate trimer⁴². Our data have been treated with a calibration coefficient of 10^{10} cm⁻³, based upon 486 an earlier calibration⁴³, and presented with a systematic uncertainty of +50%/-33%, in line with 487 other publications. No calibration was applied to the amine data, as calibrations and sensitivities are 488 not currently well constrained. Similarly, CI-APi-ToF data taken aboard the cruise showed a 489 sensitivity issue and as no in-situ calibration was applied, only ion signals are reported for these 490 measurements. Peak fits and correlations of amines and ammonia in its two measured forms 491 (clustered with the nitrate dimer and trimer) are plotted in Extended Data Figure 1. No blanks were 492 performed *in situ*. However, we calculate the concentrations of sulphuric acid-amine clusters that 493 494 would form through clustering during the 200 ms residence time in the inlet as significantly below the instrumental LOD with 3.107 cm⁻³ DMA (applying the calibration coefficient of ref. 42 to our 495 own data) and 7^{-10⁶} cm⁻³ H₂SO₄ (peak hourly concentration on averaged NPF days, Fig. 1a), and 496 collision coefficients between sulphuric acid, DMA and their clusters in the range 4-6 10⁻¹⁵ m³ s⁻¹ 497 29,37 . Our laboratory blanks run with 30 lpm CP grade N₂ as sheath and inlet flows produce C₂ & C₄ 498 499 amine signals at slightly below, and a factor of 3 above the mean for our Antarctic campaign respectively, hence we can eliminate our N₂ carrier flow as an amine source, as these N₂ flows are 500 orders of magnitude greater than that used for the Antarctic sampling campaign. Further, if the 501 sampling apparatus were a major amine source, we would have seen a steady decline in amine 502

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

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

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

515 Where the first term on the right-hand side comprises the rate at which particles enter the size d_p ,

and the latter two terms represent losses from this size by coagulation and growth, respectively. See

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
$$J_{1.7(t)} = J_{x(\Delta t+t)} \cdot \exp\left(\frac{\cos g_{d_{p1.7}}}{g_{R_{1.7}}} \cdot d_{p1.7} \cdot \gamma\right)$$
(3)

where $J_{1.7}$ is the formation rate to be calculated at 1.7 nm , $CoagS_{dp1.7}$ is the coagulation sink at that size, $GR_{1.7}$ is the growth rate between 1.7 nm and 4.5 nm calculated from condensation of H₂SO₄, MSA and HIO₃, J_x is the original particle formation rate, and Δt is determined using a time-delay method using sulphuric acid. γ is a factor defined as

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

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

526 background particle population

527
$$m = \frac{\log(coagS_{d_{px}}/coagS_{d_{p1.7}})}{\log(d_{px}/d_{p1.7})}$$
(5)

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

529
$$n = \frac{\log(GR_{d_{px}}/GR_{d_{p1,7}})}{\log(d_{px}/d_{p1,7})}$$
(6)

530 Systematic uncertainties on our calculated values of $J_{1.7}$ include a factor of $\pm 100\%$ / -50% on the 531 calculated growth rates, a factor of $\pm 25\%$ on dp 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
$$GR = \frac{ddp}{dt}$$
(7)

Two methods to determine the GR of particles were employed here. The first was growth rates 537 determined from the lognormal distribution function method outlined in ref. 44, wherein a 538 lognormal distribution function was fitted to the new mode of particles. The increase to the 539 geometric mean of the diameter of this mode over time, once corrected for coagulation effects, 540 gives the condensational growth rate, this gave $GR_{4,5-10}$. Secondly, as equation 3 requires growth 541 rates from the critical diameter upwards (here presumed 1.7 nm, but is typically estimated 1.5 ± 0.4 542 nm), we calculated theoretical growth rates due to both H₂SO₄ condensation, and condensation of 543 H₂SO₄, MSA, and HIO₃ through the method of Nieminen et al., 2010⁴⁶. At our measured relative 544 humidity, sulphuric acid favours binding to 3 H₂O molecules⁴⁷. As amine concentrations are likely 545 limited, we presume no mass from amines in the condensing species. For simplicity, the properties 546 of MSA regarding density and hydration were presumed the same as H₂SO₄, whereas HIO₃ was 547 presumed the same, with enhanced density¹⁸, with this we produce both $GR_{1.7-4.5}$, and $GR_{4.5-10}$. 548

