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Permalink
https://escholarship.org/uc/item/17j6m436

Journal
Journal of Geophysical Research, 109(D22)

ISSN
0148-0227

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Publication Date
2004-11-01

DOI
10.1029/2004JD004686

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

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[1] Carbonyl sulfide (COS) and other trace gases were measured in firn air collected near South Pole (89.98°S) and from air trapped in ice at Siple Dome, Antarctica (81.65°S). The results, when considered with ambient air data and previous ice core measurements, provide further evidence that atmospheric mixing ratios of COS over Antarctica between 1650 and 1850 A.D. were substantially lower than those observed today. Specifically, the results suggest annual mean COS mixing ratios between 300 and 400 pmol mol^{-1} (ppt) during 1650–1850 A.D. and increases throughout most of the twentieth century. Measurements of COS in modern air and in the upper layers of the firn at South Pole indicate ambient, annual mean mixing ratios between 480 and 490 ppt with substantial seasonal variations. Peak mixing ratios are observed during austral summer in ambient air at South Pole and Cape Grim, Tasmania (40.41°S). Provided COS is not produced or destroyed in firn, these results also suggest that atmospheric COS mixing ratios have decreased 60–90 ppt (10–16%) since the 1980s in high latitudes of the Southern Hemisphere. The history derived for atmospheric mixing ratios of COS in the Southern Hemisphere since 1850 is closely related to historical anthropogenic sulfur emissions. The fraction of anthropogenic sulfur emissions released as COS (directly or indirectly) needed to explain the secular changes in atmospheric COS over this period is 0.3–0.6%. *INDEX TERMS:* 0325 Atmospheric Composition and Structure: Evolution of the atmosphere; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* atmosphere composition, carbonyl sulfide, stratosphere sulfate aerosol

1. Introduction

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

[3] Although some human activities are sources of atmospheric COS, natural fluxes have a strong influence on observed mixing ratios of this trace gas [*Watts*, 2000]. For example, the largest sink of COS is believed to be loss to vegetation via hydrolysis by the enzymes primarily involved in photosynthesis [*Protoschill-Krebs et al.*, 1996; *Kettle et al.*, 2002]. Although understanding long-term trends and variability for COS can provide insight into the human influence on atmospheric sulfur in the form of COS, it also could provide information on the variability of certain biogeochemical cycles.

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

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

Sample Type	Location	Collection Times	Sample Depths	Compounds Measured	Sample Container Type
Firn air (deep holes)[a]	near South Pole (89.98°S)	January 2001	0–120 m in two holes	COS, CO_2, $\delta^{15}N$ of N_2[b]	glass flasks and three Al cylinders
Firn air (near surface)[c]	South Pole (90.00°S)	January, August, and October 2003	0.3–16.3 m	COS[b]	paired glass flasks
Ice core	Siple Dome, Antarctica (81.65°S)	December 1995	56.8–90.7 m[d]	COS,[b] CO_2,[e] $\delta^{15}N$ of N_2[e]	not applicable
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

[a]Air was sampled with the inflatable bladder technique described by *Schwander et al.* [1993] and *Battle et al.* [1996].

[b]Additional gases were measured in these samples but are not considered here (CH_4, CO, N_2O, SF_6, chlorofluorocarbons, hydrochlorofluorocarbons, hydrofluorocarbons, chlorinated solvents, methyl halides, halons, and benzene).

[c]Air was sampled from eight permanent tubes installed in January of 1998 [*Severinghaus et al.*, 2001].

[d]COS ice core measurements from 82.3 to 90.7 m were published previously by *Aydin et al.* [2002].

[e]Compounds were used in the modeling of Siple Dome firn; data were published previously by *Butler et al.* [1999].

