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Chemical Speciation of Sulfur in Marine Cloud Droplets and Particles: Analysis of Individual Particles from Marine Boundary Layer over the California Current

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1 **Chemical Speciation of Sulfur in Marine Cloud Droplets and Particles:**
2 **Analysis of Individual Particles from the Marine Boundary Layer over**
3 **the California Current.**

4
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32 **ABSTRACT**

33 Detailed chemical speciation of the dry residue particles from individual cloud
34 droplets and interstitial aerosol collected during the Marine Stratus Experiment (MASE) was
35 performed using a combination of complementary microanalysis techniques. Techniques
36 include computer controlled scanning electron microscopy with energy dispersed analysis of
37 X-rays (CCSEM/EDX), time-of-flight secondary ionization mass spectrometry (TOF-
38 SIMS), and scanning transmission X-ray microscopy with near edge X-ray absorption fine
39 structure spectroscopy (STXM/NEXAFS). Samples were collected at the ground site located
40 in Point Reyes National Seashore, approximately 1 km from the coast. This manuscript
41 focuses on the analysis of individual particles sampled from air masses that originated over
42 the open ocean and then passed through the area of the California current located along the
43 northern California coast. Based on composition, morphology, and chemical bonding
44 information, two externally mixed, distinct classes of sulfur containing particles were
45 identified: chemically modified (aged) sea salt particles and secondary formed sulfate
46 particles. The results indicate substantial heterogeneous replacement of chloride by
47 methanesulfonate (CH_3SO_3^-) and non-sea salt sulfate (nss-SO_4^{2-}) in sea-salt particles with
48 characteristic ratios of $\text{nss-S/Na} > 0.10$ and $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-} > 0.6$.

49

50 1. **INTRODUCTION**

51 Aerosols in the unpolluted marine boundary layer (MBL) result from two major
52 sources. First, sea salt particles generated from wave action, which are typically micrometers
53 or larger in size. Second, acidic sulfate aerosol formed by nucleation, with sizes on the order
54 of tenths of a micrometer. This mixture of particle types evolves with time due to a number
55 of processes, including deposition of condensable species, uptake of gas-phase species and a
56 variety of heterogeneous gas-to-particle and homogeneous in-particle chemical reactions.
57 Increased interest in the chemical composition and heterogeneity of marine aerosols stems
58 from their regional and global impact on sulfur oxidation in the MBL, in addition to climate
59 effects arising from light scattering and cloud condensation nuclei (CCN) activity [Covert, *et*
60 *al.*, 1992; Gong, 2003; Gong and Barrie, 2003; Gong, *et al.*, 1997; Gong, *et al.*, 2002; Lewis and
61 Schwartz, 2004; Murphy, *et al.*, 1998; Quinn, *et al.*, 1993; Sievering, *et al.*, 1991; Sievering, *et al.*,
62 2004].

63 The major gaseous precursor for marine sulfur-containing aerosol is dimethyl sulfide
64 (DMS). DMS is produced and emitted into the atmosphere by marine phytoplankton [Keller,
65 *et al.*, 1989]. Current estimates of global emissions indicate that DMS is the largest source of
66 natural sulfur [Bates, *et al.*, 1992; Kettle, *et al.*, 1999], produced at a rate of $\sim 12 \text{ Tg S yr}^{-1}$ [Spiro,
67 *et al.*, 1992]. In the atmosphere, DMS undergoes a complex sequence of gas-phase oxidation
68 reactions, producing a wide variety of oxidized products, which in turn interact with marine
69 cloud droplets and aerosols. These interactions include nucleation of new particles and the
70 alteration of pre-existing droplets and aerosols through condensation and multiphase
71 chemistry. Due to its large flux, the atmospheric cycle of DMS significantly impacts the
72 radiative budget over oceans on regional and global scales [Charlson, *et al.*, 1987; Shaw, 1983].

73 The atmospheric chemistry of DMS and its possible impact on aerosols and cloud
74 droplets is the subject of many studies. Understanding its major reactions has been achieved
75 through computer kinetic modeling studies [*Charlson, et al.*, 1987; *Kerminen, et al.*, 1998; *Koga*
76 *and Tanaka*, 1993; 1996; 1999; *Koga, et al.*, 1991; *Lucas and Prinn*, 2002; 2003; 2005a; b; *Shaw*,
77 1983; *von Glasow and Crutzen*, 2004; *von Glasow, et al.*, 2002a; b; *Yin, Grosjean, Flagan, et al.*, 1990;
78 *Yin, et al.*, 1986; *Yin, Grosjean and Seinfeld*, 1990; *Zaveri*, 1997], focused laboratory studies
79 [*Arsene, et al.*, 2002; *Barnes, et al.*, 1994; *Barone, et al.*, 1996; *Hynes, et al.*, 1995; *Hynes and Wine*,
80 1996; *Hynes, et al.*, 1986; *Ravishankara, et al.*, 1997; *Stickel, et al.*, 1992; *Turnipseed, et al.*, 1997;
81 *Urbanski, et al.*, 1998; *Yin, et al.*, 1986; *Zhao, et al.*, 1996; *Zhu, et al.*, 2006; *Zhu, et al.*, 2003], and
82 field observations [*M. O. Andreae and Raemdonck*, 1983; *T. W. Andreae, et al.*, 1993; *Bandy, et al.*,
83 1992; *Bandy, et al.*, 2002; *Barnard, et al.*, 1982; *Cooper and Saltzman*, 1991; 1993; *Spicer, et al.*,
84 1996; *Zemmelink, et al.*, 2002]. A simplified schematic diagram illustrating DMS chemistry and
85 its climate links is presented in Figure 1. In the ambient atmosphere, oxidation of DMS is
86 initiated by reaction with a variety of atmospheric free radicals. These radicals include, but
87 are not limited to, OH, NO₃, O(³P), Cl, Br, and BrO. Such reactions proceed *via* two
88 generalized reaction pathways: either addition of an O atom and/or abstraction of an H
89 atom. The branching ratio between the two generalized pathways is temperature dependent
90 with H abstraction dominating at room temperature, while O addition becomes increasingly
91 important at temperatures below 280 K [*Hynes, et al.*, 1986; *von Glasow and Crutzen*, 2004].
92 DMS gas phase oxidation products include sulfur dioxide (SO₂), sulfuric acid (H₂SO₄),
93 dimethylsulfoxide (CH₃SOCH₃), methanesulfinic acid (CH₃S(O)OH), methanesulfonic acid
94 (CH₃SO₃H, MSA), in addition to other species [*Lucas and Prinn*, 2002; *von Glasow and Crutzen*,
95 2004; *Yin, Grosjean, Flagan, et al.*, 1990; *Zaveri*, 1997].

96 Under atmospheric conditions, H₂SO₄ is the only DMS oxidation product that forms
97 new non-sea salt sulfate (nss-SO₄²⁻) particles (new CCN) that could potentially increase the
98 cloud albedo. All other products condense onto pre-existing particles, primarily sea salt,
99 leading to changes in particle composition and particle size without formation of new CCN.
100 Fewer and larger particles of mixed sea salt/CH₃SO₃⁻/nss-SO₄²⁻ composition would reduce
101 cloud albedo and increase the wash-out of particles due to collision coalescence, therefore
102 reducing cloud lifetime. Hence, the partitioning between DMS oxidation products in
103 different atmospheric environments may affect the number and size of CCN, which impacts
104 the chemistry-cloud-climate feedback in the marine atmosphere. For the remainder of this
105 work, methanesulfonate and sulfate are referred to as the anions CH₃SO₃⁻ and SO₄²⁻
106 respectively, as in our samples they are present in crystalline form. Their cation pairing may
107 include an array of ions typical for sea salt, i.e. Na⁺, Mg²⁺, K⁺ and others that are omitted for
108 clarity.

109 For a specific set of atmospheric conditions, consecutive uptake of the DMS
110 oxidation products onto cloud droplets and their subsequent oxidation in the aqueous phase,
111 results in different partitioning between CH₃SO₃⁻ and nss-SO₄²⁻. Kinetic modeling studies of
112 the CH₃SO₃⁻/nss-SO₄²⁻ partitioning in marine aerosol predict formation of minor amounts
113 of CH₃SO₃⁻ and favor production of nss-SO₄²⁻ in sea salt particles under a variety of
114 atmospheric conditions [*Hertel, et al., 1994; Kerminen, et al., 1998; Kloster, et al., 2006; Koga and*
115 *Tanaka, 1996; 1999; Lucas and Prinn, 2002; Yin, Grosjean, Flagan, et al., 1990; Zaveri, 1997*].
116 Measured values of CH₃SO₃⁻/nss-SO₄²⁻ ratios in bulk samples typically span a range from
117 0.001 (low latitudes) to 0.6 (high latitudes) [*Allen, et al., 1997; Berresheim, et al., 1990;*
118 *Burgermeister and Georgii, 1991; Galloway, et al., 1993; Ganor, et al., 2000; Kouvarakis and*
119 *Mihalopoulos, 2002; Li and Barrie, 1993; Li, Barrie and Sirois, 1993; Li, Barrie, Talbot, et al., 1993;*

120 *Li, et al.*, 1996; *Mihalopoulos, et al.*, 1992; *Saltzman, et al.*, 1985; 1986; *Saltzman, et al.*, 1983;
121 *Sciare, et al.*, 2000; *Wylie and deMora*, 1996]. Recent modeling studies indicate that under
122 certain conditions $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratios as high as 1.2 – 3.3 in marine droplets can occur
123 [*von Glasow and Crutzen*, 2004]. Specifically, high $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ values resulted from
124 model simulations for the cloudy MBL in winter conditions (surface temperature of 3-8°C
125 over the ocean). The authors concluded that these high ratios could result from previously
126 overlooked halogen chemistry that favors production of CH_3SO_3^- under cold cloud
127 scenarios.

128 The high level of detail used in this model was in principle sufficient to distinguish
129 and predict $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratios in droplets and particles of different origin, *i.e.* sea salt
130 *versus* sulfate particles [*von Glasow and Crutzen*, 2004]. However, validation of these
131 calculations requires field or laboratory data with a similar level of specificity. In this
132 manuscript we report results from single particle analysis of dry residues of cloud droplets
133 and interstitial aerosol that provide information on $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratios in individual
134 marine particles for the first time.

135 Samples were collected during the Marine Stratus Experiment (MASE) of July 2005
136 at the Point Reyes National Seashore located north of San Francisco [*MASE*, 2005]
137 (<http://www.asp.bnl.gov/MASE.html>). This field study provided an excellent opportunity to
138 sample marine particles under relatively cold cloudy conditions, which according to the
139 modeling predictions of *von Glasow and Crutzen* [*von Glasow and Crutzen*, 2004], could display
140 elevated $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratios. At the northern coast of California, cold ocean currents
141 produce preferential upwelling, resulting in low ocean temperatures (~10-15° C) even during
142 summer time. In addition, low altitude clouds form and typically shroud this region during
143 the summer months. This region is also an area of phytoplankton bloom, resulting in

144 efficient DMS production [Strub, et al., 1990; A. Thomas and Strub, 2001; A. C. Thomas and
145 Strub, 1990]. These factors provide a unique opportunity for field studies of CH_3SO_3^- and
146 nss-SO_4^{2-} partitioning in marine cloud droplets and particles representative of relatively cold
147 marine atmosphere over an area rich in DMS.

148 The complementary capabilities of three analytical techniques provide complete
149 chemical speciation of the field collected marine particles, with the aim of identifying the
150 chemical forms of particulate sulfur. The three data sets are consistent with one another and
151 indicate enhanced formation of particulate CH_3SO_3^- in sea salt droplets and particles
152 collected during MASE. This unique combination of single-particle measurements enables
153 quantitative assessment of $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratios in individual particles.

