

1 A 350-year atmospheric history for carbonyl sulfide inferred 2 from Antarctic firn air and air trapped in ice

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6 [1] Carbonyl sulfide (COS) and other trace gases were measured in firn air collected near
7 South Pole (89.98°S) and from air trapped in ice at Siple Dome, Antarctica (81.65°S). The
8 results, when considered with ambient air data and previous ice core measurements,
9 provide further evidence that atmospheric mixing ratios of COS over Antarctica between
10 1650 and 1850 A.D. were substantially lower than those observed today. Specifically, the
11 results suggest annual mean COS mixing ratios between 300 and 400 pmol mol⁻¹ (ppt)
12 during 1650–1850 A.D. and increases throughout most of the twentieth century.

13 Measurements of COS in modern air and in the upper layers of the firn at South Pole
14 indicate ambient, annual mean mixing ratios between 480 and 490 ppt with substantial
15 seasonal variations. Peak mixing ratios are observed during austral summer in ambient air
16 at South Pole and Cape Grim, Tasmania (40.41°S). Provided COS is not produced or
17 destroyed in firn, these results also suggest that atmospheric COS mixing ratios have
18 decreased 60–90 ppt (10–16%) since the 1980s in high latitudes of the Southern
19 Hemisphere. The history derived for atmospheric mixing ratios of COS in the Southern
20 Hemisphere since 1850 is closely related to historical anthropogenic sulfur emissions. The
21 fraction of anthropogenic sulfur emissions released as COS (directly or indirectly) needed
22 to explain the secular changes in atmospheric COS over this period is 0.3–0.6%. INDEX

23 TERMS: 0325 Atmospheric Composition and Structure: Evolution of the atmosphere; 0365 Atmospheric
24 Composition and Structure: Troposphere—composition and chemistry; KEYWORDS: atmosphere composition,
25 carbonyl sulfide, stratosphere sulfate aerosol

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30 1. Introduction

31 [2] Carbonyl sulfide (COS) is a long-lived trace gas that
32 is believed to contribute sulfur to the stratospheric aerosol
33 layer [Crutzen, 1976; Chin and Davis, 1995; Ko *et al.*,
34 2003]. This aerosol layer affects stratospheric ozone and
35 influences the radiative balance of the atmosphere [Ko *et al.*,
36 2003]. By determining historical trends in atmospheric
37 COS, we hope to understand better the amount of strato-
38 spheric sulfate contributed by COS, how this contribution
39 has changed over time, and how it might change in the
40 future.

41 [3] Although some human activities are sources of atmo-
42 spheric COS, natural fluxes have a strong influence on

observed mixing ratios of this trace gas [Watts, 2000]. For 43
example, the largest sink of COS is believed to be loss to 44
vegetation via hydrolysis by the enzymes primarily 45
involved in photosynthesis [Protoschill-Krebs *et al.*, 1996; 46
Kettle *et al.*, 2002]. Although understanding long-term 47
trends and variability for COS can provide insight into the 48
human influence on atmospheric sulfur in the form of COS, 49
it also could provide information on the variability of 50
certain biogeochemical cycles. 51

[4] Atmospheric histories for COS dating back to the 52
early to mid twentieth century were first inferred from 53
analyses of firn air collected by Sturges *et al.* [2001]. Their 54
results suggested fairly constant COS mixing ratios during 55
the early to mid twentieth century in both hemispheres, 56
although in the oldest samples they collected in the South- 57
ern Hemisphere (SH) COS was as much as 60 pmol mol⁻¹ 58
(ppt) (or 12%) lower than the 480 ppt measured at the 59
surface. The deepest firn air samples exhibited high vari- 60
ability in COS, however, and prevented a firm conclusion 61
regarding an increase in atmospheric COS during the mid- 62
1900s. Sturges *et al.* [2001] also suggested that mixing 63
ratios of COS decreased by 8 ± 5% during the 1990s in the 64
Arctic, although no similar recent decrease was apparent in 65
their Antarctic firn results. 66

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t1.1 **Table 1.** Overview of Carbonyl Sulfide (COS) Measurements in Firm Air, Ice Bubble Air, and Ambient Air

t1.2	Sample Type	Location	Collection Times	Sample Depths	Compounds Measured	Sample Container Type
t1.3	Firm air (deep holes) ^a	near South Pole (89.98°S)	January 2001	0–120 m in two holes	COS, CO ₂ , $\delta^{15}\text{N}$ of N ₂ ^b	glass flasks and three Al cylinders
t1.4	Firm air (near surface) ^c	South Pole (90.00°S)	January, August, and October 2003	0.3–16.3 m	COS ^b	paired glass flasks
t1.5	Ice core	Siple Dome, Antarctica (81.65°S)	December 1995	56.8–90.7 m ^d	COS, ^b CO ₂ , ^e $\delta^{15}\text{N}$ of N ₂ ^e	not applicable
t1.6	Ambient air	South Pole (90.00°S), and Tasmania (40.41°S)	~2.5 times per month at Tasmania during 2000–2003, less often at South Pole (see Figure 4)	at Tasmania, ~15 m above ground; at South Pole, ~18 m above snow	COS ^b	paired glass and stainless steel (Tasmania only) flasks

t1.7 ^aAir was sampled with the inflatable bladder technique described by Schwander *et al.* [1993] and Battle *et al.* [1996].

t1.8 ^bAdditional gases were measured in these samples but are not considered here (CH₄, CO, N₂O, SF₆, chlorofluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons, chlorinated solvents, methyl halides, halons, and benzene).

t1.9 ^cAir was sampled from eight permanent tubes installed in January of 1998 [Severinghaus *et al.*, 2001].

t1.10 ^dCOS ice core measurements from 82.3 to 90.7 m were published previously by Aydin *et al.* [2002].

t1.11 ^eCompounds were used in the modeling of Siple Dome firm; data were published previously by Butler *et al.* [1999].

67 [5] Aydin *et al.* [2002] reported the first measurements of
68 COS in air from an Antarctic ice core. They found COS
69 mixing ratios of 373 ± 37 ppt during 1616–1694 A.D. in
70 Antarctica, about 23% lower than observed in the modern
71 atmosphere.

72 [6] Here we report additional measurements of COS from
73 Antarctic firm and ice that supplement published ice and firm
74 atmospheric histories. They provide further evidence for
75 substantially lower atmospheric mixing ratios of COS
76 during preindustrial times and suggest substantial declines
77 during recent years in the SH atmosphere.

78 2. Methods

79 2.1. Firm Air Collection

80 [7] Firm air near South Pole (SPO) (89.98°S) was
81 sampled from two deep holes 30 m apart during January
82 2001 using established methods [Schwander *et al.*, 1993;
83 Bender *et al.*, 1994; Battle *et al.*, 1996; Butler *et al.*, 1999]
84 (Table 1). Glass flasks (2 L) and aluminum cylinders (29 L,
85 Aculife treated; Scott Specialty Gases, Inc.) were pressur-
86 ized with firm air from various depths down to the firm-ice
87 transition. Fill pressures were about 300 kPa in glass flasks
88 and 375 kPa in aluminum cylinders.

89 [8] Firm air samples were also drawn periodically from
90 eight permanent tubes located in the upper 20 m of the firm
91 at SPO (90.00°S) (tubes installed by J. Severinghaus in
92 1998) (Table 1). Paired glass flasks were filled from these
93 tubes with a minimum amount of flushing (~100 L) to
94 avoid disturbing mixing ratio gradients in the surface
95 snowpack [Severinghaus *et al.*, 2001].