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

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

2. Methods

2.1. Firn Air Collection

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

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

2.2. Firn Air Analysis

[9] Flasks filled with firn air were analyzed in the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) Boulder laboratory with gas chromatography-mass spectrometry (GC-MS) instrumentation that has allowed measurements of halocarbons in firn air and in the modern atmosphere [*Butler et al.*, 1999; *Montzka et al.*, 1999]. Selected flasks were reanalyzed up to 4 months after the 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 (≤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 ≤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 H_2O) in electropolished, stainless steel tanks (Essex Cyrogenics, 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 firn air from these same deep holes. Some were analyzed with mass spectrometry for $\delta^{15}N$ of N_2 (among other species) at the Princeton laboratory to allow for gravitational corrections on firn air measurements [*Bender et al.*, 1994], while others were analyzed for CO_2 by NOAA CMDL [*Tans et al.*, 2002]. These data, along with the atmospheric CO_2 record of *Etheridge et al.* [1996] and *Tans et al.* [2002], were incorporated into one-dimensional firn 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 firn air samples, especially near bubble close off [*Butler et al.*, 1999; *Sturges et al.*, 2001]. This contamination was detected by elevated amounts of CO_2, 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

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

2.3. Analysis of Ice Core Air

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

2.4. Ambient Air Measurements of COS

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

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

2.5. Model Calculations for Deriving Atmospheric Histories for COS

[16] We derived multiple histories for atmospheric COS with various combinations of measurements from firn air, ice core air, and ambient air at SPO and Siple Dome (Table 2). Because the movement of trace gases through firn is dominated by molecular diffusion [*Schwander et al.*,

1988; *Schwander*, 1989; *Bender et al.*, 1994], histories were derived with an inverse approach based on one-dimensional forward diffusion models [*Battle et al.*, 1996; *Aydin et al.*, 2004]. As in those studies, we used independently measured atmospheric CO_2 histories [*Etheridge et al.*, 1996; *Tans et al.*, 2002] and measurements of CO_2 in firn air to infer the relationship between diffusivity and depth. Although the 'tuned' diffusivity profiles at South Pole and Siple Dome are similar to those derived solely from snow density [e.g., *Trudinger et al.*, 1997], they allow for a more accurate representation of gas movement through the complex and highly variable crystalline structure of firn. The resulting diffusivity profiles, along with porosity values derived from in situ density measurements, were used without further modification as input values for the one-dimensional diffusion model calculations.

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

[17] Two histories, H1 and H2, were derived for COS in the Antarctic atmosphere based upon measurements of SPO firn air, ambient air measurements collected through the firn air sampling apparatus in January 2001, and knowledge of seasonal changes observed for COS in the ambient atmosphere (Table 2). To derive these atmospheric histories, we assumed that the true history of atmospheric COS mixing ratios can be described by a single mathematical function with a limited number of free parameters. A systematic and objective procedure was used to select a number of functions as candidates for providing the best fit to the firn air data. First, a preliminary history was derived from the discrete firn air measurements of COS based upon CO_2-derived mean ages assigned to each individual sample. Second, many functions (a library of more than 3400 functions; TableCurve2D) were sorted based upon how well they fit the preliminary history; those giving the best fits were selected for further consideration. These trial functions, and a few additional ones that included or excluded inflection points in an atmospheric history, were considered in the derivation of a best estimate history. They included log normal, extreme value (EV), sigmoidal (SIG), asymmetric logistic (H1 and H2), Pearson VII, asymmetric double sigmoidal, Lorentzian cumulative, extreme value cumulative, asymmetric sigmoidal, asymmetric sigmoidal with reverse asymmetry, and Weibull. All of these functions include a constant offset (allowed to vary) and have six or fewer free parameters. These functions were chosen for their ability to describe a wide range of possible atmospheric histories including monotonic increases, transitions from low to high values, and increases followed by decreases. The functions all have a small number of free parameters (relative to the number of firn air measurements), and are well behaved with respect to small variations in their free parameters.