154

155 2. EXPERIMENTAL

156 2.1. **Meteorological Conditions and Sample Collection.** Particle samples were
157 collected continuously during the cloudy period between July 6th 17:00 –July 7th 9:00 Pacific
158 Standard time (July 7th 01:00 – 17:00, UTC) on a seashore site within one kilometer of the
159 Pacific Ocean at the Point Reyes National Seashore, N38°5', W122°57.43'. This site is
160 shrouded in cold clouds much of the time, as illustrated in Figure 2, and is well situated for
161 sampling cloud droplets and aerosols. Figure 2 shows backward trajectory calculations
162 performed using the HYSPLIT model [Draxler and Rolph, 2003], that end at the sampling site
163 on July 6, 21:00 PST (red) and July 7, 09:00 PST (blue). The trajectories indicate that during
164 the 36 hours preceding collection, the air mass passed over open areas of the ocean and then
165 along the northern shore of California. Backward trajectories calculated for 5 days prior to
166 collection revealed that the sampled air traveled over the Pacific Ocean and did not enter
167 continental areas in exception to ~1-2 km of the shore area adjacent to the sampling site.

168 Over the time frame of the backward trajectory calculation shown in Figure 2b, the relative
169 humidity was above 78%, the air temperature was 13-16°C and the height of boundary
170 mixing layer was 250-400 meters.

171 During sampling, the cloud/fog droplets and (interstitial) aerosol were first separated
172 using a counter-flow virtual impactor (CVI) [Ogren, *et al.*, 1985] that directs the flow of small
173 (interstitial) particles and relatively large cloud droplets into two different sampling lines: the
174 CVI line for particles (drops) larger than $\sim 5 \mu\text{m}$ and the aerosol observing system (AOS)
175 line for particles smaller than $\sim 5 \mu\text{m}$. The particles were first dried inside the CVI and AOS
176 probe lines, and the resulting dehydrated particles were collected by two compact time
177 resolved aerosol collectors (TRAC) [Laskin, *et al.*, 2006; Laskin, Iedema, *et al.*, 2003] attached
178 to each of the lines. The TRAC is a conventional one stage jet-to-plate impactor that
179 deposits particles on a rotating impaction plate containing pre-arranged substrates. In this
180 study, each substrate was exposed for 12 minutes of sample collection. The effective
181 aerodynamic cut-off size D_{50} of the TRAC is $\sim 0.36 \mu\text{m}$. Three different types of substrates
182 were used in this study: (a) Copper 400 mesh TEM grids coated with Carbon Type-B films
183 (Ted Pella, Inc.) for the CCSEM/EDX analysis, (b) silicon wafer chips (Silson Ltd, Inc.) for
184 the TOF-SIMS analysis, and (c) silicon wafer frames with silicon nitride windows (Silson
185 Ltd, Inc.) for the STXM/NEXAFS analysis. After collection, impaction plates with the
186 exposed substrates were sealed and stored pending analysis.

187 In general, particle samples collected on substrates may suffer from some artifacts.
188 These include evaporation of volatile and semi-volatile species during the sampling, storage
189 and then analysis by the applied techniques as well as possible reactions between sampled
190 particles and trace gases entering the impactor. For CH_3SO_3^- and SO_4^{2-} salts, no sampling
191 artifacts due to the volatilization are expected to occur. Artifacts like the potential reactions

192 of SO₂(g), HCl(g) and NO₂(g) with the samples inside the TRAC, could not be quantified.
193 However, their possible impacts were somewhat minimized by drying particles prior to
194 collection which would decrease their reaction kinetics.

195 **2.2. Methods of laboratory analysis.** Detailed characterization of individual
196 particles required multiple techniques. As illustrated below, applications of different
197 analytical methods are interdependent; hence, the information from one method guides
198 subsequent measurements. Three analytical techniques were applied for particle analysis: (a)
199 CCSEM/EDX – for microscopy imaging of particles and quantitative speciation of their
200 elemental composition, (b) TOF-SIMS – for qualitative detection of CH₃SO₃⁻ and SO₄²⁻
201 within individual particles, and (c) STXM/NEXAFS – for quantitative speciation of the
202 CH₃SO₃⁻ to SO₄²⁻ partitioning within individual particles.

203 A FEI XL30 digital field emission gun environmental scanning electron microscope
204 was used in this work. The microscope is equipped with an EDAX PV7761/54 ME X-ray
205 spectrometer (EDAX, Inc) with a Si(Li) detector with an active area of 30 mm² and an
206 ATW2 window. In addition to the standard SEM/EDX mode of operation, the instrument
207 can also operate in computer-controlled (CCSEM/EDX) mode for analysis of individual
208 particles. In the CCSEM/EDX mode, selected samples are inspected automatically and
209 individual particles are recognized by an increase in the detector signal above a threshold
210 level. The program then acquires an X-ray spectrum from each detected particle. In this
211 work, particles with an equivalent circle diameter larger than $\geq 0.35 \mu\text{m}$ were measured by
212 the software. The X-ray spectra were acquired for 10 s, at a beam current of $\sim 500 \text{ pA}$ and an
213 accelerating voltage of 20 kV. Additional details of the CCSEM/EDX approach employed
214 for the analysis of particles deposited onto carbon coated TEM grids can be found in our
215 recent review article [Laskin, *et al.*, 2006] and references therein.

216 A TRIFT II time-of-flight secondary ion mass spectrometer (TOF-SIMS), (Physical
217 Electronics, Inc.) was used in this work. TOF-SIMS analysis entails impacting a pulsed
218 primary ion beam onto a solid sample in vacuum and collecting secondary ions of one
219 polarity (positive or negative), using a time-of-flight (TOF) mass analyzer. The particles
220 collected on the silicon wafer chips were placed in the sample holder and subject to a $^{69}\text{Ga}^+$
221 source of primary ions in high spatial resolution mode. An accelerating voltage of 15 kV was
222 used for spectral measurements and 25 kV for mapping. The dose rate was 9.8×10^{12} ions
223 cm^{-2} . A combination of static and dynamic modes of operation allowed molecular speciation
224 of different forms of sulfur-containing compounds within individual particles.

225 STXM/NEXAFS measurements were performed at the carbon (C) (280 – 320 eV)
226 and nitrogen (N) (395 – 430 eV) K-absorption edges and at the sulfur (S) (168 – 176 eV) L-
227 absorption edge. STXM instruments at beamlines 5.3.2 (C, N) and 11.0.2. (C, N, S) of the
228 Advanced Light Source of Lawrence Berkeley National Laboratory were used for these
229 experiments. The intensity of X-rays transmitted through the sample at a fixed energy is
230 measured as the sample is raster scanned to record an image. Sequences of images are
231 acquired at closely spaced energies to record a “stack” of images, which is essentially a three-
232 dimensional map in position, energy and transmission. NEXAFS spectra from individual
233 pixels or particular regions of interest on the sample image are extracted from the stack. The
234 absorption through the sample is obtained by converting the signal (Beer-Lambert Law)
235 using the reference flux measured through a sample free region. This mapping of chemical
236 bonding information in individual particles [Hopkins, Tivanski, Marten, *et al.*, 2007; Tivanski, *et*
237 *al.*, 2007; Maria, *et al.*, 2004; Russell, *et al.*, 2002] allows a quantitative assessment of the
238 apportionment between different molecular forms of the same element, *i.e.* CH_3SO_3^- and
239 SO_4^{2-} in this work. For comparison purposes, particles of reference materials were examined

240 using TOF-SIMS and STXM/NEXAFS, including sodium sulfate (Na_2SO_4) (99.99% pure),
241 sodium methanesulfonate ($\text{CH}_3\text{SO}_3\text{Na}$) (98% pure) and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$)
242 (99.99% pure) purchased from Sigma-Aldrich.

243

244 3. EXPERIMENTAL RESULTS AND DISCUSSIONS

245 Twelve samples (6 CVI and 6 AOS samples with time intervals of ~ 1.5 -2 hours
246 between them) from the Point Reyes sampling site collected during the cloudy period were
247 analyzed using CCSEM/EDX single particle analysis. Figure 3 shows typical SEM images of
248 CVI and AOS aerosol samples. The upper images depict samples collected on silicon wafer
249 chips, while the magnified bottom images are from samples collected on TEM grid
250 supported films. As seen from the upper images, the spatial distribution of particles is
251 inhomogeneous. Larger particles are concentrated in the central region, directly under the
252 deposition nozzle and smaller particles are scattered widely from this area. Thus, a
253 statistically significant analysis of particles by CCSEM/EDX requires sampling across the
254 deposition spot, as indicated by the rectangles in the images. The elemental composition was
255 analyzed for ~ 1000 particles in a region of $500 \mu\text{m} \times 80 \mu\text{m}$ across the deposition spot for
256 each tested sample.

257 A brief inspection using manual SEM/EDX analysis indicated two prominent
258 particle classes, characteristic for both the CVI and AOS samples. The particles were mostly
259 either sea salt or sulfur-rich (S-rich) particles. S-rich particles are composed of a mixture of
260 H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$, as discussed below. Sea salt particles are easily recognized (Figure 3,
261 bottom panels) as they are typically of super micron size with cubic-shaped NaCl crystals
262 surrounded by irregularly shaped residues of other salts. In contrast, S-rich particles are

263 submicron in size and spherical. Consistent with the schematic of sulfur-aerosol-climate links
264 presented in Figure 1, larger sea salt particles dominate the CVI samples while smaller S-rich
265 particles are more abundant in the AOS samples.

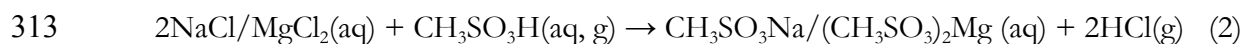
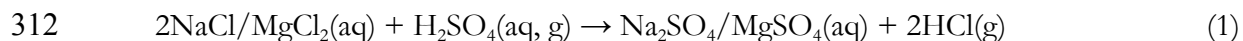
266 In this work, as illustrated in panel (a) of Figure 4, a simple rule-based assignment
267 was used to separate individual particles into three major classes. All particles (~10,000)
268 detected in the CCSEM/EDX analysis of 12 selected samples are combined in a group and
269 then all particles containing sulfur above the threshold level of 0.5 atomic percent (as
270 detected by the EDX analysis) are separated. Next, sulfur containing particles that also
271 contain sodium are assigned into the “sea salt” class, while those containing only S, O, and
272 N are assigned to the “S-rich” class. Particles in the S-rich class are expected to display
273 mixed H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ composition. All remaining particles are assigned to one, non-
274 specific class of “other” particles. Panel (b) of Figure 4 illustrates the results of this
275 classification scheme for particles sampled from the CVI and AOS lines over the cloudy
276 period studied here. In general, significant populations of sea salt particles dominate samples
277 collected from both sampling lines, indicating that even submicron particles typical for the
278 AOS samples are of sea mist origin rather than sulfates formed by nucleation. Nucleated
279 sulfates presumably fall into the “S-rich” class and their relative population ranges from
280 between 2 – 6% and 15 – 30 % in the CVI and AOS samples, respectively. Relative
281 contributions of “other” particles normally remains at the 3 – 5% level and only occasionally
282 reaches values of 8 – 9%. Particle class composition remained largely the same over the
283 entire period of the cloudy episode for both sampling lines.

284 Figure 5 illustrates particle number size distributions of sea salt and S-rich particles
285 determined from the CCSEM/EDX data, combined for the 6 CVI and 6 AOS analyzed

286 samples. The four distributions are normalized to the total number of particles. Plots
287 presented in panels (a) and (b) are shown on the same scale to facilitate comparison. Hence,
288 areas below the distribution curves indicate relative populations of each particle class. The
289 size distributions in Figure 5 indicate a mode size of $\sim 0.8 \mu\text{m}$ for residues of sea salt
290 particles in the CVI samples. A smaller mode size of $0.4\text{-}0.5 \mu\text{m}$ is observed for sea salt
291 particles in the AOS samples. The number concentration ratio of sea salt particles found in
292 the CVI samples to those in the AOS samples is approximately 2:1. The situation is reversed
293 for the S-rich particles where the concentration of S-rich particles in the AOS sample is ~ 2
294 times higher than for the CVI samples. The size distributions of S-rich particles peak at ~ 0.5
295 μm and $\sim 0.4 \mu\text{m}$ for the CVI and AOS samples, respectively. However, the abrupt fall-off of
296 the size distributions at $\sim 0.3\text{-}0.4 \mu\text{m}$ is due to the impactor cut-off function and
297 comparisons of the size distributions in Figure 5 must be made with this caveat in mind.