96 2.2. Firm Air Analysis

97 [9] Flasks filled with firm air were analyzed in the NOAA
98 Climate Monitoring and Diagnostics Laboratory (CMDL)
99 Boulder laboratory with gas chromatography-mass
100 spectrometry (GC-MS) instrumentation that has allowed
101 measurements of halocarbons in firm air and in the modern
102 atmosphere [Butler *et al.*, 1999; Montzka *et al.*, 1999].
103 Selected flasks were reanalyzed up to 4 months after the
104 initial analysis and gave results for COS that were 1–7%

(median = 2%; n = 7) greater than the initial analysis. Our
experience suggests that COS mixing ratios can increase
slowly in glass flasks filled with dry air at near ambient
pressure. Despite this, the potential mean bias on our results
from the delay between sampling and initial analysis of
glass flasks is estimated to be small ($\leq 2\%$ or 10 ppt). COS
was quantified by monitoring ion $m/z = 60$ (COS⁺). The
median replicate injection precision for COS at ambient
levels with our instrumentation is 0.4% (n~3000); 95% of
the time it is $\leq 1.3\%$ (i.e., ≤ 14 ppt).

[10] The COS results reported here are based on seven
standards prepared by us with gravimetric techniques at
mixing ratios between 263 and 732 ppt. These standards
were prepared as dry air in Aculife-treated aluminum
cylinders and as humidified air (19 torr of H₂O) in electro-
polished, stainless steel tanks (Essex Cryogenics, Inc.). The
ratios of instrument response to prepared mole fraction for
these seven standards, when analyzed on the NOAA GC-
MS, yield a standard deviation of 1.4% and are independent
of container type. This suggests a linear instrument
response, consistency in the preparation of the standards,
and reliability in their storage.

[11] Additional glass flasks were filled with firm air from
these same deep holes. Some were analyzed with mass
spectrometry for $\delta^{15}\text{N}$ of N₂ (among other species) at the
Princeton laboratory to allow for gravitational corrections
on firm air measurements [Bender *et al.*, 1994], while others
were analyzed for CO₂ by NOAA CMDL [Tans *et al.*,
2002]. These data, along with the atmospheric CO₂ record
of Etheridge *et al.* [1996] and Tans *et al.* [2002], were
incorporated into one-dimensional firm models [Battle *et al.*,
1996; Butler *et al.*, 1999; Aydin *et al.*, 2004] to infer
atmospheric histories for COS (see model descriptions
below).

[12] Past studies have shown that it is sometimes difficult
to avoid modern air contamination of firm air samples,
especially near bubble close off [Butler *et al.*, 1999; Sturges
et al., 2001]. This contamination was detected by elevated
amounts of CO₂, CO, and halocarbons in samples filled
below 118 m depth in hole 1, below 120 m depth in hole 2,
and at a depth of 89 m from hole 1. Results from these

146 depths were eliminated from further consideration (5 depths
147 out of a total of 29 depths sampled).

148 2.3. Analysis of Ice Core Air

149 [13] COS was measured in air bubbles trapped in ice from
150 a shallow core drilled at Siple Dome, Antarctica (81.65°S),
151 in December of 1995 [Aydin et al., 2002]. This paper
152 presents new measurements of COS from younger portions
153 of the same core. Similar techniques were used to analyze
154 these additional samples at the University of California,
155 Irvine (UCI), laboratories, although improvements in sam-
156 ple handling and instrument preparation resulted in signif-
157 icantly lower blank levels and smaller zero corrections in
158 the newer measurements (the mean correction was 4% (3–
159 7%) in ice data presented here compared to 7% (4–12%)
160 presented by Aydin et al. [2002]. Where the two sets of ice
161 core results overlap (~82 m depth), COS mixing ratios in
162 the newer measurements are slightly lower (20 to 30 ppt)
163 than those from Aydin et al. [2002]. This difference does not
164 appear to stem from calibration shifts over time, but may be
165 due to uncertainty in the larger background corrections that
166 were necessary in the earlier measurements [Aydin et al.,
167 2002]. Adjustments of 1.6 and 3% have been applied to the
168 data from Aydin et al. [2002] and to the more recent
169 ice measurements from UCI so that all data considered here
170 are referenced to the same scale (defined by the NOAA
171 standards).

172 2.4. Ambient Air Measurements of COS

173 [14] Since early 2000, we have measured COS from glass
174 flasks collected at SPO (air inlet ~18 m above the
175 snowpack and 2837 m above sea level (asl), 90.00°S)
176 and from glass and electropolished stainless steel flasks
177 filled at a coastal site in Australia (Cape Grim, 40.41°S,
178 94 m asl) as part of the CMDL global flask sampling
179 network [Montzka et al., 1999]. Paired flasks are filled
180 one to four times per month to pressures between 300 kPa
181 and 375 kPa. After sampling, flasks are returned to
182 Boulder and analyzed on the same instrument described
183 above for the analysis of firn air samples. Results are
184 discarded when pair disagreement is greater than 14 ppt
185 (3% of the time).

186 [15] No results for COS from electropolished stainless
187 steel flasks filled at SPO are included in this analysis
188 because COS is not stable in very dry steel containers
189 during the multiple-month delay between flask sampling
190 and analysis; such losses are not observed for COS in glass
191 flasks filled at SPO. To ascertain if mixing ratios of COS at
192 Cape Grim are dependent upon flask type, paired glass
193 flasks have been filled periodically on the same day as
194 electropolished stainless steel flasks. The mean ratio of
195 results for COS from glass flasks relative to that measured
196 from stainless steel flasks is 1.006 ± 0.007 ($n = 14$),
197 suggesting that COS mixing ratios at this more humid site
198 are independent of flask type.

199 2.5. Model Calculations for Deriving Atmospheric 200 Histories for COS

201 [16] We derived multiple histories for atmospheric COS
202 with various combinations of measurements from firn air,
203 ice core air, and ambient air at SPO and Siple Dome
204 (Table 2). Because the movement of trace gases through

205 firn is dominated by molecular diffusion [Schwander et al.,
206 1988; Schwander, 1989; Bender et al., 1994], histories were
207 derived with an inverse approach based on one-dimensional
208 forward diffusion models [Battle et al., 1996; Aydin et al.,
209 2004]. As in those studies, we used independently measured
210 atmospheric CO₂ histories [Etheridge et al., 1996; Tans et
211 al., 2002] and measurements of CO₂ in firn air to infer the
212 relationship between diffusivity and depth. Although the
213 ‘tuned’ diffusivity profiles at South Pole and Siple Dome
214 are similar to those derived solely from snow density [e.g.,
215 Trudinger et al., 1997], they allow for a more accurate
216 representation of gas movement through the complex and
217 highly variable crystalline structure of firn. The resulting
218 diffusivity profiles, along with porosity values derived from
219 in situ density measurements, were used without further
220 modification as input values for the one-dimensional diffu-
221 sion model calculations.