[18] For each of the functions listed above, we adjusted the free parameters according to the method of Levenberg and Marquardt [*Press et al.*, 1992] to optimize the agreement between observations and predictions of a forward model run. For the few functions exhibiting the best fits, multiple runs were attempted with different starting parameters and the same minima were obtained. To reduce our sensitivity to errors in the inferred diffusivity-depth profile, we optimized agreement between the

Table 2. Description of Model-Derived Histories

History	Input COS Data	Period, years	Output
H1	firn air from deep holes drilled near South Pole (89.98°S) in January 2001; ambient air sampled through firn 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 firn air data for COS and CO_2
H2	same as H1 but with firn 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
H3	firn 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 firn at South Pole and in ice at Siple Dome

[a]Dates are applied to air trapped in Siple Dome ice through an understanding of trace gas diffusion timescales through the Siple Dome firn. These timescales were derived from an analysis of CO_2 measurements discussed elsewhere [*Butler et al.*, 1999].

data and model for COS as a function of CO_2 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 firn measurements between 60 m and 110 m depth and not on instrumental analysis uncertainty (which is smaller). Calculations with the one-dimensional firn model suggest that at these depths diffusion is rapid enough in the SPO firn 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 firn 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; CO_2 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 10^5 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 $[\chi^2_{min}]/[$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 Firn Air Measurements

[22] Additionally, a 350-year atmospheric history (H3) for COS was derived with a separate, one-dimensional, forward model of a firn column [*Schwander et al.*, 1988] that was constrained by all available COS data. These included data from ice cores at Siple Dome, from deep firn air at SPO, and from ambient air at SPO (Table 2). The physical properties of the firn at Siple Dome and SPO are different; therefore the model was initiated separately to simulate these two firn columns. As was the case for the one-dimensional model used to derive H1 and H2, H3 was derived with porosity profiles from firn column density measurements, and diffusivity profiles were adjusted to provide good consistency between measured CO_2 within the firn column and CO_2 mixing ratios calculated from the model based upon the indepen-
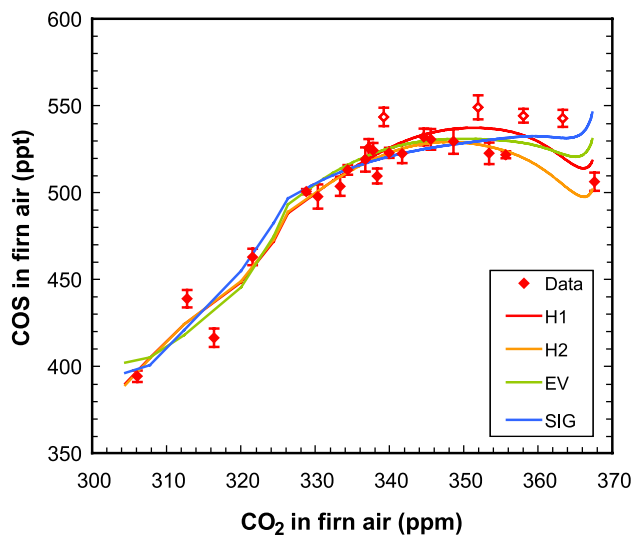
Figure 1. The measured (red diamonds) and modeled (lines) relationship between mixing ratios of COS and CO_2 in South Pole firn air (89.98°S). Modeled relationships reflect optimized, 100-year histories of carbonyl sulfide (COS) and the known history for CO_2 [*Etheridge et al.*, 1996; *Tans et al.*, 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 CO_2 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 CO_2 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).

dently measured atmospheric CO_2 history [*Etheridge et al.*, 1996; *Tans et al.*, 2002]. Firn air measurements of CO_2 from December of 1996 were used to optimize diffusivity in the firn column above the ice at Siple Dome (provided by *Butler et al.* [1999]). This procedure is necessary for assigning dates to the ice core results from this site. To test these optimizations and this slightly different modeling approach, firn air mixing ratios of CFC-12 were considered. Good consistency was observed for measured firn air mixing ratios of CFC-12 at South Pole and Siple Dome [*Butler et al.*, 1999] and for those calculated with the model based upon an estimate of its atmospheric history [*Walker et al.*, 2000]. The accumulation rate at Siple Dome and ice ages below the firn-ice

transition were estimated from visual stratigraphy (R. B. Alley, unpublished data, 2001).

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

[24] The oldest 100 years of the 350-year atmospheric history are shifted by about 30 years from the dates derived by *Aydin et al.* [2002]. This is because diffusivity in the firn diffusion model at South Pole and Siple Dome was not tuned by considering CO_2 in firn air and its known atmospheric history in the earlier work of *Aydin et al.* [2002].