298 The CCSEM/EDX analysis indicates sulfur enrichment in sea salt particles. Figure 6
299 shows the CCSEM/EDX measured S/Na elemental ratios for sea salt particles detected in
300 the CVI (upper panel) and AOS (bottom panel) samples. The dashed horizontal line is the
301 nominal ratio of $S/Na = 0.06$, typical for sea water [CRC, 1999]. The solid curved line
302 indicates the experimentally determined deviation of the S/Na ratios for large sea salt
303 particles. This deviation is a result of ZAF sensitivity effects [Goldstein, *et al.*, 2003], which
304 were omitted from the quantification method [Laskin and Cowin, 2001; Laskin, *et al.*, 2006].
305 The S/Na elemental ratios are systematically higher than expected for unreacted sea salt
306 particles. This indicates cloud and chemical processing of sea salt particles with sulfur
307 compounds, which is consistent with the DMS chemistry expected in the region of this field
308 campaign.

309 For cloud and chemically processed sea salt particles, chemical reactions of sea salt
310 components and added sulfuric and/or methanesulfonic acids can be presented by the
311 following, highly simplified, albeit illustrative reactions:



314 These reactions liberate HCl gas to the atmosphere, leaving particles enriched in sulfur and
315 depleted in chloride. Additional sulfur-halogen processes could also lead to similar changes
316 in the elemental composition of sea salt particles [Finlayson-Pitts, 2003; Finlayson-Pitts and
317 Hemminger, 2000]. However, a full discussion of the detailed reaction mechanism and its
318 kinetics is beyond the scope of this manuscript.

319 The sulfur enrichment is larger for sea salt particles in the CVI samples, compared to
320 those in the AOS samples. This is likely a result of the greater activation of particles (larger
321 droplets and higher water content) sampled in the CVI line, compared to the smaller sizes
322 sampled in the AOS line. If so, the higher water content would provide an enhanced
323 capacity for soluble species in larger droplets, and therefore higher S/Na ratios in the CVI
324 samples of dry residues would be expected.

325 CCSEM/EDX analysis provides quantitative data on the S/Na ratios over a
326 statistically significant number of particles. However, no molecular information on the
327 chemical forms of sulfur can be inferred from EDX spectroscopy. Molecular speciation of
328 sulfur-containing compounds is revealed by complementary analysis of individual particles
329 using TOF-SIMS. To identify chemical forms of sulfur, TOF-SIMS ionic maps were
330 produced for selected ions indicative of sulfate (SO_4^- , HSO_4^-), methanesulfonate (SO_3^- ,
331 CH_3SO_3^-), sodium (Na^+) and ammonium (NH_4^+). Figure 7 shows ionic maps ($100 \mu\text{m} \times 100$

332 μm) characteristic for CVI samples collected during this cloudy period. The maps indicate
333 that methanesulfonate (SO_3^- , CH_3SO_3^-) ions are co-located with Na^+ ions, while sulfate
334 (SO_4^{2-} , HSO_4^-) ions are co-located with NH_4^+ ions. Furthermore, the characteristic locations
335 of sulfate and the methanesulfonate ions do not overlap. These observations support the
336 conclusion that methanesulfonate is present in relatively large sea salt particles, while the
337 characteristic sulfate ions are primarily generated from smaller $(\text{NH}_4)_2\text{SO}_4$ particles. To
338 confirm this conclusion, TOF-SIMS negative spectra integrated from the areas of sea salt
339 and $(\text{NH}_4)_2\text{SO}_4$ particles were compared with those acquired from laboratory prepared
340 samples of $\text{CH}_3\text{SO}_3\text{Na}$ and $(\text{NH}_4)_2\text{SO}_4$ particles. This comparison is shown in Figure 8. The
341 characteristic spectra of field collected particles match those of the standard materials nearly
342 perfectly. Although not shown here, negative spectra of Na_2SO_4 , $\text{CH}_3\text{SO}_4\text{Na}$, and HO-
343 $\text{CH}_2\text{SO}_3\text{Na}$ particles were also measured (see supplement A), and did not match the spectra
344 measured in the field samples.

345 However, these TOF-SIMS observations should be interpreted with some caution.
346 Particles were examined with a low primary ion dose (static mode of operation), resulting in
347 an analysis depth of 3 – 5 nm, thus corresponding to the outermost atomic layers of the
348 particles. As particles dry out, the less soluble salts precipitate first and form the core of the
349 particle, while more soluble salts are present in the outer layer. Thus, the observed abundant
350 mass spectrometry signal originating from the highly soluble $\text{CH}_3\text{SO}_3\text{Na}$ salt does not
351 confirm the absence of sulfates in these sea salt particles as sulfates could be present at the
352 particle core, and therefore not detectable in this operating mode of the TOF-SIMS
353 instrument. Nevertheless, the important observation is that the $(\text{NH}_4)_2\text{SO}_4$ particles show
354 little or no signal of CH_3SO_3^- characteristic for methanesulfonate salts.

355 In principle, a combination of static and dynamic modes of operation of the TOF-
356 SIMS allows monitoring of chemical speciation of compounds within particles [*Gaspar, et al.,*
357 2004; *Laskin, Gaspar, et al., 2003; Lin, et al., 2007*]. However, these experiments are technically
358 challenging, and inherently qualitative, providing no quantitative information on the
359 concentrations of different species within particles. An alternative approach uses
360 STXM/NEXAFS analysis to study chemical bonding information of different elements for
361 individual particles. Supported by the TOF-SIMS observations, this enables the speciation of
362 different elements within particles allowing quantification of $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$ ratios in
363 individual particles.

364 Figure 9(a) shows a representative STXM image ($12\ \mu\text{m} \times 12\ \mu\text{m}$) recorded at 290.8
365 eV of a sample region containing two particle classes observed in our experiments. Contours
366 of the sea salt and the S-rich particles in the STXM image are marked by squares and circles,
367 respectively. Maps generated by principle component analysis (PCA) of the acquired
368 STXM/NEXAFS spectra are shown, with colors corresponding to X-ray absorbance regions
369 specific for nitrogen, carbon and sulfur. In contrast to the TOF-SIMS maps, these PCA
370 maps generated from STXM/NEXAFS analysis are indicative of the entire composition of
371 sampled particles due to the fact that transmitted intensity through the sample is measured.
372 Comparison of the PCA maps presented in Figure 9(b) and (c) shows that these particles
373 either contain carbon or nitrogen, but not both elements. This observation is consistent with
374 particles having either mixed sea salt/ $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$ (red) or mixed $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$
375 (black) composition. The spectral contours of the N K-edge NEXAFS spectra of the mixed
376 $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ and purchased $(\text{NH}_4)_2\text{SO}_4$ are nearly identical (unpublished data), which
377 is further evidence that these small round particles are mixed $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$. The low
378 carbon absorption in purchased $\text{CH}_3\text{SO}_3\text{Na}$ and the sea salt/ $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ particles

379 made peak assignments in their spectra ambiguous, thus preventing comparisons of the C-K
380 edge NEXAFS spectra. The PCA maps presented in Figure 9(d) indicate two different types
381 of sulfur characteristic for two particle classes. The particles which contain nitrogen (black)
382 display a sulfur L-edge NEXAFS spectrum indicative of SO_4^{2-} which is consistent with these
383 particles being assigned as mixed $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$. The particles which contain carbon
384 (red) display a sulfur L-edge spectrum that is intermediate of CH_3SO_3^- and SO_4^{2-} . This is
385 consistent with these particles having a mixed sea salt/ $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$ composition.

386 Furthermore, combined data sets from CCSEM/EDX and STXM/NEXAFS
387 measurements, enable quantification of the $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$ ratios on an individual particle
388 basis. Elemental analysis performed using CCSEM/EDX measures the total S/Na ratio for a
389 large number of particles. Separately, STXM/NEXAFS analysis provides quantification of
390 the partitioning between CH_3SO_3^- and total- SO_4^{2-} (nss and ss) on an individual particle basis.
391 Combining these two data sets, in addition to the literature reported value for ss- $\text{SO}_4^{2-}/\text{Na}$
392 = 0.06 [CRC, 1999], enables the total- SO_4^{2-} to be decoupled into nss and ss components,
393 leading to the quantitative assessment of $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratios in particles as will be
394 described below.

395 Figure 10(a) presents S L-edge NEXAFS spectra of the Na_2SO_4 and $\text{CH}_3\text{SO}_3\text{Na}$
396 reference particles respectively. The Na_2SO_4 spectrum displays three distinct peaks at 170.9
397 eV, 172.1 eV and 172.9 eV, in good agreement with literature data [Hitchcock, *et al.*, 1990].
398 Sulfur spectra recorded from $(\text{NH}_4)_2\text{SO}_4$ and Na_2SO_4 , both of which have an oxidation state
399 of +6, were identical to one another. However, the $\text{CH}_3\text{SO}_3\text{Na}$ spectrum is considerably
400 different, its broad contour has no resolvable peaks and the peak maximum occurs at lower
401 energy. The peak maximum of the Na_2SO_4 spectrum (or sulfate in general) appears at higher
402 energy because of its higher oxidation state (+6 for Na_2SO_4 versus +5 for $\text{CH}_3\text{SO}_3\text{Na}$).

403 These differences in the spectral contours of SO_4^{2-} and CH_3SO_3^- are advantageous for
404 determining the partitioning between these two species in individual particles. Mixing of
405 CH_3SO_3^- and SO_4^{2-} in particle spectra would lead to a broadening of the resolved peaks
406 present in SO_4^{2-} and a change in the relative intensities of the three peaks. These changes in
407 spectral contours as a function of the proportion of CH_3SO_3^- and SO_4^{2-} were used to
408 quantify the amount of CH_3SO_3^- and total- SO_4^{2-} present in individual particles. For
409 example, the $\text{CH}_3\text{SO}_3^-/\text{total-SO}_4^{2-}$ ratio from the single particle pertinent to Figure 10(b) is
410 determined as 20:80%. The corresponding spectrum modeled for 20% CH_3SO_3^- and 80%
411 total- SO_4^{2-} is shown for comparison. A good agreement between the spectral contours is
412 observed. Further details about the sulfur L-edge spectroscopy are provided in Supplement
413 B.

414 As STXM/NEXAFS is significantly more time and labor intensive than
415 CCSEM/EDX, a single CVI sample from the studied time period was selected for
416 quantitative analysis. A CVI sample was chosen due to the higher proportion of mixed sea
417 salt/ $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ particles. Several other CVI and AOS samples from this time
418 period were surveyed using STXM/NEXAFS, and confirmed qualitative observations
419 reported for the selected sample in this publication. The STXM/NEXAFS analysis method
420 was applied to sulfur L-edge spectra recorded from ~ 100 individual mixed sea
421 salt/ $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ particles to determine their $\text{CH}_3\text{SO}_3^-/\text{total-SO}_4^{2-}$ ratio. In Figure
422 11 the $\text{CH}_3\text{SO}_3^-/\text{total-SO}_4^{2-}$ ratio is plotted against the average particle diameter. As most
423 particles are irregular in shape, the equivalent circle diameter was calculated from the particle
424 projection area. The error bars displayed in Figure 11 represent the standard deviation in the
425 mean $\text{CH}_3\text{SO}_3^-/\text{total-SO}_4^{2-}$ ratio, which is derived from the calibration plot presented in
426 Supplement B. No obvious size dependence was observed in the $\text{CH}_3\text{SO}_3^-/\text{total-SO}_4^{2-}$ ratio

427 for the particles studied, which ranged from $\sim 1 - 5 \mu\text{m}$ in diameter. Hence, the mean
428 $\text{CH}_3\text{SO}_3^-/\text{total-SO}_4^{2-}$ ratio, represented by the solid black line in Figure 11 (the two dashed
429 lines are the standard deviation from the mean), yield a value of 0.52 with a standard
430 deviation of ± 0.30 , assuming invariance with particle size.