222 2.5.1. The 100-Year Atmospheric Histories Derived 223 From Measurements of South Pole Firn Air

224 [17] Two histories, H1 and H2, were derived for COS in
225 the Antarctic atmosphere based upon measurements of SPO
226 firn air, ambient air measurements collected through the firn
227 air sampling apparatus in January 2001, and knowledge of
228 seasonal changes observed for COS in the ambient atmo-
229 sphere (Table 2). To derive these atmospheric histories, we
230 assumed that the true history of atmospheric COS mixing
231 ratios can be described by a single mathematical function
232 with a limited number of free parameters. A systematic and
233 objective procedure was used to select a number of func-
234 tions as candidates for providing the best fit to the firn air
235 data. First, a preliminary history was derived from the
236 discrete firn air measurements of COS based upon CO₂-
237 derived mean ages assigned to each individual sample.
238 Second, many functions (a library of more than 3400
239 functions; TableCurve2D) were sorted based upon how well
240 they fit the preliminary history; those giving the best fits
241 were selected for further consideration. These trial func-
242 tions, and a few additional ones that included or excluded
243 inflection points in an atmospheric history, were considered
244 in the derivation of a best estimate history. They included
245 log normal, extreme value (EV), sigmoidal (SIG), asym-
246 metric logistic (H1 and H2), Pearson VII, asymmetric
247 double sigmoidal, Lorentzian cumulative, extreme value
248 cumulative, asymmetric sigmoidal, asymmetric sigmoidal
249 with reverse asymmetry, and Weibull. All of these functions
250 include a constant offset (allowed to vary) and have six or
251 fewer free parameters. These functions were chosen for their
252 ability to describe a wide range of possible atmospheric
253 histories including monotonic increases, transitions from
254 low to high values, and increases followed by decreases.
255 The functions all have a small number of free parameters
256 (relative to the number of firn air measurements), and are
257 well behaved with respect to small variations in their free
258 parameters.

259 [18] For each of the functions listed above, we adjusted
260 the free parameters according to the method of Levenberg
261 and Marquardt [Press et al., 1992] to optimize the agree-
262 ment between observations and predictions of a forward
263 model run. For the few functions exhibiting the best fits,
264 multiple runs were attempted with different starting param-
265 eters and the same minima were obtained. To reduce our
266 sensitivity to errors in the inferred diffusivity-depth profile,

t2.1 **Table 2.** Description of Model-Derived Histories

t2.2	History	Input COS Data	Period, years	Output
t2.3	H1	firm air from deep holes drilled near South Pole (89.98°S) in January 2001; ambient air sampled through firm air collection apparatus near South Pole in January 2001; magnitude of seasonality in ambient air described by long-term measurements at South Pole and Cape Grim, Tasmania	100	a single function describing a 100-year atmospheric history that results in the smallest chi square fit to the firm air data for COS and CO ₂
t2.4	H2	same as H1 but with firm air results from four depths removed (collected at 20, 39, 60, and 100 m depth) to ascertain their influence on the derived history	100	same as H1 but function derived by considering four fewer data points
t2.5	H3	firm air data from South Pole used in H2 (i.e., H1 minus outliers); ice bubble data from Siple Dome minus four outliers (at 59.6, 61.5, 66.5, and 85 m); ^a annual mean mixing ratios measured during 2000–2002 at South Pole and Tasmania	350	multiple polynomials describing a single 350-year contiguous atmospheric history that is consistent with recent ambient air data and the measured depth profiles of COS in firm air at South Pole and in ice at Siple Dome

^aDates are applied to air trapped in Siple Dome ice through an understanding of trace gas diffusion timescales through the Siple Dome firm. These timescales were derived from an analysis of CO₂ measurements discussed elsewhere [Butler *et al.*, 1999].

we optimized agreement between the data and model for COS as a function of CO₂ measured from this same hole, rather than as a function of depth (Figure 1). Optimizing agreement is equivalent to minimizing χ^2 . To provide meaningful estimates of χ^2 we assumed that each observation carries an uncertainty of 8.34 ppt; this value is based on the scatter in the firm measurements between 60 m and 110 m depth and not on instrumental analysis uncertainty (which is smaller). Calculations with the one-dimensional firm model suggest that at these depths diffusion is rapid enough in the SPO firm that any short-term atmospheric variations should be extensively smoothed. Thus mixing ratio variability in this region characterizes our ability to extract information from the firm archive more completely than instrumental analysis precision.

[19] We find that the data are matched best if we assume that the atmosphere is described by an asymmetric logistic function (Figures 1–3; history H1), with $\chi^2_{\min} = 41.9$ for 19 (24–5) degrees of freedom. A second history (H2) was derived with this same technique in order to determine if four, suspiciously high observations biased H1 substantially (observations at 20 m, 39 m, 60 m and 100 m; CO₂ mixing ratios of 339, 352, 358, and 363 ppm). Although the fit improves markedly when these four observations are excluded ($\chi^2_{\min} = 15.4$ for H2; 15 (20–5) degrees of freedom), the inferred atmospheric history does not change substantially (Figure 2, compare history H1 and H2).

[20] To quantify the uncertainty in the atmospheric history H1, we determined (through 10⁵ trials) correlated values of the free parameters on the asymmetric logistic function that lead χ^2 to increase by 5.89 units above its minimum value, thereby encompassing 68.3% of probability space for a five-parameter fit [see, e.g., Bevington and Robinson, 1992]. We note that the minimum found in the five-dimensional search was not significantly different from that found initially using the Levenberg-Marquardt method, indicating that the initial minimum was in fact a true or global, rather than local, minimum.

[21] The method of inversion described here is limited by the ability of our suite of functions to describe an atmospheric history of arbitrary shape. Inversion techniques employing adjoint equations [Rommelaere *et al.*, 1997] or Bayesian synthesis inversion [Trudinger *et al.*, 2002] are more general and do not suffer from this particular limitation. Nonetheless, we are confident that our method objectively provides a close approximation of the true atmospheric history. This confidence is based on three observations: (1) the low values of χ^2_{\min} achieved (e.g., the $[\chi^2_{\min}]/[\text{degree of freedom}]$ is ~ 1.0 for H2), (2) the similarities of the atmospheric histories inferred from functions that differ significantly in their mathematical structure, and (3) the high values of χ^2_{\min} for the functions that cannot describe particular atmospheric features. Specifically, those functions that cannot describe a rise and subsequent fall in atmospheric COS give χ^2_{\min} values that are at least 25 units higher than those functions that can describe a rise and fall in atmospheric COS (Figure 2). This gives us confidence that the available data imply a recent decrease in atmospheric COS over Antarctica.