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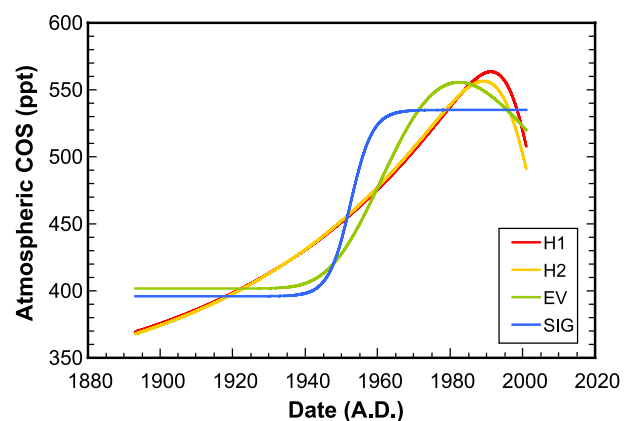

Figure 2. Optimized, 100-year histories for COS in Antarctic ambient air calculated with asymmetric logistic (H1 and H2), SIG, and EV functions (described in Figure 1 caption). These histories, when incorporated into the one-dimensional South Pole firn model, provide the smallest residuals (χ^2, listed for the different functions in the caption to Figure 1) between measured mixing ratios of COS and CO_2 in the firn for the chosen functional form (given the known atmospheric history of CO_2 [*Etheridge et al.*, 1996; *Tans et al.*, 2002]).
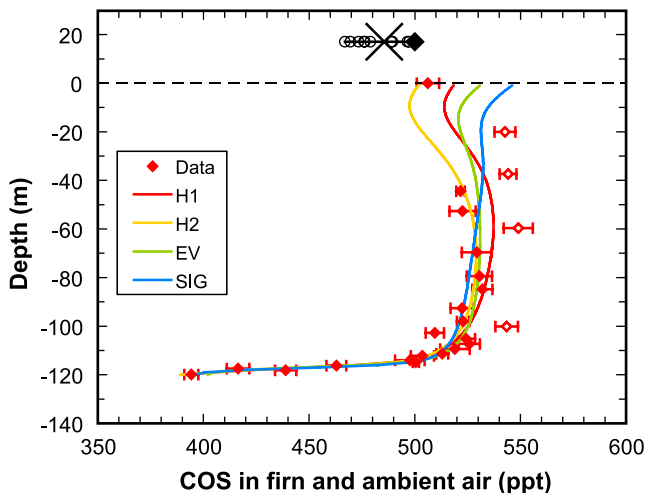
Figure 3. Measured and calculated COS mixing ratios in SPO firn air (89.98°S) (symbols the same as Figure 1) and ambient air at South Pole (90.00°S). Calculated depth profiles (lines) are derived from the one-dimensional firn model and the optimized, 100-year histories shown in Figure 2. The solid red 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 (circles), and (3) the monthly mean during January (the solid diamond).
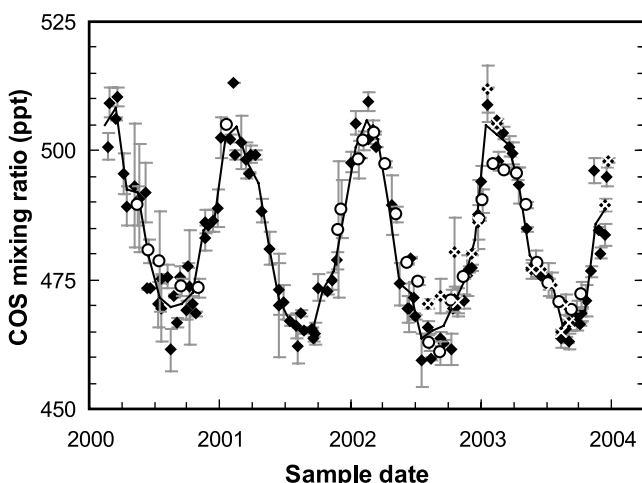

Figure 5. Carbonyl sulfide mixing ratios in air trapped in ice collected at Siple Dome, Antarctica, in December 1995 (81.65°S) (solid and open circles [*Aydin et al.*, 2002]) and additional measurements from this same core (solid and open squares (this work)). Points suspected of being contaminated were 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.