431 Figure 12(a) presents the normalized distribution of the total-S/Na ratios detected in
432 over 7000 individual sea salt/ $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ particles using the CCSEM/EDX
433 technique. The frequency of particles displaying a particular total S/Na ratio is normalized to
434 the total number of particles examined. This data is plotted for different size bins with
435 particle diameters ranging from 0.3 to $> 2 \mu\text{m}$. The size bins are set using the $\log(D_p)$ scale
436 with an even spacing of 0.2, where D_p represents particle diameter. The total S/Na ratio is
437 between 0.05 – 1 and peaks at 0.15 for particles in all size bins. This peak total S/Na value of
438 0.15 is higher than that characteristic for sea water (0.06) [CRC, 1999]. The higher observed
439 value can be understood by considering acid displacement reactions of NaCl/MgCl₂ present
440 in sea water with H₂SO₄ and CH₃SO₃H, which increase the total S present in the particles.
441 Sea salt fully reacted with H₂SO₄ would yield a total S/Na ratio of 0.59. Clearly, the range of
442 total S/Na values observed in these multi-component particles exceeds this, reaching values
443 as high as 1. Again, this higher observed value can be understood by considering reactions of
444 NaCl/MgCl₂ with CH₃SO₃H, which may yield a total S/Na ratio of 1.18. An enhancement in
445 the fraction of particles displaying total S/Na ratios > 0.15 is observed for smaller particles
446 that display larger surface-to-volume ratios. This observation could suggest that surface area
447 controls the uptake of gas-phase CH₃SO₃H by liquid sea salt particles. The longer average
448 atmospheric residence times of smaller particles may also increase the probability of reaction
449 resulting in CH_3SO_3^- and nss-SO_4^{2-} enrichment.

450 As noted above, calculation of the $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratio relies on a combination
 451 of data recorded using both STXM/NEXAFS and CCSEM/EDX. The method for
 452 combining this data is presented here. For the mixed sea salt/ $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ particles,
 453 the total S/Na ratio is equal to the sum of $\text{ss-SO}_4^{2-}/\text{Na}$, $\text{nss-SO}_4^{2-}/\text{Na}$ and $\text{CH}_3\text{SO}_3^-/\text{Na}$
 454 ratios, as described by equation 3:

455

$$456 \quad \frac{[\text{total-S}]}{[\text{Na}]} = \underbrace{\frac{[\text{ss-SO}_4^{2-}]}{[\text{Na}]}}_{=0.06} + \frac{[\text{nss-SO}_4^{2-}]}{[\text{Na}]} + \frac{[\text{CH}_3\text{SO}_3^-]}{[\text{Na}]} \quad (3)$$

457

458 The $\text{ss-SO}_4^{2-}/\text{Na}$ ratio is 0.06 [CRC, 1999], leaving two unknowns in this equation. The
 459 $\text{CH}_3\text{SO}_3^-/\text{total-SO}_4^{2-}$ ratio is determined as 0.52 ± 0.30 using the STXM/NEXAFS
 460 technique. This ratio can be written as follows:

461

$$462 \quad \frac{[\text{CH}_3\text{SO}_3^-]}{[\text{total-SO}_4^{2-}]} = \frac{[\text{CH}_3\text{SO}_3^-]/[\text{Na}]}{[\text{total-SO}_4^{2-}]/[\text{Na}]} = \frac{[\text{CH}_3\text{SO}_3^-]/[\text{Na}]}{0.06 + [\text{nss-SO}_4^{2-}]/[\text{Na}]} \quad (4)$$

463 This leaves the same two unknowns as in equation 3. These two equations can now be
 464 solved to determine values for both $[\text{CH}_3\text{SO}_3^-]/[\text{Na}]$ and $[\text{nss-SO}_4^{2-}]/[\text{Na}]$.

465 This analysis method is applied to the data presented in Figure 12(a) to yield Figure
 466 12(b), which displays the distribution of $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ in individual particles for
 467 different size bins. As particle diameter increases, the distribution of $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$
 468 shifts to higher values, *i.e.* sulfur in larger particles is mostly in the form of CH_3SO_3^- , while
 469 sulfur content in smaller particles is dominated by the SO_4^{2-} form.

470 The peak of the distribution presented in Figure 12(b), which uses the mean
471 $\text{CH}_3\text{SO}_3^-/\text{total-SO}_4^{2-}$ ratio of 0.52, yields a $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ partitioning ratio of 0.6.
472 Using the standard deviation in the mean $\text{CH}_3\text{SO}_3\text{Na}/\text{total-SO}_4^{2-}$ ratio of ± 0.30 , the lower
473 and upper limits on the $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratio are calculated as 0.30 and 1.10. The large
474 variation in this ratio could be attributed to differences in the individual particle history, the
475 long duration over which the particles were sampled, the uncertainty associated with the
476 measurement and the assumptions associated with invariance of $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$ with
477 particle size.

478 Therefore, all the observations presented in this manuscript so far, can be
479 summarized as follows. Particles collected during the cloudy period between July 6th 17:00-
480 July 7th 9:00 (PST) can be divided in two major particle classes: (a) sea salt particles
481 composed of a mixture of sea salt/ $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$ and (b) S-rich particles of mixed
482 $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ composition. Qualitatively, these observations are in agreement with the
483 schematic of the sulfur-aerosol-climate links in the MBL in Figure 1. Indeed, the presence of
484 CH_3SO_3^- in sea salt particles indicates substantial formation and fast uptake of $\text{CH}_3\text{SO}_3\text{H}$ by
485 activated droplets containing sea salt presumably resulting from the oxygen addition channel
486 in the DMS oxidation mechanism. Formation of mixed $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ particles is
487 indicative of H_2SO_4 nucleation resulting from the H abstraction channel of DMS oxidation.
488 Therefore, the quantitative assessment of partitioning between two different forms of sulfur,
489 *i.e.* CH_3SO_3^- and nss-SO_4^{2-} , is important for kinetic modeling as it is an inherent indicator of
490 the pathways of DMS oxidation in the environment of the given geographic location. The
491 partitioning between these reaction products is important for climate considerations as the
492 result impacts the number and size of CCN produced in the marine atmosphere.

493 The $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-} > 0.6$ ratios in sea salt particles reported in this study are high
494 compared to previous measurements at similar latitudes. The reported ratios are similar to
495 those from polar latitudes where the temperature is lower, a factor known to enhance the
496 addition pathway leading to formation of CH_3SO_3^- . The results presented here are somewhat
497 comparable with model calculations which predict higher $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratios in the
498 summer for pristine marine air sampled under cold (276 K), cloudy conditions and implying
499 additional oxidation reactions of DMS with halogen radicals [*von Glasow and Crutzen, 2004*].
500 However, there is an important aspect of the presented data that contradicts modeling study
501 of *von Glasow and Crutzen* [2004]. The TOF-SIMS analysis of particle samples (see Fig. 7)
502 indicate that CH_3SO_3^- is exclusively associated with sea salt particles, but not with
503 $(\text{NH}_4)_2\text{SO}_4$ particles. This finding disagrees with the modeling results that indicate significant
504 formation of CH_3SO_3^- in sulfate particles as a result of their smaller size and higher surface-
505 to-volume ratio compared that typical for sea salt particles. Furthermore, despite their
506 different starting sizes, the sulfate and the sea salt particles would grow to aqueous droplets
507 that are roughly of the same size, if activated. As a result, the condensed compounds should
508 be quite similar in the different activated particles. This observed selectivity of CH_3SO_3^- to
509 sea salt particles is quite puzzling and additional studies are required to understand this
510 discrepancy.

511 The discrepancy is even more intriguing given that our numerical model calculations
512 of the atmospheric chemistry occurring in the area of the field experiment suggests that
513 consideration of cloud chemistry is essentially required to explain the high $\text{CH}_3\text{SO}_3^-/\text{nss-}$
514 SO_4^{2-} and S/Na ratios reported in this study. These modeling results are presented and
515 discussed below.

516 During the cloudy period studied here, meteorological data indicate that air parcels
517 arriving to the sampling site were first swiftly transported from the open ocean area and then
518 turned southbound along the coastline of northern California (Figure 2) where it remained
519 for ~12-18 hours prior to sampling. A systematic analysis of phytoplankton pigment
520 concentrations in this area (derived from satellite based multi-annual records) indicate an
521 order of magnitude higher phytoplankton concentration in the narrow latitudinal range
522 adjacent to the shore. Specifically, within 100-200 km of the coast, typical concentrations of
523 phytoplankton of ~5 µg/l are reported, while 300-400 km offshore these decrease to ~0.5
524 µg/l [A. C. Thomas and Strub, 1990]. Therefore, the key factor determining the $\text{CH}_3\text{SO}_3^-/\text{nss-}$
525 SO_4^{2-} and total-S/Na ratios in sea salt particles is most likely the amount of time the air mass
526 spent in the area of high DMS emissions (high phytoplankton concentrations) which is in
527 the order of ~18 hours or less prior to sampling at Pt. Reyes.

528 A Lagrangian box-model [Zaveri, 1997] was used to simulate atmospheric oxidation
529 of DMS in the air mass that originated over unpolluted open ocean areas and entered the
530 region of high DMS concentration ~18 hour prior to the sampling which corresponds to ~
531 6 am local time. Two model scenarios were examined: (a) gas-phase chemistry only, and (b)
532 coupled gas- and cloud-phase chemistry. The initial conditions for model runs and a brief
533 description of the model are given in supplement C.

534 Figure 13 shows the temporal evolution of DMS, $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$, and total
535 S/Na for gas-chemistry only and coupled gas- and cloud-phase chemistry scenarios. A few
536 hours are required to build up the SO_2 concentration from gas-phase DMS oxidation in the
537 relatively clean air mass as it was advected along the coast over high DMS emissions region
538 for the next 12-18 hours. During this time, CH_3SO_3^- is efficiently formed in particles, while
539 formation of nss-SO_4^{2-} is somewhat delayed. The gas-chemistry-only model results indicate

540 that the $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratio in sea salt particles reaches a maximum of ~ 0.18 during the
541 early stages of DMS oxidation (< 6 hours) because formation of $\text{CH}_3\text{SO}_3\text{H}$ proceeds more
542 rapidly early in the day when compared to H_2SO_4 formation. Later, as both OH and SO_2
543 concentrations increase, formation of H_2SO_4 begins to exceed that of $\text{CH}_3\text{SO}_3\text{H}$, resulting in
544 a decrease in the particulate $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratio to a quasi-steady-state value of ~ 0.13 ,
545 which is about a factor of 5 lower than the observed ratios seen in Figure 11b. Also, a
546 negligible increase in the modeled values of the total-S/Na ratio is seen even after 18 hours
547 of processing, which is at odds with the measurements for the field-collected sea salt
548 particles as seen in Figure 11a.

549 Atmospheric conditions during our field study most likely resemble the coupled gas
550 and cloud chemistry scenario. Indeed, the coupled gas- and cloud-phase model results show
551 that the $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ bulk ratio in sea salt particles reached a maximum of ~ 0.3 in ~ 6
552 hours and then remained fairly steady for the rest of the simulation period. This value is
553 comparable within a factor of ~ 2 to our measurements. Also, the total-S/Na bulk ratio is
554 predicted to increase up to ~ 0.09 in 12 hours, which is similar to the observed values. These
555 results therefore suggest that cloud-phase oxidation of SO_2 , DMS, DMSO, MSIA, and MSA
556 played an important role under the atmospheric conditions encountered during this field
557 study.