549	Calculated rates per day are shown in Extended Data Figure 2. Measured growth of partic	les in the
550	range 4.5-10 nm is within error for both sets of calculations. The efficiency of condensation	on of
551	MSA and HIO ₃ onto particles of sizes 1.7 through 4.5 nm has not been studied in detail, h	iowever,
552	they are non-negligible, and so here we presume they condense with the same efficiency a	as H ₂ SO ₄
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 are presented with errors of $+100\%/-50\%^{46}$, and growth rates are presented with errors of $+100\%/-50\%^{46}$, and growth rates are presented with errors of $+100\%/-50\%^{46}$, and growth rates are presented with errors of $+100\%/-50\%^{46}$, and growth rates are presented with errors of $+100\%/-50\%^{46}$, and growth rates are presented with errors of $+100\%/-50\%^{46}$, and growth rates are presented with errors of $+100\%/-50\%^{46}$.	wth rates
556	fitted to SMPS data given an error of $\pm 50\%$ ($\pm 25\%$ from fitting, $\pm 25\%$ from instrument er	rors ⁴⁸ .
557 558	Condensation sink	
559	The condensation sink (CS) represents the rate at which a vapour phase molecule will coll	lide with
560	pre-existing particle surface, and was calculated from the size distribution data as follows	⁴⁴ :
561	$CS = 2\pi D \sum_{d_p} \beta_{m,d_p} d_p N_{d_p} ,$	(8)

where D is the diffusion coefficient of the diffusing vapour (assumed H_2SO_4), β_m is a transition regime correction, d_p is particle diameter, and N_{dp} is the number of particles at diameter d_p .

565 Back trajectories and sea ice extent

The NOAA HYSPLIT model was used to calculate 4 day back-trajectories for air masses arriving at the sampling sites. Each back-trajectory data point was assigned to sea ice concentration percentage on a 12.5 km grid from microwave satellite data, providing a sea ice concentration from 0 - 100%(5% width)⁴⁹. These air masses were then clustered using an angle-based distance matrix to produce 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
$$\sigma_{ij} = \sqrt{l/t_s}$$
(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

Extended Data Figure 4 shows the PMF solution for 8 factors. Factors 1 & 2 relate to daytime 583 photochemistry, the latter containing dicarboxylic acids of marine origin, and the former 584 corresponding to daytime oxidation of DMS and VOCs. Due to the mass range selected, 585 deprotonated MSA and H₂SO₄ are not included, but their clusters with NO₃⁻, and with other species 586 (MSA-HSO₄⁻ cluster, HSO₄⁻ amine clusters etc) are. Contaminant peaks as identified below are 587 absent in these factors, and the dominant wind direction was from the north (the station was located 588 to the south-east) confirming the absence of contaminants in our analysis of nucleation mechanisms, 589 and confirm the role of marine air masses in the production of sulphuric acid, methanesulphonic 590 acid, and oxygenated organics. 591

592

The remaining factors belonged to contaminants from either station activities, or from instrument contamination. Most of these factors comprised of just a few large peaks, and thus we identify several contaminant ions through this method. Contaminants arose partially from a narrow wind sector from the station, with factors 3, 4, & 5 being associated with a narrow south easterly air mass band, containing emissions from the nearby station (~250 m distance). Dicarboxylic acids such as the C₄H₄O₄-NO₃⁻ ion, which may be fumaric acid, a food additive, is found in factor 3, and factor 5 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.

602 METHOD REFERENCES

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603

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

- 631 UBIRA eData repository at <u>https://doi.org/10.25500/edata.bham.00000400.</u> Daily sea ice
- 632 concentrations⁴⁹ are available from NSIDC at <u>https://doi.org/10.7265/N5K072F8</u>.
- 633
- 634 **Code availability:** Code required to produce the figures is available from the authors upon
- 635 reasonable request.

EXTENDED DATA

Date	H ₂ SO ₄ (10 ⁶ cm ⁻³)	J _{4.5} (cm ⁻³ s ⁻ 1)	J _{1.7} (cm ⁻³ s ⁻	GR4.5-105MPS (nm h ⁻¹)	GR4.5-10Acids (nm h ⁻¹)	GR4.5- 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

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	HSO4 ⁻		1:0
111.947	SO5		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	H2SO4HSO4C2H7N ⁻	C ₂ amine	2:1
257.012	H2SO4HSO4(CH5N)2	Methylamine, methylamine	2:2
268.020	H2SO4HSO4C4H11N ⁻	C_4 amine	2:1
271.031	H2SO4HSO4C2H7NCH5N-	C ₂ amine, methylamine	2:2
285.044	H2SO4HSO4(C2H7N)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	H2SO4HSO4(C3H9N)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	H2SO4HSO4(C4H11N)2	2 C4 amines, C3 + C5 amine, C2 + C6 amine, methylamine + C7 amine	2:2