2.5.2. A 350-Year Atmospheric History From Ice Core and Firm Air Measurements

[22] Additionally, a 350-year atmospheric history (H3) for COS was derived with a separate, one-dimensional, forward model of a firm column [Schwander *et al.*, 1988] that was constrained by all available COS data. These included data from ice cores at Siple Dome, from deep firm air at SPO, and from ambient air at SPO (Table 2). The physical properties of the firm at Siple Dome and SPO are different; therefore the model was initiated separately to simulate these two firm columns. As was the case for the one-dimensional model used to derive H1 and H2, H3 was derived with porosity profiles from firm column density measurements, and diffusivity profiles were adjusted to provide good consistency between measured CO₂ within the firm column and CO₂ mixing ratios calculated from the model based upon the independently measured atmospheric

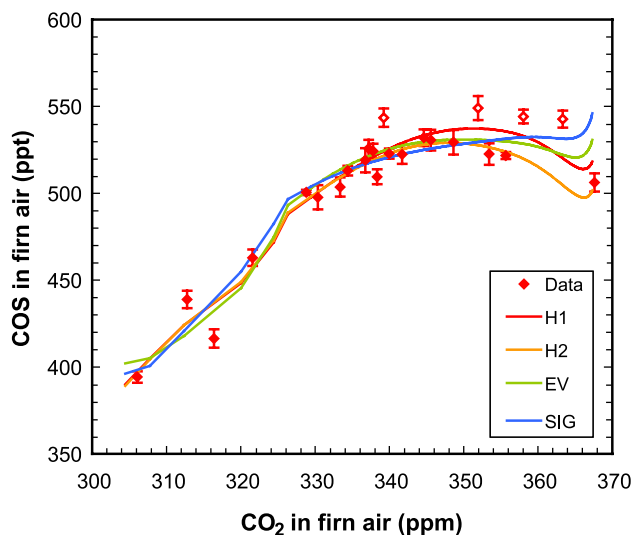


Figure 1. The measured (red diamonds) and modeled (lines) relationship between mixing ratios of COS and CO₂ in South Pole firn air (89.98°S). Modeled relationships reflect optimized, 100-year histories of carbonyl sulfide (COS) and the known history for CO₂ [Etheridge *et al.*, 1996; Tans *et al.*, 2002] that are allowed to become incorporated into the firn with use of the one-dimensional forward firn model. The corresponding atmospheric histories for COS appear in Figure 2. The calculated relationships between COS and CO₂ in the firn that arise from an optimized history are shown for only three of the many different functions considered: asymmetric logistic (H1, $\chi^2 = 42$, and H2, $\chi^2 = 15$), sigmoidal (SIG, $\chi^2 = 67$), and extreme value (EV, $\chi^2 = 48$). Results for the optimized SIG and EV functional forms are shown here and in Figures 2 and 3 in addition to the best fit, asymmetric logistic functions (H1 and H2) because SIG and EV represent the wide range of different functional forms encompassed by those considered (see text for complete listing). One asymmetric logistic history, H2, was derived by ignoring data suspected of being slightly contaminated for COS (indicated as open red diamonds, these anomalies were not unique to either hole). Curvature in the modeled results at the highest CO₂ mixing ratios arises from including a mean seasonal variation in calculated atmospheric COS mixing ratios. This seasonality is based upon ambient air observations at South Pole and Cape Grim, Tasmania (see Figure 4).

343 CO₂ history [Etheridge *et al.*, 1996; Tans *et al.*, 2002]. Firn
 344 air measurements of CO₂ from December of 1996 were
 345 used to optimize diffusivity in the firn column above the ice
 346 at Siple Dome (provided by Butler *et al.* [1999]). This
 347 procedure is necessary for assigning dates to the ice core
 348 results from this site. To test these optimizations and this
 349 slightly different modeling approach, firn air mixing ratios
 350 of CFC-12 were considered. Good consistency was ob-
 351 served for measured firn air mixing ratios of CFC-12 at
 352 South Pole and Siple Dome [Butler *et al.*, 1999] and for
 353 those calculated with the model based upon an estimate of
 354 its atmospheric history [Walker *et al.*, 2000]. The accumu-
 355 lation rate at Siple Dome and ice ages below the firn-ice

transition were estimated from visual stratigraphy (R. B. 356
 Alley, unpublished data). 357

[23] The 350-year history for COS was derived with 358
 different procedures and constraints than the 100-year 359
 histories to provide a second estimate of the COS history 360
 (Table 2). Although histories H1 and H2 represent opti- 361
 mized histories from a single functional form, the 350-year 362
 history was derived from multiple polynomial functions 363
 (second to fourth order) covering sequential time periods. 364
 Parameters on nine polynomials were adjusted iteratively to 365
 improve the agreement between measured and calculated 366
 depth profiles for COS in the SPO firn and for COS in the 367
 Siple Dome ice. Furthermore, H3 was derived with the 368
 additional constraint that annual mean mixing ratios during 369
 2000–2002 were defined by the CMDL measurements at 370
 Cape Grim and SPO (Figure 4). Ambient air collected 371
 through the firn sampling apparatus in January of 2001, 372
 however, was not included in the H3 calculation because 373
 this history was derived without consideration of seasonal 374
 variation in ambient COS. Finally, the optimization was 375
 done manually to facilitate a fit to data from three different 376
 domains: the projection of the atmospheric history onto the 377
 Siple Dome and SPO firn columns was assessed simulta- 378
 neously, and annual mean mixing ratios from ongoing 379
 ambient air measurements were implemented as a boundary 380
 condition. 381

[24] The oldest 100 years of the 350-year atmospheric 382
 history are shifted by about 30 years from the dates derived 383
 by Aydin *et al.* [2002]. This is because diffusivity in the 384
 diffusion model at South Pole and Siple Dome was not 385
 tuned by considering CO₂ in firn air and its known 386
 atmospheric history in the earlier work of Aydin *et al.* 387
 [2002]. 388

[25] Several samples from both the firn and ice core were 389
 not considered in the derivation of the 350-year atmospheric 390

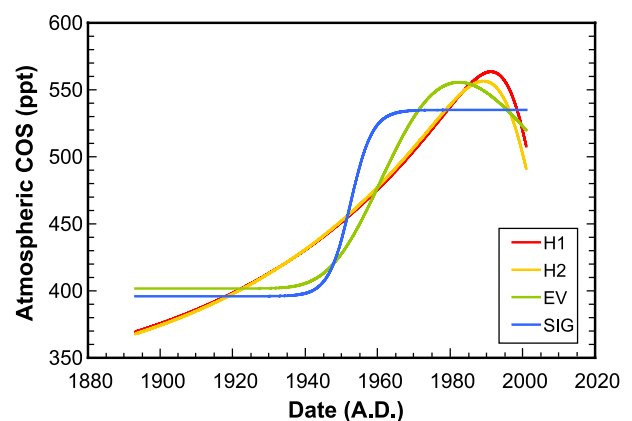


Figure 2. Optimized, 100-year histories for COS in Antarctic ambient air calculated with asymmetric logistic (H1 and H2), SIG, and EV functions (described in Figure 1 caption). These histories, when incorporated into the one-dimensional South Pole firn model, provide the smallest residuals (χ^2 , listed for the different functions in the caption to Figure 1) between measured mixing ratios of COS and CO₂ in the firn for the chosen functional form (given the known atmospheric history of CO₂ [Etheridge *et al.*, 1996; Tans *et al.*, 2002]).

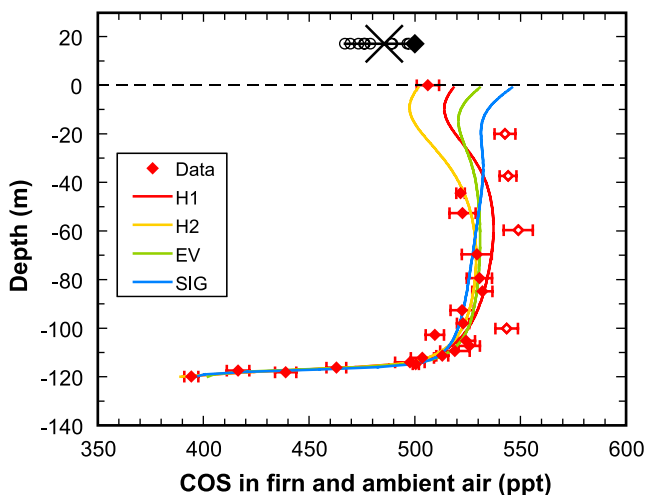


Figure 3. Measured and calculated COS mixing ratios in SPO firn air (89.98°S) (symbols the same as Figure 1) and ambient air at South Pole (90.00°S). Calculated depth profiles (lines) are derived from the one-dimensional firn model and the optimized, 100-year histories shown in Figure 2. The solid red diamond appearing at 0 m depth represents the mean of two samples of ambient air filled through the firn air sampling apparatus during the firn sampling expedition (January 2001). Ambient air mixing ratios for COS during 2000–2003 at SPO are also shown (at +18 m) for comparison and include (1) the annual mean during 2000–2003 (the black cross), (2) monthly means (open gray circles), and (3) the monthly mean during January (the solid diamond).