558 We note that the purpose of these modeling calculations is to evaluate the feasibility
559 of the plausible hypothesis rather than providing detailed cross-comparison between field
560 and modeling data, which lies beyond the scope of this manuscript. With this regard, it is
561 important to note that modeled $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ and total-S/Na ratios is sensitive to a
562 number of parameters, which include DMS flux, temperature, sea-salt particle concentration
563 and size distribution, and photolysis rate. Additionally, halogen chemistry and nucleation

564 (new particle formation) were neglected in the present model, but may play an important
565 role. The influence of these parameters are interesting topics for more detailed modeling
566 studies where the field data provided here could be used for validation.

567

568 **5. CONCLUSIONS AND ATMOPHERIC IMPLICATIONS**

569 This study presents the first observations of both CH_3SO_3^- and SO_4^{2-} sulfur
570 compounds in marine aerosol, identified on a single particle basis. Both TOF-SIMS and
571 STXM/NEXAFS techniques indicate an external mixture consisting primarily of two
572 particle classes; mixed sea salt/ $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$ and S-rich particles of mixed
573 $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ composition. Unambiguous, qualitative speciation of sulfur containing
574 compounds and quantitative assessment of the $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratios are facilitated
575 using combined data sets from three techniques: CCSEM/EDX – quantitative assessment of
576 elemental composition of individual particles, TOF-SIMS – qualitative molecular speciation
577 of sulfur-containing compounds in individual particles, STXM/NEXAFS – quantitative
578 assessment of different forms of sulfur within individual particles. The data provided by
579 these techniques offer a rich set of qualitative and quantitative information that is of primary
580 importance to atmospheric processes in the MBL involving sea salt and marine sulfate
581 particles.

582 For the first time, size-dependent nss-S/Na and $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-}$ ratios are
583 reported for marine particles. Characteristic ratios of $\text{nss-S/Na} > 0.10$ are reported for sea
584 salt particles, with higher values observed for smaller particles, indicating more extensive
585 formation of sulfur-containing salts. Characteristic ratios of $\text{CH}_3\text{SO}_3^-/\text{nss-SO}_4^{2-} > 0.60$ are
586 reported for sea salt particles of all sizes, with higher values for large particles. This indicates

587 that CH_3SO_3^- salts are likely the dominant form of nss-sulfur in large particles while SO_4^{2-} is
588 more common in smaller particles.

589 In the past, much attention has been given to the hygroscopic and optical properties
590 of sea salt aerosol and the corresponding mixed sea salt/sulfate particles that can be formed
591 as a result of the $\text{DMS} \rightarrow \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4$ reaction sequence that is assumed to dominate in the
592 mid-latitude marine boundary layer. However, our analysis of field collected sea salt particles
593 and presented in this manuscript indicate that DMS conversion to MSA can result in
594 $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-} > 0.6$ and $\text{nss-S/Na} > 0.1$ ratios, as were observed under specific conditions
595 of the coastal area north of San Francisco. These findings indicate that modeling of the
596 marine boundary layer (MBL) aerosols and cloud formation processes require extensive data
597 on the hygroscopic and CCN properties of mixed sea salt/ $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$ and perhaps other
598 organo-sulfur particles. These data are fairly scarce and require future research.

599

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619 **Supplemental Information Available:**

620 Supplement A - TOF-SIMS spectra of particles prepared from purchased standard materials.
621 Supplement B - Determination of $\text{CH}_3\text{SO}_3^-/\text{total-SO}_4^{2-}$ ratio in individual sea salt particles
622 Supplement C - Description of the model and key constraints.

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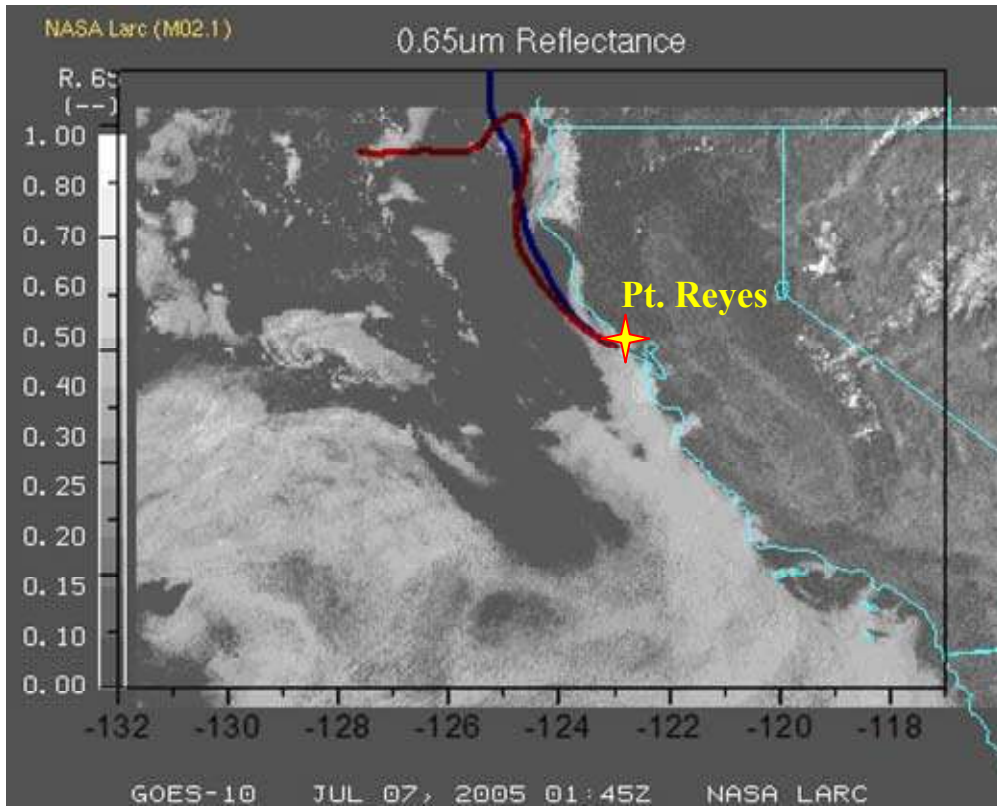
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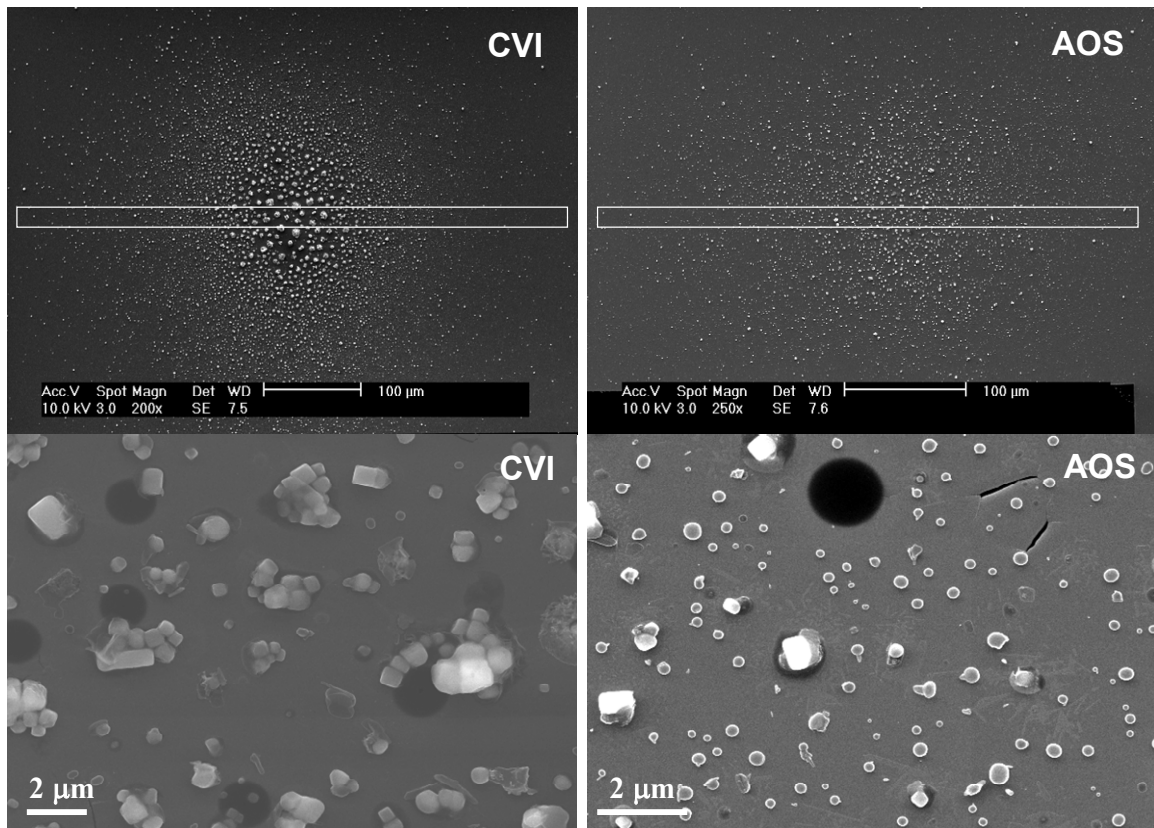


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942 **Figure 2** GOES-10 satellite image (0.65 micron cloud reflectivity at 4 km resolution) of the
943 California coast, at July 6, 17:45 PST (July 7, 1:45 UTC), showing extensive coastal stratus
944 typical of this region. Superimposed on this image are 48 hour HYSPLIT backtrajectories
945 starting at 10 m AGL on July 6, 21:00 PST (red) and July 7, 09:00 PST (blue)

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951 **Figure 3** SEM images of two samples collected from the CVI and AOS sampling lines
952 during the cloudy period on July 7, 2005. The upper images are the entire samples and
953 illustrate the spatial inhomogeneity of the deposition spot. Rectangles indicate the regions
954 inspected by CCSEM/EDX analysis. The lower images are magnified fields of view,
955 showing representative particles from the central areas of the samples. Sea salt particles are
956 larger, irregularly shaped supermicron particles with NaCl cubic crystal cores. Ammonium
957 sulfate particles are spherical submicron particles.