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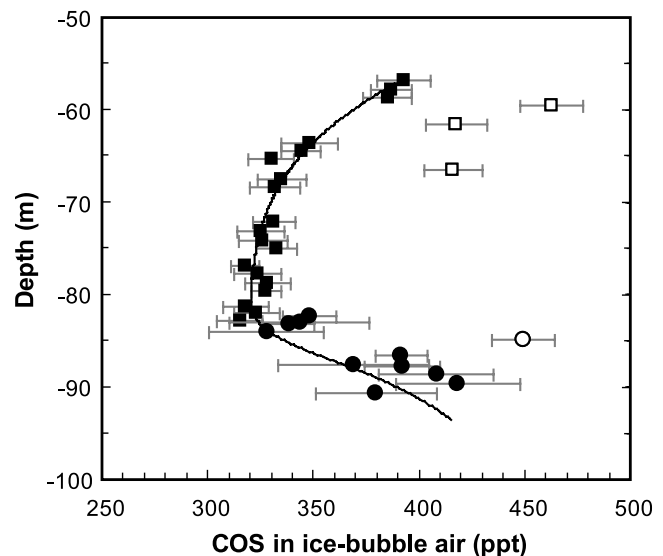
atmospheric history. COS mixing ratios in four ice samples (at 59.6, 61.5, 66.5, and 85 m) were unusually high compared to the running mean of the remaining data. Tests with a firn model suggest that short-duration atmospheric increases (e.g., potentially from volcanoes) would be extensively smoothed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

3. Results and Discussion

3.1. Depth Profiles for COS in Firn and Ice

[26] In firn air the lowest COS mixing ratios were measured in the deepest samples that showed no modern air contamination (Figure 3). In these deep and clean samples, COS averaged 416 ± 5 ppt from hole 1 (at 117.5 m depth), and 394 ± 8 ppt from hole 2 (at 120 m depth). These mixing ratios are about 16% lower than annual means observed in ambient air at SPO and Cape Grim, Tasmania (CGO) (40.41°S) during 2000–2003 (485 ppt) (Figures 3 and 4). Even lower mixing ratios were measured in ice bubbles collected from Siple Dome (Figure 5) [*Aydin et al.*, 2002]. In the deepest section of this ice core, *Aydin et al.* [2002] reported a mean mixing
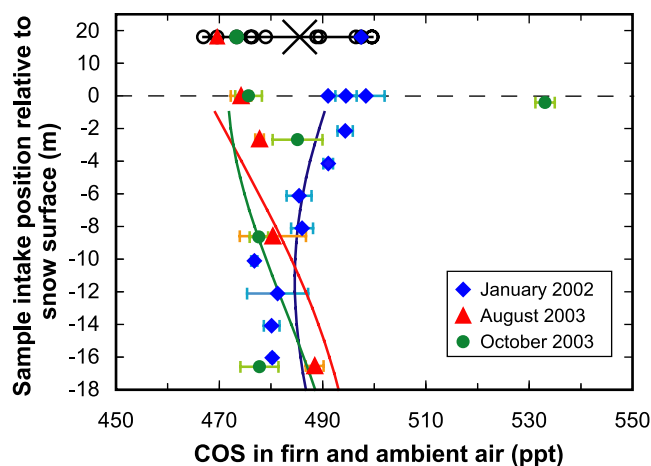
Figure 6. Carbonyl sulfide mixing ratios in firn air collected from tubes permanently installed in the upper 17 m of the firn at South Pole. These tubes were sampled at different times in the past, as indicated by the different colors (blue diamonds, January 2002; red triangles, August 2003; green circles, October 2003). Each firn 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 firn 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).

ratio for COS of 373 ± 37 ppt. Here we report additional measurements of COS from this same core, but in younger ice (57−83 m depth) (Figure 5). The mean COS mixing ratio in these shallower samples was 340 ± 39 ppt, which is lower than was measured in the deep ice. A mean minimum COS mixing ratio of 322 ± 10 ppt is calculated from the measurements between 63 and 84 m (excluding the apparently contaminated result at 66.47 m). Provided COS is neither degraded nor produced in firn or ice, these mixing ratio−depth profiles from both SPO and Siple Dome provide further evidence that the atmospheric mixing ratio of COS was once substantially lower than observed in Antarctica today.