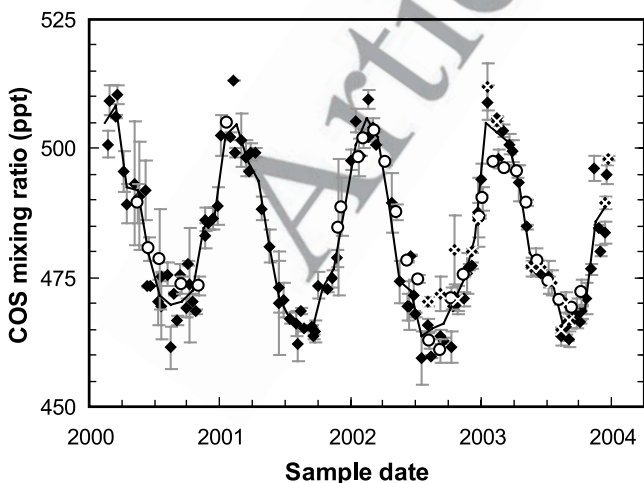


Figure 4. Carbonyl sulfide mixing ratios in ambient air at South Pole (90.00°S) (circles) and Cape Grim (40.41°S) (diamonds) in recent years as measured from paired flask samples. The solid line connects Cape Grim monthly means derived from the flask data. While all results from South Pole are from glass flasks, those at Cape Grim are from both electropolished stainless steel (diamonds) and glass flasks (white cross over a diamond). Error bars represent ± 1 standard deviation of the paired sample flasks.

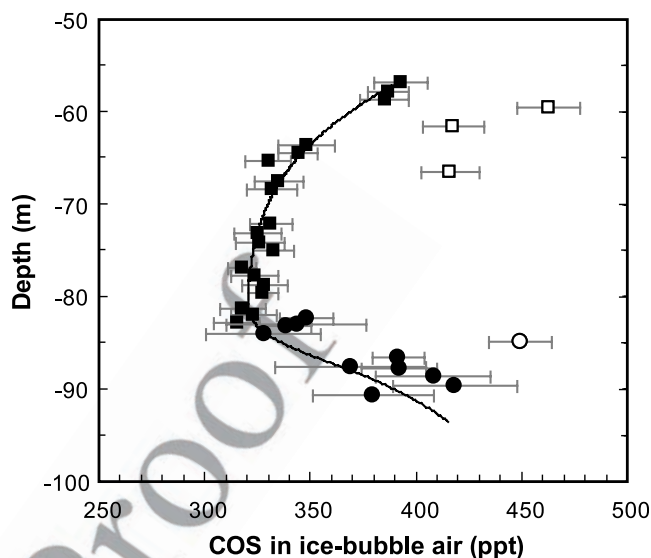


Figure 5. Carbonyl sulfide mixing ratios in air trapped in ice collected at Siple Dome, Antarctica, in December 1995 (81.65°S) (solid and open circles [Aydin et al., 2002]) and additional measurements from this same core (solid and open squares (this work)). Points suspected of being contaminated were not included in model calculations (open symbols). Error bars represent measurement uncertainty (analysis uncertainty of ± 1 standard deviation plus a blank uncertainty as described by Aydin et al. [2004]). The solid line is the depth profile calculated for COS in Siple Dome ice from the 350-year history, H3. The depth of the firn-to-ice transition at this site is 56 m.

history. COS mixing ratios in four ice samples (at 59.6, 391
61.5, 66.5, and 85 m) were unusually high compared to the 392
running mean of the remaining data. Tests with a firn model 393
suggest that short-duration atmospheric increases (e.g., 394
potentially from volcanoes) would be extensively smoothed 395
in the firn before being incorporated in ice. We conclude 396
that these spikes are likely the result of contamination, 397
perhaps as a result of undetected cracks in the ice core 398
(ice samples with visible cracks showed elevated COS 399
mixing ratios). In addition, similar to the 100-year history 400
H2, firn observations at 20, 39, 60 and 100 m were excluded 401
during the development of the H3 history. 402

3. Results and Discussion 404

3.1. Depth Profiles for COS in Firn and Ice 405

[26] In firn air the lowest COS mixing ratios were 406
measured in the deepest samples that showed no modern 407
air contamination (Figure 3). In these deep and clean samples, 408
COS averaged 416 ± 5 ppt from hole 1 (at 117.5 m depth), 409
and 394 ± 8 ppt from hole 2 (at 120 m depth). These mixing 410
ratios are about 16% lower than annual means observed in 411
ambient air at SPO and Cape Grim, Tasmania (CGO) 412
(40.41°S) during 2000–2003 (485 ppt) (Figures 3 and 4). 413
Even lower mixing ratios were measured in ice bubbles 414
collected from Siple Dome (Figure 5) [Aydin et al., 2002]. 415
In the deepest section of this ice core, Aydin et al. [2002] 416
reported a mean mixing ratio for COS of 373 ± 37 ppt. Here 417
we report additional measurements of COS from this same 418

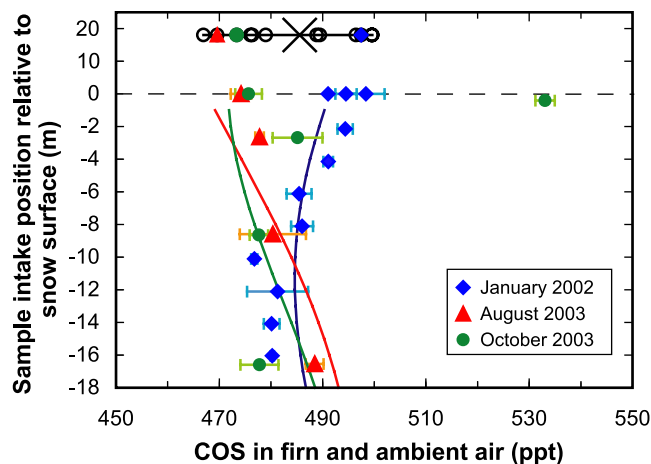


Figure 6. Carbonyl sulfide mixing ratios in firm air collected from tubes permanently installed in the upper 17 m of the firn at South Pole. These tubes were sampled at different times in the past, as indicated by the different colors (blue diamonds, January 2002; red triangles, August 2003; green circles, October 2003). Each firm air point is a mean of two glass flasks filled in series. Lines are calculated depth profiles (from the H1 history scaled to an annual mean ambient mixing ratio of 485 ppt, different colors correspond to months as for firm data). Mean ambient air mixing ratios at SPO during 2000–2003 are also shown (at +18 m) for comparison: annual mean (black cross), monthly means (open circles), January mean (blue diamond), August mean (red triangle), and October mean (green circle). All ambient air data were collected at 18 m above the snowpack (note y axis scale change above snow surface).