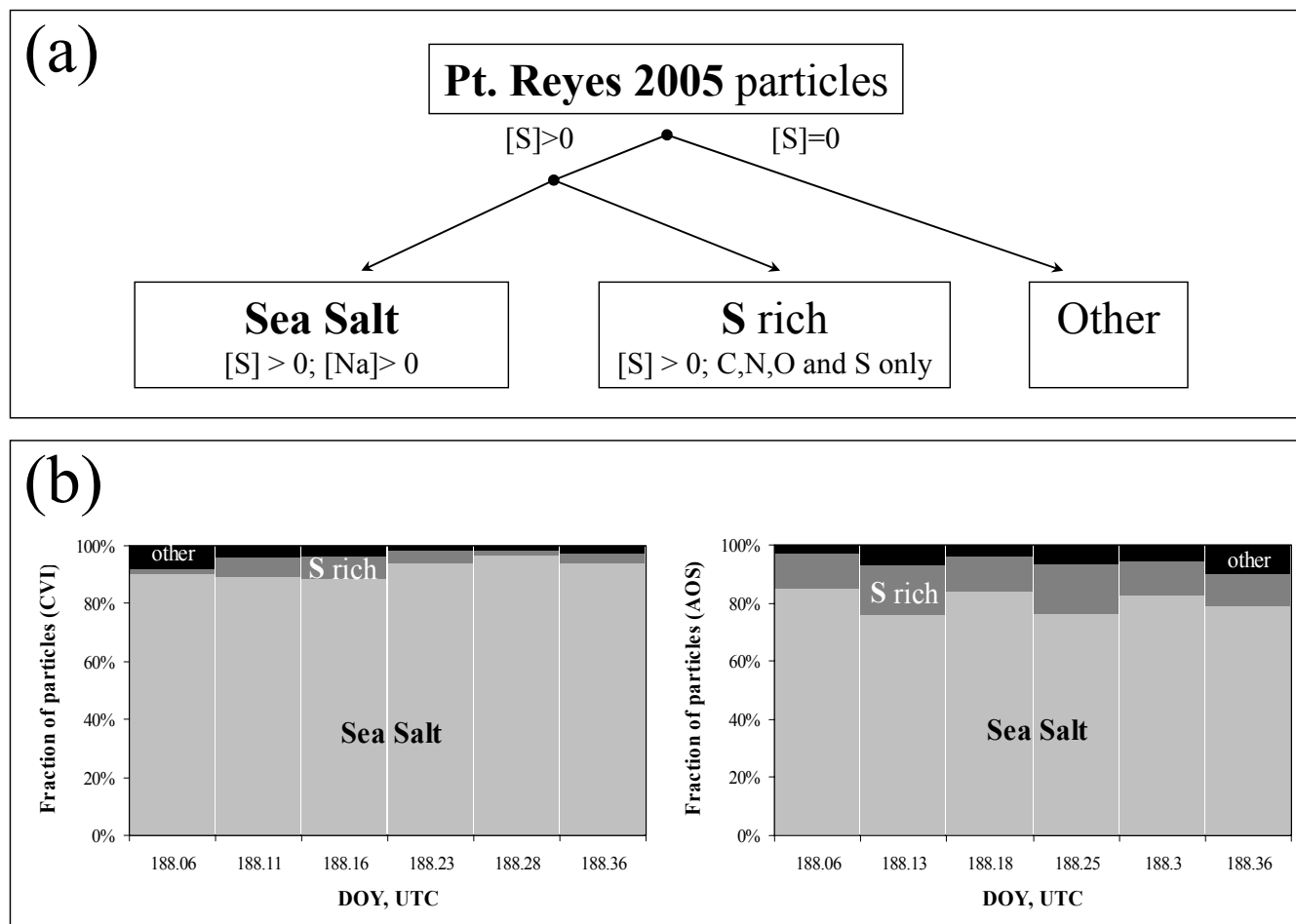


Figure 4 (a) Classification scheme applied to the samples collected during the cloudy period on the night of July 7, 2005 (Point Reyes 2005). (b) Stacked column chart diagram of particle-classes present in the CVI (left panel) and the AOS (right panel) samples.

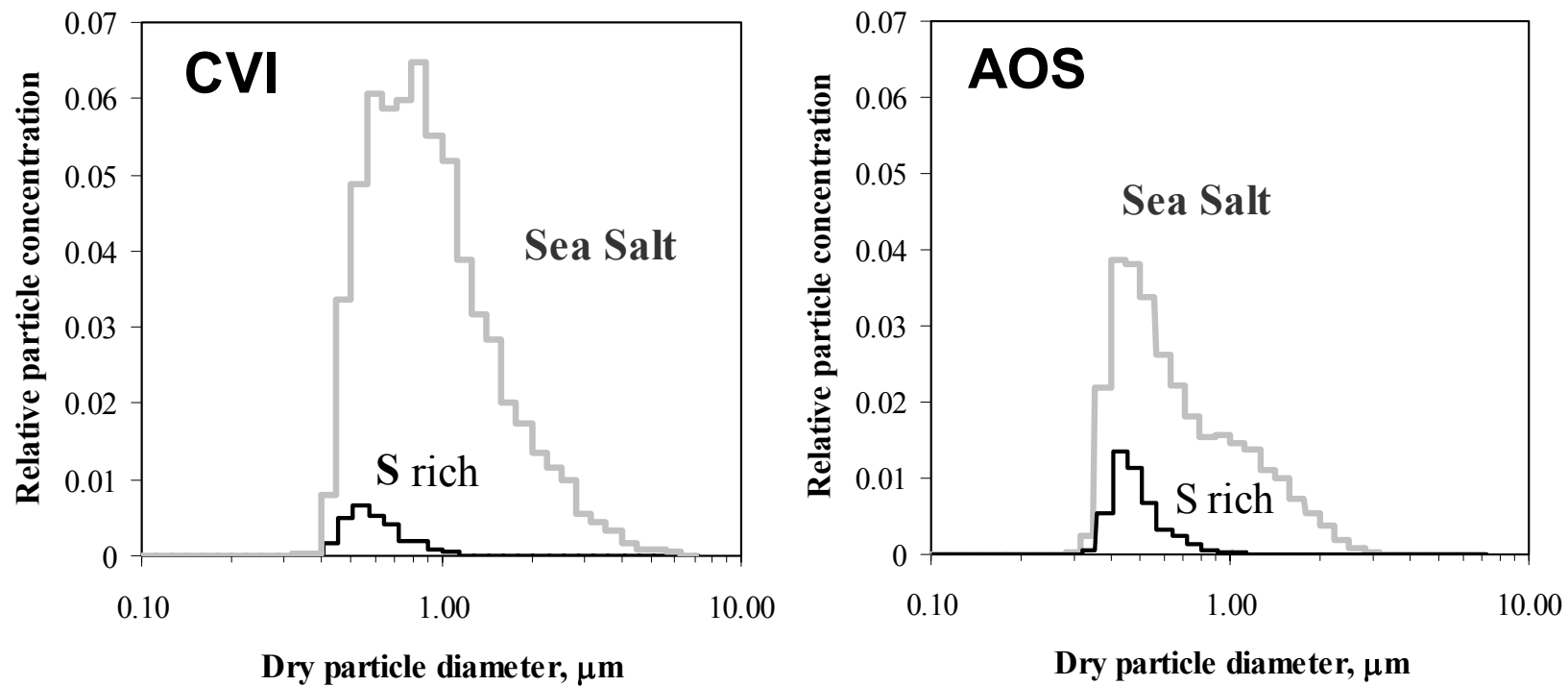


Figure 5 Number distributions of sea salt and S-rich particles in CVI (left panel) and AOS (right panel) samples measured by the CCSEM/EDX analysis. For comparison purposes, all distributions are normalized to the total number of analyzed particles.

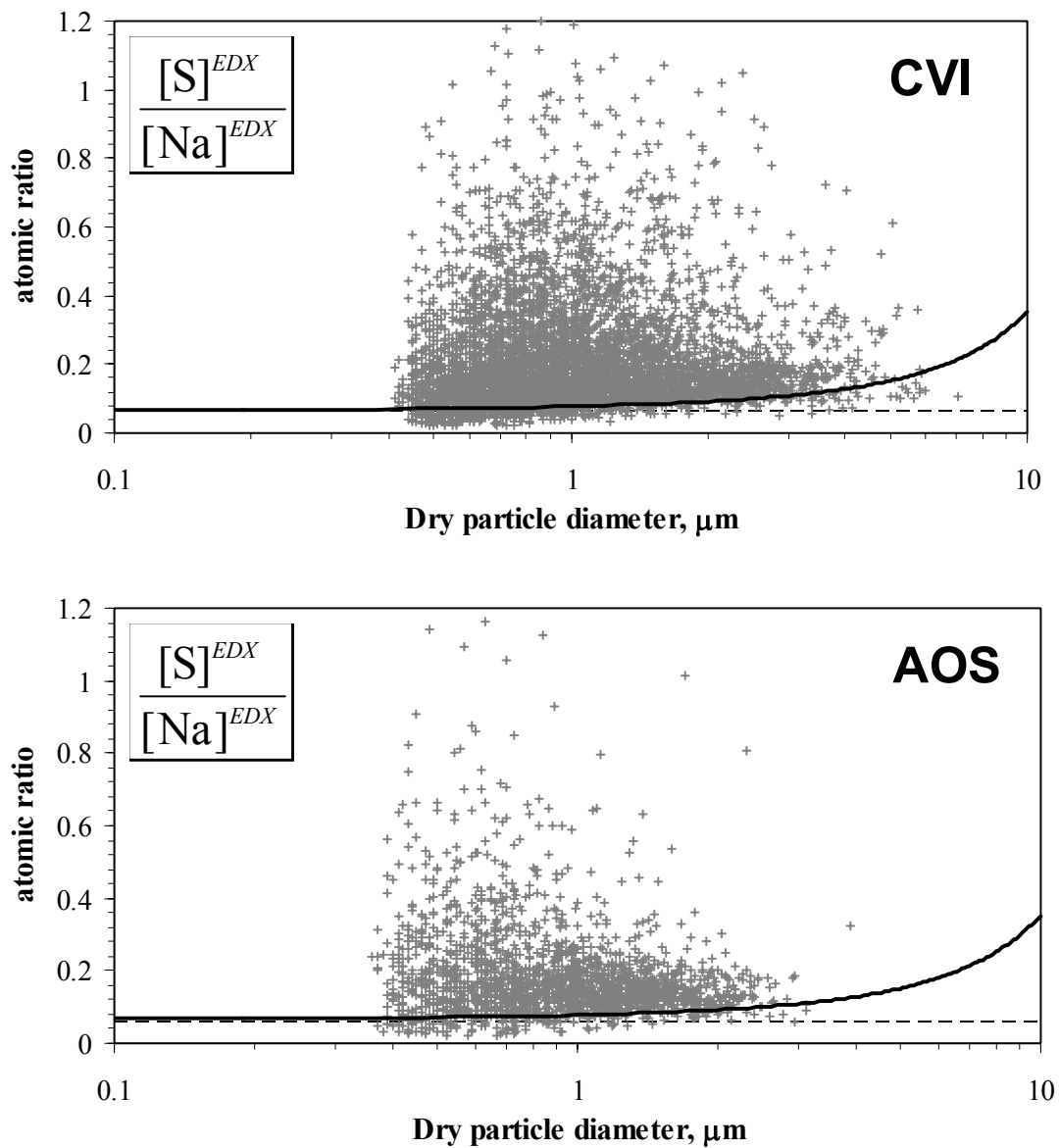


Figure 6 Elemental ratios of S/Na measured by CCSEM/EDX analysis in sea salt particles found in the CVI (upper panel) and the AOS (lower panel) samples. The dashed lines indicate the ratio of 0.06 nominal to sea water. The solid lines indicate expected experimental deviation from the nominal line from sensitivity effects that impact results of EDX particle analysis. See text for further discussion.