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

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

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

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

3.2. Atmospheric Histories Inferred for COS Over Antarctica

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

[31] Some of the differences between the derived histories arise because different constraints were imposed while performing the inversions (Table 2). The 350-year history (H3) was developed by considering both the ice core and firn data, and also the ambient air data from SPO during 2000−2003. Seasonal variability, however, was not considered. H1 and H2 were derived with measurements of SPO firn air and samples of ambient air collected through the firn air sampling apparatus in January 2001. These summertime samples were treated on an equal footing with the subsurface firn data. Furthermore, H1 and H2 allowed for a seasonally varying
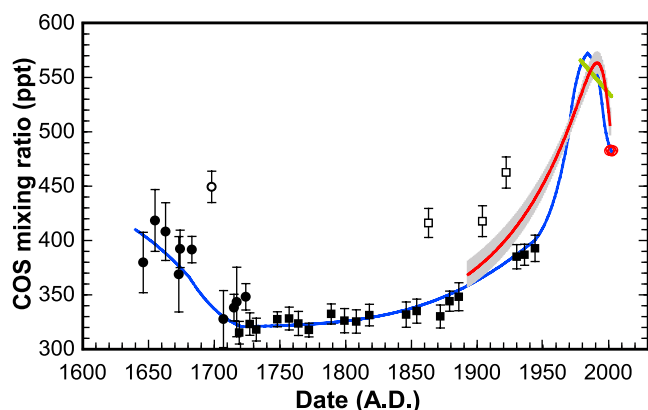
Figure 7. Atmospheric histories inferred for COS from firn air measurements (H1, red line with 68.3% uncertainty bound indicated by gray shading) and from a combination of ice core, firn air, and ambient air data (H3, blue line). Dated ice core results (solid black circles [*Aydin et al.*, 2002]; solid 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.

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

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

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

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

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

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

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

3.3. Interpreting Historical Atmospheric Trends

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

[38] The atmospheric history derived from the firn and ice data suggests preindustrial COS mixing ratios that are 34–43% ([485−320]/485 to [565−320]/565, Figure 7) lower than observed in modern time. This difference is larger than
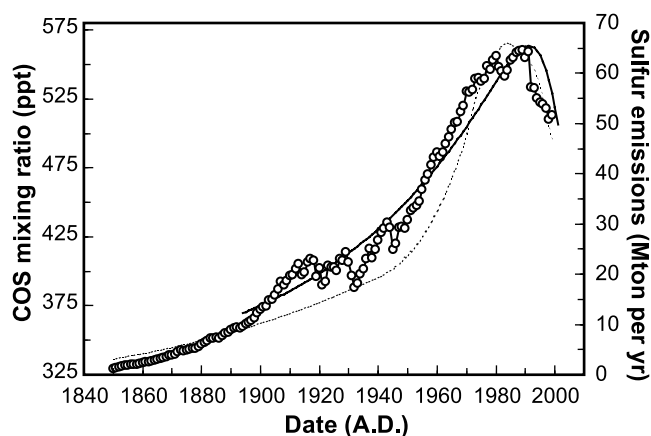
Figure 8. Histories for atmospheric COS mixing ratios derived in this work compared to estimates of global sulfur emissions [*Stern*, 2001] (history H1, solid line; history H3, dashed line; and emission estimates, points connected by lines). The similarity suggests a relationship between atmospheric COS and sulfur emissions of 3.5 ppt COS/ megaton of S emitted.