419 core, but in younger ice (57–83 m depth) (Figure 5).
 420 The mean COS mixing ratio in these shallower samples was
 421 340 ± 39 ppt, which is lower than was measured in the deep
 422 ice. A mean minimum COS mixing ratio of 322 ± 10 ppt is
 423 calculated from the measurements between 63 and 84 m
 424 (excluding the apparently contaminated result at 66.47 m).
 425 Provided COS is neither degraded nor produced in firm or
 426 ice, these mixing ratio–depth profiles from both SPO and
 427 Siple Dome provide further evidence that the atmospheric
 428 mixing ratio of COS was once substantially lower than
 429 observed in Antarctica today.

430 [27] Previous firm air measurements [Sturges *et al.*, 2001]
 431 did not indicate substantial increases for COS over the last
 432 50 or more years, but the oldest firm air sampled by Sturges
 433 *et al.* [2001] represented a younger mean age than the
 434 deepest samples we obtained from SPO. This conclusion
 435 is based on concurrent firm air measurements of CFC-12, a
 436 gas for which the atmospheric abundance increased mono-
 437 tonically during most of the twentieth century [Butler *et al.*,
 438 1999]. Sturges *et al.* [2001] measured 80 ppt of CFC-12 in
 439 their deepest Arctic sample, and 28 ppt in their deepest
 440 Antarctic sample. In contrast, at SPO in January 2001 we
 441 measured 5 ppt of CFC-12 in the oldest and deepest firm air
 442 sampled.

443 [28] Within the firm air column at SPO, the highest COS
 444 mixing ratios were measured between 20 m and 110 m

below the snow surface (Figure 3). The mean mixing ratio
 445 in this region of the firn was 530 ± 12 ppt, which is 50 ppt
 446 higher than the annual mean measured at SPO in modern air
 447 (Figures 3 and 4) [Montzka *et al.*, 2001]. Provided COS is
 448 not produced or destroyed in firm, this offset suggests a
 449 decline in ambient air COS mixing ratios at SPO during
 450 recent years.
 451

452 [29] High mixing ratios of COS can be observed
 453 temporarily very close to the surface of the firn during
 454 October (sunrise) at SPO (Figure 6). These temporary
 455 elevations are inconsistent with a firm model calculation
 456 in which a seasonally varying atmosphere is considered.
 457 These results indicate that COS can be produced or
 458 released from the snowpack surface during sunrise. Such
 459 an effect could bias COS mixing ratios in the firn and
 460 interfere with the derivation of past atmospheric trends.
 461 Swanson *et al.* [2002] have shown that processes occur-
 462 ring at the snow surface in Greenland can affect firm air
 463 mixing ratios of some trace gases, although no mention
 464 of COS was made in their study. Our data suggest that
 465 any offset for COS in SPO firm air is small, however,
 466 because (1) the enhancement is fairly small and short-
 467 lived (we have observed an enhancement only in October
 468 and November, in December and months thereafter it is
 469 not noticeable), (2) firm air mixing ratios below 15 m,
 470 where seasonal effects are reduced, are not biased high
 471 relative to ambient air annual means measured in recent
 472 years at this site, and (3) the general pattern of measured
 473 seasonality at depths below 5 m in the firn is consistent
 474 with the seasonal changes observed in the atmosphere and
 475 the one-dimensional model calculation (Figure 6). We
 476 conclude that ambient air mixing ratios of COS become
 477 incorporated into the firn at SPO without significant
 478 production or loss.

3.2. Atmospheric Histories Inferred for COS Over Antarctica

481 [30] We derived three different histories for COS in
 482 Antarctic air using different combinations of the available
 483 COS data (H1, H2, and H3; Figures 2 and 7; and
 484 Table 2). The inferred histories imply that mixing ratios
 485 of COS have increased and decreased at different times in
 486 the past. The measurements from ice cores suggest that
 487 COS mixing ratios decreased during the 1600s and
 488 reached a minimum of about 320 ppt in the 1700s (H3,
 489 Figure 7). All histories derived here indicate substantial
 490 increases in atmospheric COS after 1850. Although some
 491 discrepancies are apparent between H1 and H3 where
 492 they overlap, the general pattern of past changes inferred
 493 for COS is consistent.

494 [31] Some of the differences between the derived his-
 495 tories arise because different constraints were imposed
 496 while performing the inversions (Table 2). The 350-year
 497 history (H3) was developed by considering both the ice
 498 core and firm data, and also the ambient air data from
 499 SPO during 2000–2003. Seasonal variability, however,
 500 was not considered. H1 and H2 were derived with
 501 measurements of SPO firm air and samples of ambient
 502 air collected through the firm air sampling apparatus in
 503 January 2001. These summertime samples were treated on
 504 an equal footing with the subsurface firm data. Further-
 505 more, H1 and H2 allowed for a seasonally varying

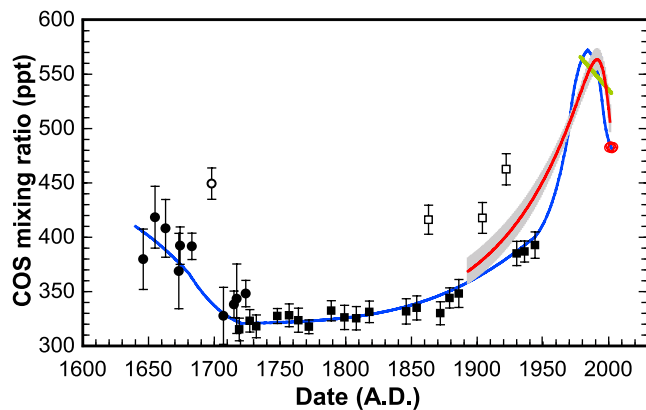


Figure 7. Atmospheric histories inferred for COS from firn air measurements (H1, red line with 68.3% uncertainty bound indicated by gray shading) and from a combination of ice core, firn air, and ambient air data (H3, blue line). Dated ice core results (solid black circles [Aydin *et al.*, 2002]; solid black squares (this work); open black circle and squares were not considered in the calculation of the H3 history) are plotted as individual points but represent a mean mixing ratio over a range of years owing to the diffusive nature of the firn at Siple Dome (the full width at half height of the age distribution for these ice core observations is estimated from the firn modeling to be about 20 years). Meaningful dates cannot be similarly assigned to individual SPO firn air samples and so are not shown. Annual means from flask measurements at South Pole since 2000 are shown as red circles. A fit to the long-term decline reported by Rinsland *et al.* [2002] for the Northern Hemisphere is included for comparison (green line, mean seasonality on the fit not included). Adjustments of 1.6 and 3% have been applied to the data from Aydin *et al.* [2002] and the more recent ice data from University of California, Irvine, respectively, to put all data on a consistent scale.

506 atmosphere based upon the mean seasonality observed at
507 SPO in recent years (Figure 4).