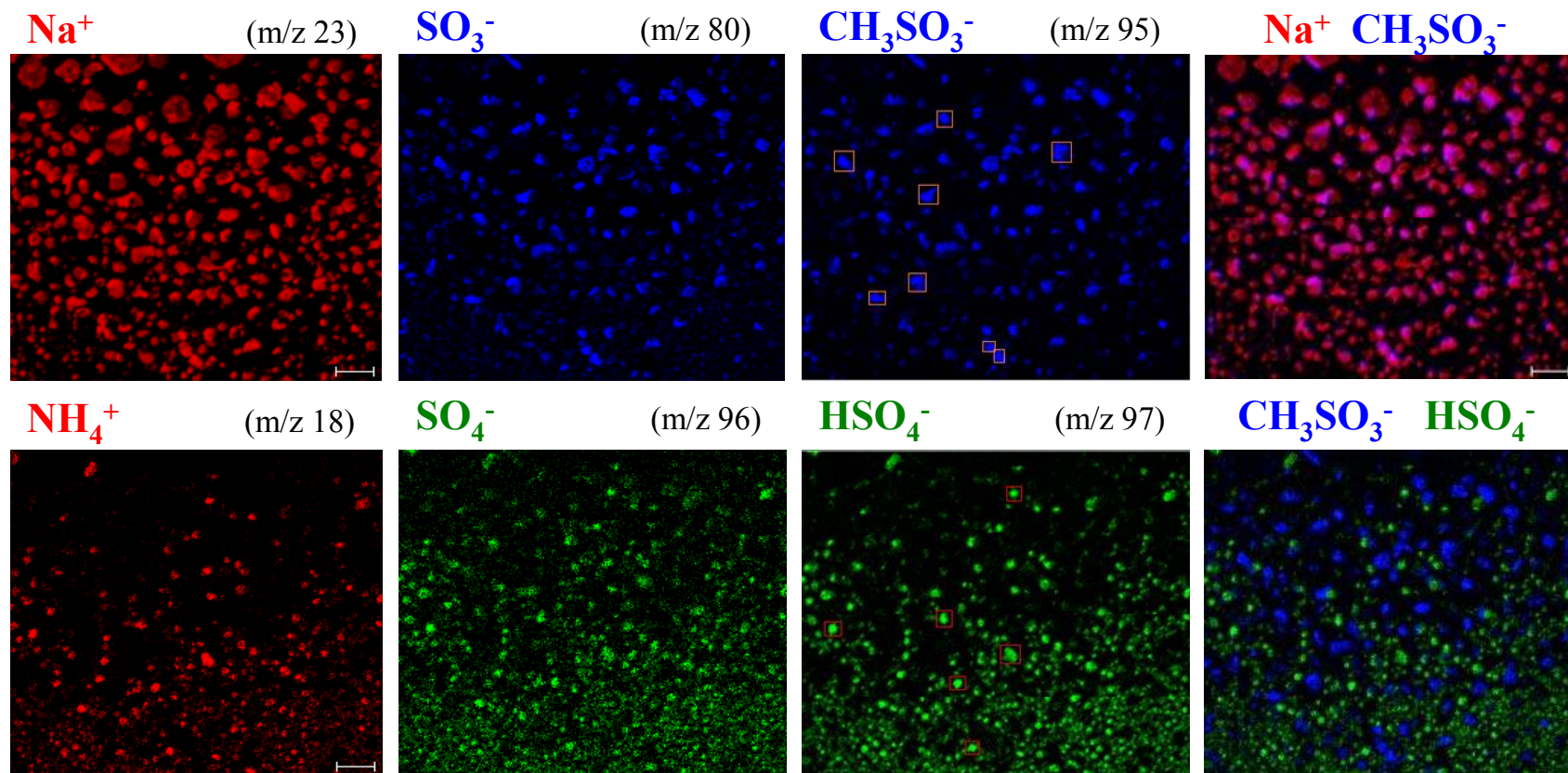


Figure 7 TOF-SIMS maps of typical samples collected from the CVI line. Upper three left images are maps produced for characteristic ions of sodium (Na^+) and methanesulfonate (SO_3^- , CH_3SO_3^-). The upper right image shows overlaid maps of the Na^+ and CH_3SO_3^- ions. Their close overlap indicates formation of methanesulfonate in sea salt particles. The lower three left images are maps produced for characteristic ions of ammonia (NH_4^+) and sulfate (SO_4^- , HSO_4^-) originating from H_2SO_4 / $(\text{NH}_4)_2\text{SO}_4$ particles. The lower right image shows overlaid maps of CH_3SO_3^- and HSO_4^- ions and indicates external mixing of sea salt and ammonium sulfate particles. Maps are $100 \mu\text{m} \times 100 \mu\text{m}$. See text for additional details.

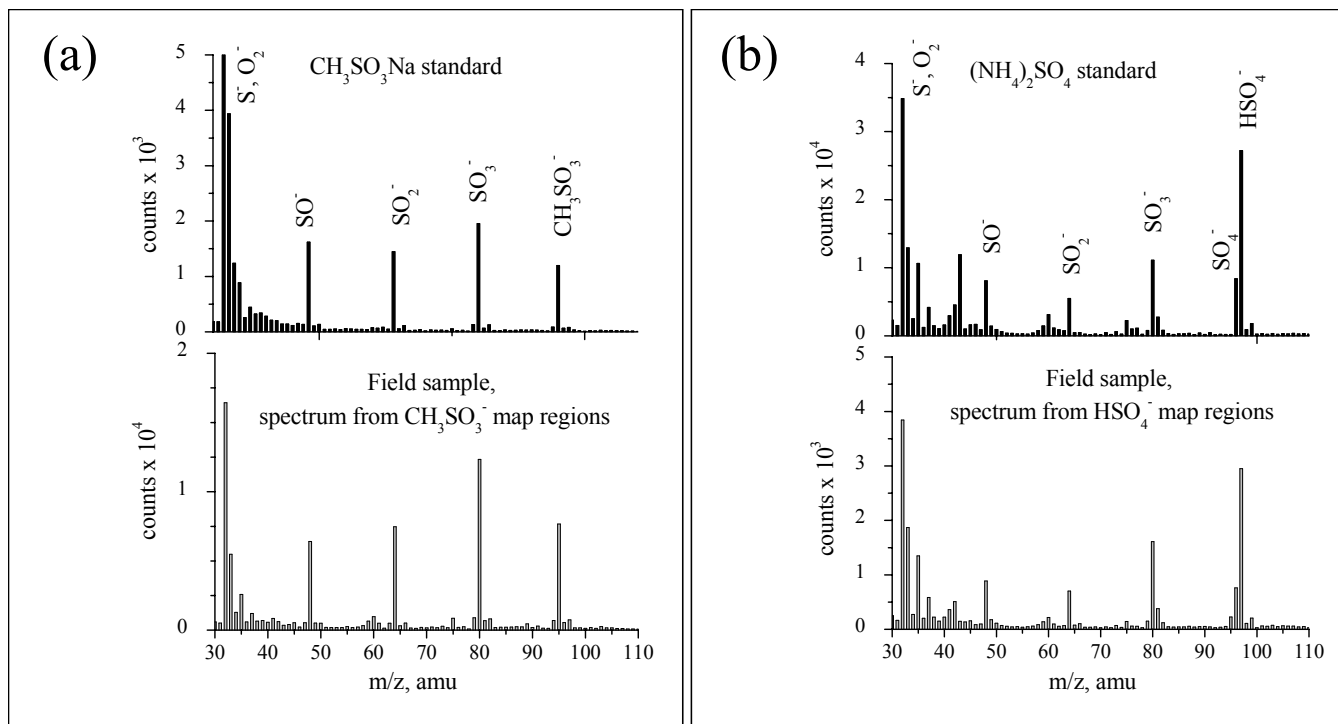


Figure 8 (a) TOF-SIMS spectrum characteristic of sea salt particles (see upper panel of Fig. 7) shown with the reference spectrum obtained from laboratory prepared $\text{CH}_3\text{SO}_3\text{Na}$ particles. (b) TOF-SIMS spectrum characteristic of ammonium sulfate particles (see bottom panel of Fig. 7) plotted along with the reference spectrum obtained from laboratory prepared $(\text{NH}_4)_2\text{SO}_4$ particles.

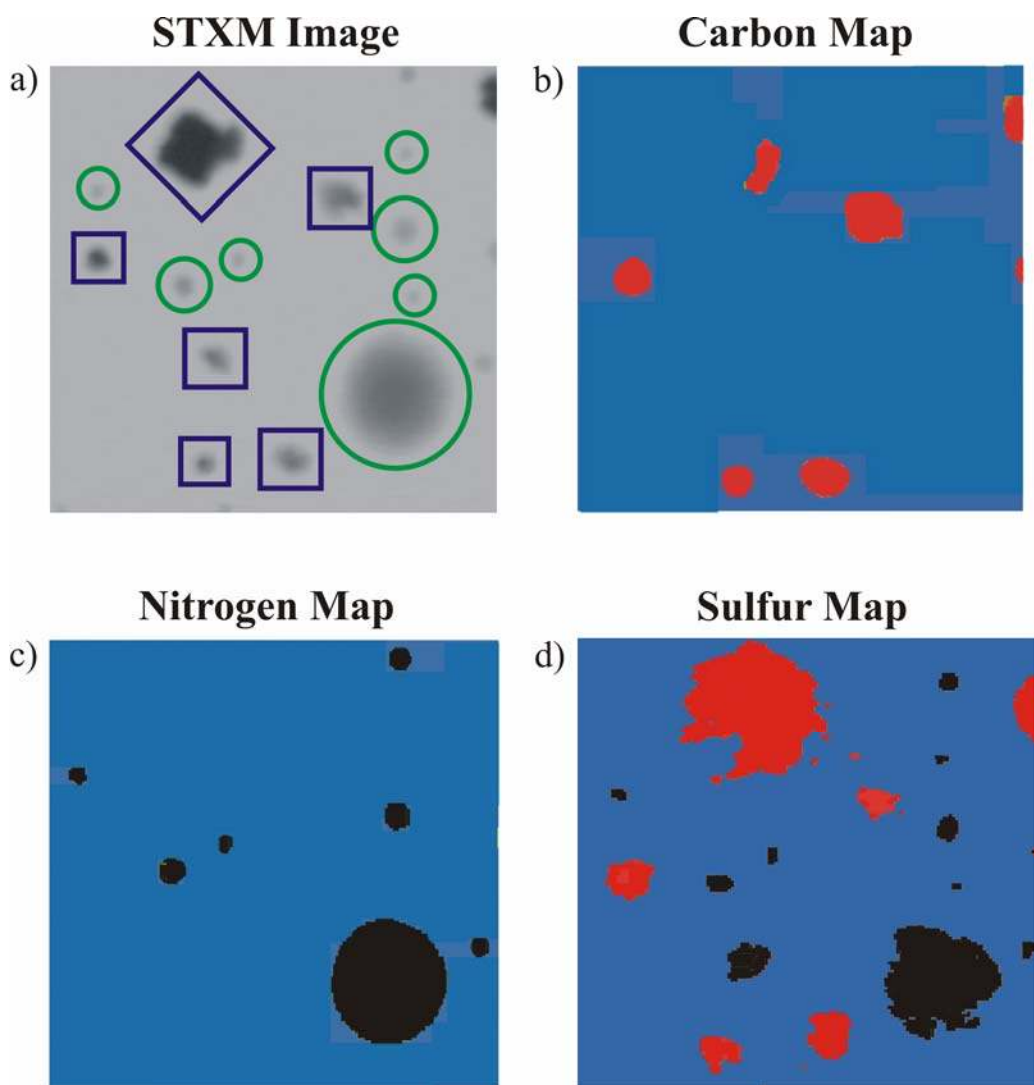


Figure 9 (a) STXM image ($12\ \mu\text{m} \times 12\ \mu\text{m}$) of externally mixed sea salt/ $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$ (marked by squares) and $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ (marked by circles) particles, b) C K-edge STXM/NEXAFS map of sea salt/ $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$ particles, c) N K-edge STXM/NEXAFS map of $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ particles, d) S L-edge STXM/NEXAFS map of sea salt/ $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$ particles (red) and $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ particles (black).