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

[39] The largest anthropogenic source of COS is believed to be atmospheric oxidation of industrially produced CS_2, which is derived primarily from the manufacture of viscose rayon [*Watts*, 2000; *Sturges et al.*, 2001]. Viscose rayon production began in 1910 and was fairly constant from 1970–1990 [*Sturges et al.*, 2001]. The magnitude of the atmospheric increase inferred from the SH ice core and firn data suggest that changes in rayon production alone could not be responsible for the increases in atmospheric COS [see also *Sturges et al.*, 2001].

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

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

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

[42] Substantial historical changes are also possible for atmospheric losses of COS. The largest sinks for atmospheric COS are believed to be photosynthesizing plants [*Kettle et al.*, 2002]. Thus it is likely that past changes in climate and land use would have affected the lifetime and atmospheric abundance of COS. For example, deforestation during the 1900s may have lengthened the lifetime of COS and resulted in increasing atmospheric mixing ratios over this period. Furthermore, during the "Little Ice Age" from 1550 to 1850 A.D. CO_2 mixing ratios were reduced compared to other years [*Etheridge et al.*, 1996]; it seems possible that such changes in climate or terrestrial vegetation may have caused the decline inferred for COS during the 1600s (Figure 7). While such explanations are speculative, they suggest that COS fluxes and mixing ratios may be affected by changes in the biosphere brought about by changes in global climate and land use.

3.4. Interpreting Recent Atmospheric Trends

[43] Firn air data from the Arctic [*Sturges et al.*, 2001], and multiyear records measured by FTIR at Kitt Peak (31.9°N) and the Jungfraujoch (46.5°N) (update of *Mahieu et al.* [1997] and *Rinsland et al.* [2002]) all suggest that Northern Hemispheric (NH) mixing ratios of COS decreased by 6 to 8% during the past 10 to 20 years. The longest available measurement record from Kitt Peak shows a mean decline of 0.25% (±0.04%) yr^{-1} for COS during 1978 to 2002 at this midlatitude, NH site (Figure 7). Recent trends in the SH are less well defined. Long-path absorbance data above Lauder, New Zealand, exhibit a decrease over time, but *Griffith et al.* [1998] suggest that this decrease may result from an instrument artifact. On the basis of Antarctic firn air data, *Sturges et al.* [2001] suggest no substantial decline in COS mixing ratios over the Antarctic since the 1980s. Their conclusion may need revisiting, however, given the seasonal variations apparent in ambient air over Antarctica. In contrast to these studies, the measurements presented here suggest a substantial decline for COS above Antarctica since the mid-1980s (Figure 7).

[44] The underlying cause for a decline in COS in the Southern Hemisphere during recent years is not well understood. *Sturges et al.* [2001] suggested that recent NH declines of 8 ± 5% over the past decade might arise in part from the 24% decrease in viscose rayon production during the 1990s. However, they also noted that SH mixing ratios of COS would likely be affected minimally by the magnitude of this production decline. The work of *Stern* [2001] and *Smith et al.* [2004] suggest, however, that sulfur emissions from other processes also have declined recently. Owing to reduced SO_2 emissions in Europe and North America, and to the collapse of Eastern European and Asian economies, *Stern* [2001] and *Smith et al.* [2004] estimate that global sulfur emissions decreased 15–20% over the past 20–30 years. While the burning of coal with lower

sulfur content and the implementation of flue-gas desulfurization technology likely decreased global COS emissions, the magnitude of these potential changes on COS emissions is not known.

3.5. Relevance to the Stratospheric Sulfate Burden

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

4. Conclusions

[46] Histories derived from firn air and ice core measurements suggest that COS mixing ratios in the Southern Hemisphere have changed substantially in the past. Reasonable consistency was observed for a history derived from SPO firn air and for results from an ice core drilled at Siple Dome, Antarctica, during the period when the results overlap. Provided COS is neither produced nor degraded significantly within the firn and ice, the derived histories indicate a substantial increase in COS mixing ratios from the mid 1800s to the late 1900s. Although this increase is larger than expected based upon current understanding of the anthropogenic contribution to COS sources, the derived atmospheric increase for COS over this period is closely related to global anthropogenic sulfur emissions.

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

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

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