508 [32] Despite these differences, all three derived histories
509 suggest a decline in COS over Antarctica of about 60–90 ppt
510 during the past 10 to 15 years. Although peak mixing ratios in
511 the model-derived atmospheric histories are larger than those
512 measured in firn air (compare Figure 3 to Figures 2 or 7,
513 for example), mixing ratios in the firn are influenced
514 substantially by molecular diffusion. The diffusivity in the
515 shallow firn is high enough so that rapid changes in atmo-
516 spheric mixing ratios are incompletely expressed (i.e.,
517 smoothed) in the firn. Because of these effects, the inferred
518 histories include mixing ratios above 550 ppt despite the fact
519 that we measured only lower mixing ratios in firn air.

520 [33] The inferred atmospheric decline during recent years,
521 however, is sensitive to differences between mixing ratios
522 measured in firn air and those measured in ambient air. If
523 COS were produced within the firn or at the air-firn
524 interface, or if biases were introduced in sampling firn air,
525 for example, the resulting offset between firn air and
526 ambient air could be interpreted erroneously to suggest a
527 recent decline in atmospheric mixing ratios. Aware of these
528 sensitivities, we searched for COS artifacts in firn air and in

our sampling apparatus but found none to be significant. For
529 example, COS mixing ratios in ambient air collected
530 through the firn air sampling apparatus were within 2%
531 (or 10 ppt) of those from ongoing measurements at SPO and
532 CGO at this time of year (Figure 3). This consistency
533 suggests that firn air mixing ratios were accurately sampled
534 with the firn air sampling apparatus.
535

[34] Detecting processes in the firn and ice that might bias
536 COS mixing ratios, such as hydrolysis or slow production
537 over long periods, is more difficult. As discussed above, we
538 studied the incorporation of COS into the upper layers of
539 the firn and found that unusual and temporary enhance-
540 ments can be observed shortly after sunrise at SPO
541 (Figure 6). This enhancement appears to be quite small,
542 however, and apparently does not substantially affect firn
543 air COS mixing ratios below a few meters depth.
544

[35] The long-term stability of COS in the firn or ice has
545 not been proven in our studies. Aydin *et al.* [2002] suggest
546 that the ice core data argue against rapid loss. The fact that
547 ice core COS levels exhibit a minimum during the 1700s
548 and 1800s suggests that in situ, first-order losses are not
549 responsible for the observed COS variability on timescales
550 of a few hundred years. The histories derived here were
551 calculated with the assumption that COS is neither produced
552 nor destroyed within the firn and ice.
553

[36] Although the scatter observed for COS in the upper
554 firn is large compared to measurement uncertainty (Figures 1
555 and 3), the decreasing trend inferred from the available data
556 for atmospheric COS since the mid-1980s appears robust. A
557 separate history (H2) was calculated as was H1 but with the
558 highest firn air results from 20, 37.4, 59.6, and 100.2 m
559 depth excluded (Figures 1–3). Although the χ^2 for the
560 history derived with these points removed ($\chi^2 = 15.4$ for
561 H2) is much smaller than for H1 ($\chi^2 = 42$), both inferred
562 histories suggest substantial declines in atmospheric COS
563 over Antarctica in recent years (Figure 2). The large, recent
564 decline in atmospheric COS is suggested by the firn results
565 because mixing ratios in all firn samples between 20 and
566 114 m depth are higher than annual means measured at SPO
567 during 2000–2002. Our firn data would have to be errone-
568 ously high by 50 ppt for the inversion calculations to not
569 show this recent decline. Given the results of the tests we
570 performed on firn air and our sampling apparatus, we
571 consider this possibility unlikely.
572

3.3. Interpreting Historical Atmospheric Trends 573

[37] Attributing past changes in southern hemispheric
574 COS to specific sources or sinks is difficult because COS
575 fluxes are numerous and poorly quantified. Watts [2000]
576 reviewed COS sources and sinks and suggested that anthro-
577 pogenic sources account for $26 \pm 12\%$ of all known sources.
578 More recent work by Yvon-Lewis and Butler [2002]
579 concerning oceanic loss rates for COS suggests that the
580 gross ocean-to-atmospheric flux for COS is over 2 times as
581 large as the net oceanic flux of 0.3 Tg yr^{-1} considered by
582 Watts [2000]. This would imply that anthropogenic emis-
583 sions comprise a slightly smaller fraction ($\sim 20\%$) of total
584 emissions.
585

[38] The atmospheric history derived from the firn and ice
586 data suggests preindustrial COS mixing ratios that are 34–
587 43% ([485–320]/485 to [565–320]/565, Figure 7) lower
588 than observed in modern time. This difference is larger than
589

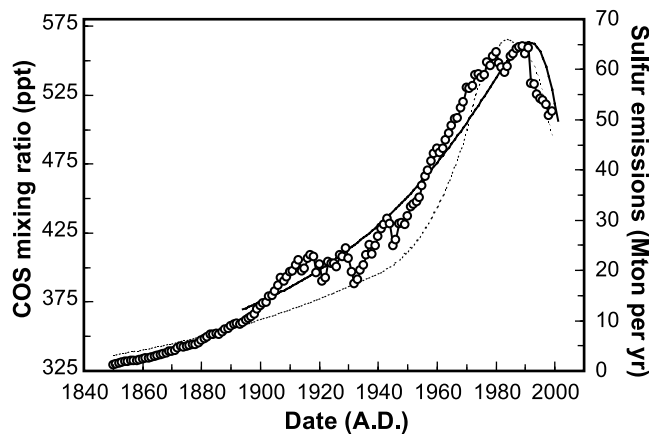


Figure 8. Histories for atmospheric COS mixing ratios derived in this work compared to estimates of global sulfur emissions [Stern, 2001] (history H1, solid line; history H3, dashed line; and emission estimates, points connected by lines). The similarity suggests a relationship between atmospheric COS and sulfur emissions of 3.5 ppt COS/megatons of S emitted.

590 expected considering the estimated contribution of anthro-
 591 pogenic emissions to total COS emissions. This apparent
 592 discrepancy may reflect the large uncertainties in estimates
 593 of COS sources, or it may suggest substantial changes in
 594 nonanthropogenic fluxes over the past 150 years (such as
 595 that indicated by the ice data during 1650–1750).

596 [39] The largest anthropogenic source of COS is believed
 597 to be atmospheric oxidation of industrially produced CS₂,
 598 which is derived primarily from the manufacture of viscose
 599 rayon [Watts, 2000; Sturges et al., 2001]. Viscose rayon
 600 production began in 1910 and was fairly constant from
 601 1970–1990 [Sturges et al., 2001]. The magnitude of the
 602 atmospheric increase inferred from the SH ice core and firn
 603 data suggest that changes in rayon production alone could
 604 not be responsible for the increases in atmospheric COS
 605 [see also Sturges et al., 2001].

606 [40] Direct industrial emissions of COS from coal burn-
 607 ing, sulfur recovery processes, and motor vehicles are
 608 thought to account for the remaining anthropogenic sources.
 609 Although COS from coal combustion is thought to be a
 610 minor source of COS to the atmosphere [Watts, 2000], this
 611 estimate is based solely upon a single plume study [Khalil
 612 and Rasmussen, 1984] conducted in the western United
 613 States where coal is relatively low in sulfur.