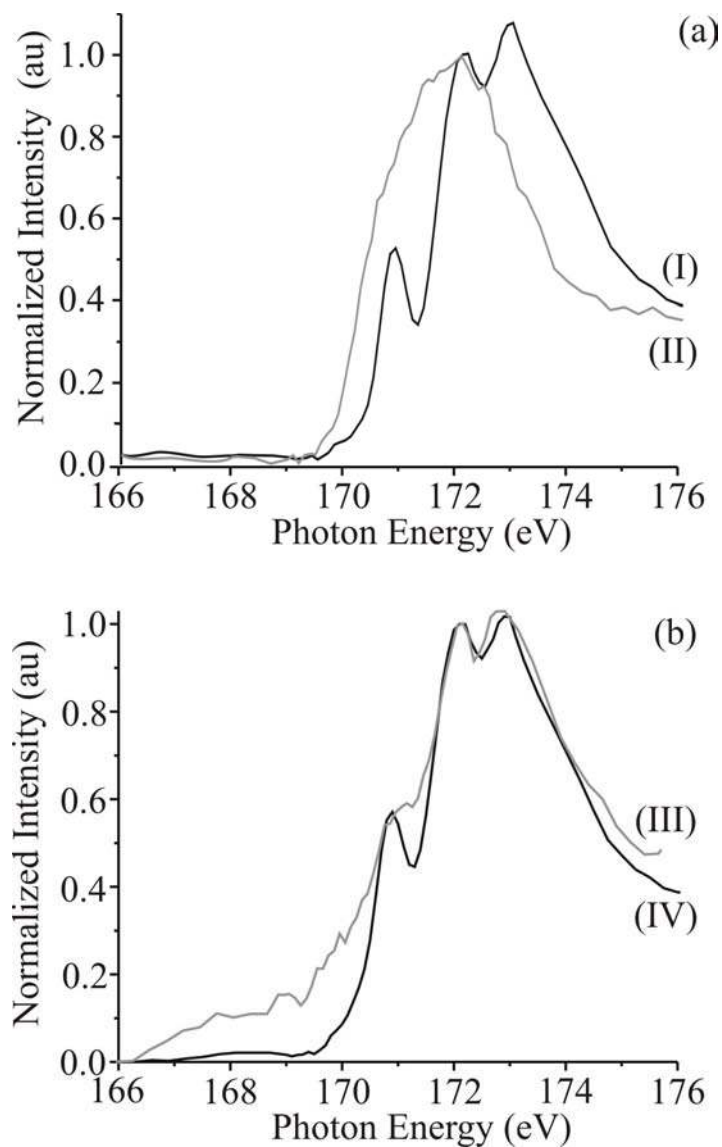


Figure 10 (a) Sulfur L-edge NEXAFS spectra recorded from reference particles of (I) Na_2SO_4 and (II) $\text{CH}_3\text{SO}_3\text{Na}$. (b) Sulfur L-edge NEXAFS spectrum recorded from a mixed (III) sea salt/ CH_3SO_3^- / nss-SO_4^{2-} particle collected at Point Reyes National Seashore, (IV) modeled spectrum for 20:80 proportion of $\text{CH}_3\text{SO}_3\text{Na}/\text{Na}_2\text{SO}_4$ particle.

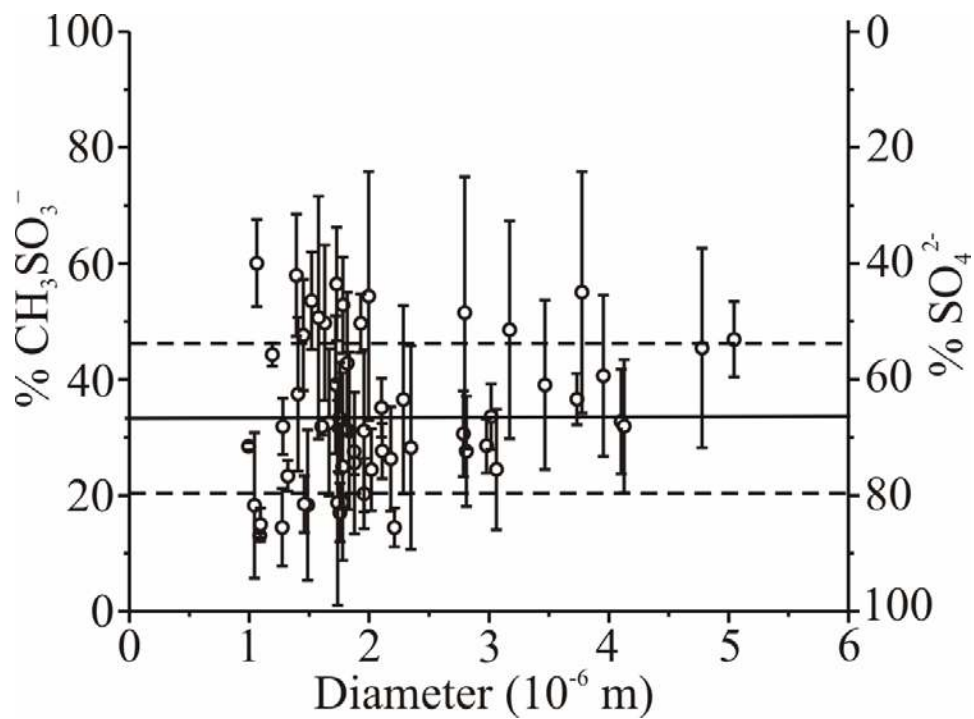


Figure 11 – Invariance in chemical composition with projected particle diameter. The solid black line indicates the mean value of the $\text{CH}_3\text{SO}_3^-/\text{SO}_4^{2-}$ ratio and the dashed lines represent one standard deviation from the mean.

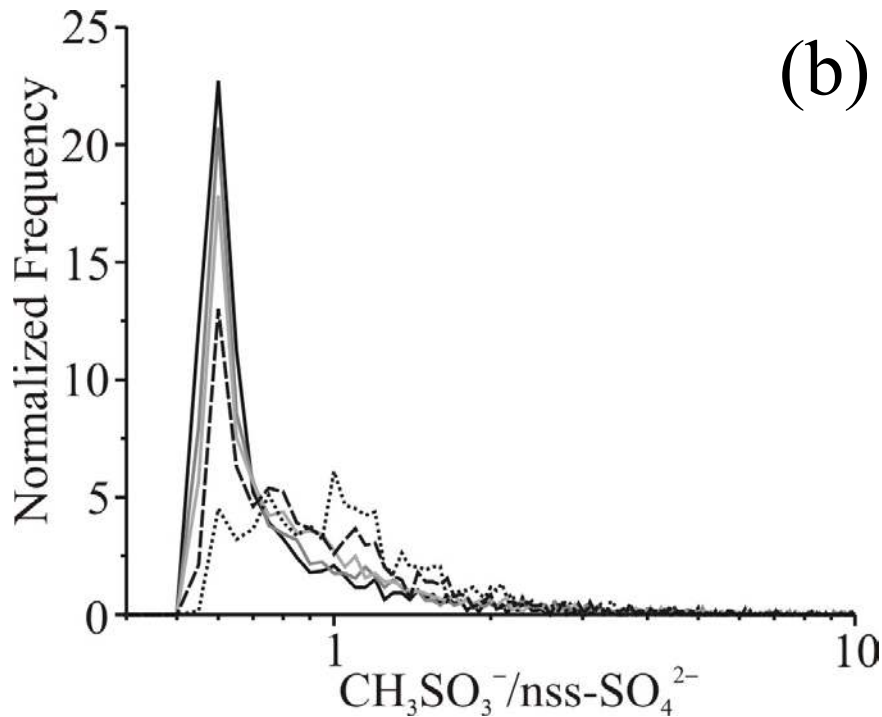
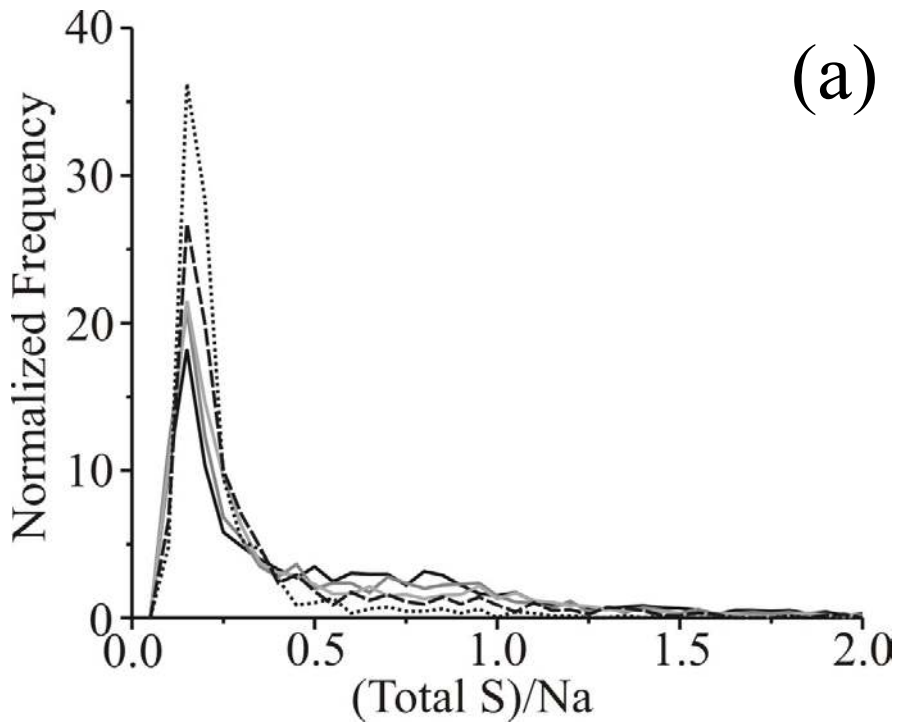


Figure 12 – Distribution of (a) total sulfur to sodium ratio and (b) CH_3SO_3^- to nss-SO_4^{2-} ratio present in particles with diameter in the range 0.31 – 0.5, 0.5 – 0.79, 0.79 – 1.26, 1.26 – 2 and $> 2 \mu\text{m}$ (black, dark grey, light grey, dashed and dotted lines, respectively).

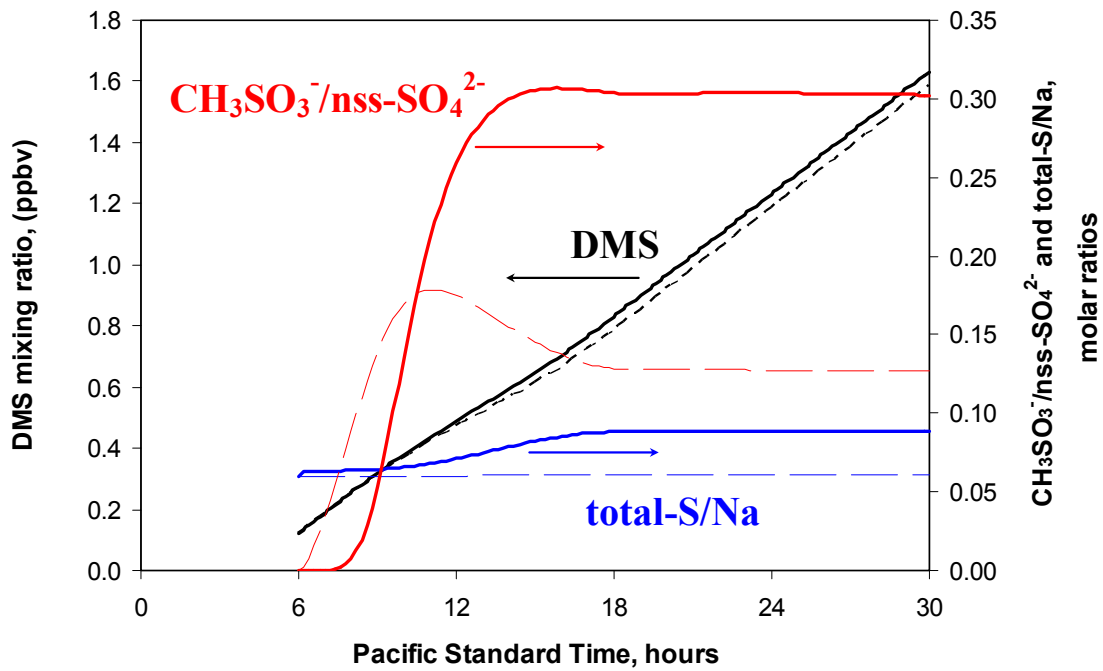


Figure 13 Temporal evolution of $[\text{CH}_3\text{SO}_3^-]/[\text{nss-SO}_4^{2-}]$ and $[\text{total-S}]/[\text{Na}]$ ratios in sea salt particles calculated using “gas-phase chemistry only” (dashed lines) and “gas and cloud chemistry” scenarios (solid lines). The model calculations are initiated at 6 am assuming $E_{\text{DMS}} = 20 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, emission rates of DMS. Temporal evolution of DMS mixing ratio is also shown.