614 [41] Although the magnitude of the increase inferred for
 615 atmospheric COS during the last 150 years is larger than
 616 expected from anthropogenic sources, the atmospheric his-
 617 tories inferred for COS over Antarctica during this period
 618 closely follow global anthropogenic sulfur emissions
 619 (Figure 8) [Lefohn et al., 1999; Stern, 2001]. Global sulfur
 620 emissions increased rapidly beginning in the mid-1800s
 621 owing to enhanced combustion of coal and other fossil
 622 fuels [Keeling, 1994; Siegenthaler and Oeschger, 1987].
 623 While sulfur emissions continued to increase until the late
 624 1900s, they have decreased by 15 to 20% over the past 20
 625 to 30 years [Stern, 2001; Smith et al., 2004]. The strong
 626 similarity between atmospheric COS and sulfur emission
 627 magnitudes suggests that anthropogenic activities played a

628 dominant role in influencing atmospheric mixing ratios of
 629 COS in the nineteenth and twentieth centuries. The history
 630 derived from the firn and ice data can be simulated
 631 reasonably well with a simple box model from 1850 to
 632 2000 if one assumes that 0.3–0.6% of global sulfur emis-
 633 sions ultimately become converted to COS (for a global
 634 COS lifetime of 3–6 years [Kettle et al., 2002]).

635 [42] Substantial historical changes are also possible for
 636 atmospheric losses of COS. The largest sinks for atmo-
 637 spheric COS are believed to be photosynthesizing plants
 638 [Kettle et al., 2002]. Thus it is likely that past changes in
 639 climate and land use would have affected the lifetime and
 640 atmospheric abundance of COS. For example, deforestation
 641 during the 1900s may have lengthened the lifetime of COS
 642 and resulted in increasing atmospheric mixing ratios over
 643 this period. Furthermore, during the “Little Ice Age” from
 644 1550 to 1850 A.D. CO₂ mixing ratios were reduced
 645 compared to other years [Etheridge et al., 1996]; it seems
 646 possible that such changes in climate or terrestrial vegeta-
 647 tion may have caused the decline inferred for COS during
 648 the 1600s (Figure 7). While such explanations are specula-
 649 tive, they suggest that COS fluxes and mixing ratios may be
 650 affected by changes in the biosphere brought about by
 651 changes in global climate and land use.

3.4. Interpreting Recent Atmospheric Trends

652 [43] Firn air data from the Arctic [Sturges et al., 2001],
 653 and multiyear records measured by FTIR at Kitt Peak
 654 (31.9°N) and the Jungfraujoch (46.5°N) (update of Mahieu
 655 et al. [1997] and Rinsland et al. [2002]) all suggest that
 656 Northern Hemispheric (NH) mixing ratios of COS de-
 657 creased by 6 to 8% during the past 10 to 20 years. The
 658 longest available measurement record from Kitt Peak shows
 659 a mean decline of 0.25% ($\pm 0.04\%$) yr⁻¹ for COS during
 660 1978 to 2002 at this midlatitude, NH site (Figure 7). Recent
 661 trends in the SH are less well defined. Long-path absor-
 662 bance data above Lauder, New Zealand, exhibit a decrease
 663 over time, but Griffith et al. [1998] suggest that this
 664 decrease may result from an instrument artifact. On the
 665 basis of Antarctic firn air data, Sturges et al. [2001]
 666 suggest no substantial decline in COS mixing ratios over the
 667 Antarctic since the 1980s. Their conclusion may need
 668 revisiting, however, given the seasonal variations apparent
 669 in ambient air over Antarctica. In contrast to these studies,
 670 the measurements presented here suggest a substantial
 671 decline for COS above Antarctica since the mid-1980s
 672 (Figure 7).

673 [44] The underlying cause for a decline in COS in the
 674 Southern Hemisphere during recent years is not well un-
 675 derstood. Sturges et al. [2001] suggested that recent NH
 676 declines of $8 \pm 5\%$ over the past decade might arise in part
 677 from the 24% decrease in viscose rayon production during
 678 the 1990s. However, they also noted that SH mixing ratios
 679 of COS would likely be affected minimally by the magni-
 680 tude of this production decline. The work of Stern [2001]
 681 and Smith et al. [2004] suggest, however, that sulfur
 682 emissions from other processes also have declined recently.
 683 Owing to reduced SO₂ emissions in Europe and North
 684 America, and to the collapse of Eastern European and Asian
 685 economies, Stern [2001] and Smith et al. [2004] estimate
 686 that global sulfur emissions decreased 15–20% over the
 687 past 20–30 years. While the burning of coal with lower
 688

689 sulfur content and the implementation of flue-gas desulfur-
690 ization technology likely decreased global COS emissions,
691 the magnitude of these potential changes on COS emissions
692 is not known.

693 3.5. Relevance to the Stratospheric Sulfate Burden

694 [45] COS is believed to account for 20–50% of the sulfur
695 in the nonvolcanic, stratospheric aerosol [Chin and Davis,
696 1995; Ko *et al.*, 2003]. Accordingly, one could expect
697 changes in the stratospheric burden of this aerosol over
698 the twentieth century as a result of the changes inferred here
699 for atmospheric COS. The available data [Chipperfield *et al.*,
700 2003] suggest that the nonvolcanic aerosol burden has
701 been fairly constant during 1970–2000, which is when
702 Southern Hemisphere COS mixing ratios and global sulfur
703 emissions changed by a relatively small amount (± 7 –10%).
704 Such small changes in nonvolcanic aerosol are difficult to
705 discern, however, because volcanic eruptions have caused
706 much larger variations in stratospheric aerosol over the past
707 25–30 years [Hofmann, 1990; Chipperfield *et al.*, 2003].
708 Given this large variability, it is not possible to relate
709 changes in stratospheric background aerosol to changes in
710 atmospheric mixing ratios of COS derived from firn and ice
711 bubble air. Despite this, our results suggest that the time-
712 dependent contribution of COS to stratospheric sulfur
713 aerosol changed during the twentieth century in concert
714 with total anthropogenic sulfur emissions.

716 4. Conclusions

717 [46] Histories derived from firn air and ice core measure-
718 ments suggest that COS mixing ratios in the Southern
719 Hemisphere have changed substantially in the past. Reason-
720 able consistency was observed for a history derived from
721 SPO firn air and for results from an ice core drilled at Siple
722 Dome, Antarctica, during the period when the results
723 overlap. Provided COS is neither produced nor degraded
724 significantly within the firn and ice, the derived histories
725 indicate a substantial increase in COS mixing ratios from
726 the mid 1800s to the late 1900s. Although this increase is
727 larger than expected based upon current understanding of
728 the anthropogenic contribution to COS sources, the derived
729 atmospheric increase for COS over this period is closely
730 related to global anthropogenic sulfur emissions.

731 [47] The results also suggest a decline in COS mixing
732 ratios during the late 1600s, before sulfur was emitted in
733 large quantities from anthropogenic activity. Although the
734 cause of this decline is not known, it seems likely that
735 preindustrial mixing ratios of COS could have been affected
736 substantially by changes in climate or terrestrial vegetation
737 coverage.

738 [48] Finally, measurements of COS in modern air and in
739 the upper layers of the firn at SPO suggest ambient air
740 mixing ratios between 480 and 490 ppt and substantial
741 seasonal variations. These observations place useful con-
742 straints on firn air data. Provided that COS is not produced
743 or destroyed in firn air, our results suggest that ambient air
744 mixing ratios of COS have decreased substantially in the
745 Southern Hemisphere during the past 20 years. These
746 atmospheric decreases coincide with declines in global
747 anthropogenic sulfur emissions of 15–20% noted by others
748 over this period.

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758

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