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Journal

Journal of Geophysical Research: Atmospheres, 119(13)

ISSN

2169-897X

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Publication Date

2014-07-16

DOI

10.1002/2014jd021618

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Peer reviewed

RESEARCH ARTICLE

10.1002/2014JD021618

Key Points:

- Carbonyl sulfide measurements made in various Antarctic ice cores
- Carbonyl sulfide is hydrolyzed in situ within the ice matrix
- Data corrected for in situ loss to recover a Holocene atmospheric history

Supporting Information:

- Readme
- Table S1
- Table S2
- Table S3
- Figure S1
- Figure S2
- Figure S3
- Figure S4

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Citation:

Aydin, M., T. J. Fudge, K. R. Verhulst, M. R. Nicewonger, E. D. Waddington, and E. S. Saltzman (2014), Carbonyl sulfide hydrolysis in Antarctic ice cores and an atmospheric history for the last 8000 years, *J. Geophys. Res. Atmos.*, *119*, 8500–8514, doi:10.1002/2014JD021618.

Received 7 FEB 2014

Accepted 2 JUN 2014

Accepted article online 9 JUN 2014

Published online 12 JUL 2014

Carbonyl sulfide hydrolysis in Antarctic ice cores and an atmospheric history for the last 8000 years

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Abstract Carbonyl sulfide (COS) was measured in Antarctic ice core samples from the Byrd, Siple Dome, Taylor Dome, and West Antarctic Ice Sheet Divide sites covering the last 8000 years of the Holocene. COS levels decrease downcore in most of these ice cores. The magnitude of the downcore trends varies among the different ice cores and is related to the thermal histories of the ice sheet at each site. We hypothesize that this is due to the temperature-dependent hydrolysis of COS that occurs in situ. We use a one-dimensional ice flow and heat flux model to infer temperature histories for the ice core samples from different sites and empirically determine the kinetic parameters for COS hydrolysis. We estimate *e*-folding lifetimes for COS hydrolysis ranging from 10² years to 10⁶ years over a temperature range of 0°C to −50°C. The reaction kinetics are used to estimate and correct for the in situ COS loss, allowing us to reconstruct paleoatmospheric COS trends during the mid-to-late Holocene. The results suggest a slow, long-term increase in atmospheric COS that may have started as early as 5000 years ago. Given that the largest term in the COS budget is uptake by terrestrial plants, this could indicate a decline in terrestrial productivity during the late Holocene.

1. Introduction

Carbonyl sulfide (COS) is the most abundant sulfur gas in the troposphere, with a global average mixing ratio of 480–490 parts per trillion (ppt) and a lifetime of 2–3 years [Montzka *et al.*, 2007]. COS is emitted from a variety of natural and anthropogenic sources. It is produced directly in the surface ocean through photochemical breakdown of organosulfur compounds. The oceans are also a large indirect source of COS via the emission and atmospheric oxidation of carbon disulfide (CS₂) and dimethylsulfide (DMS) [Watts, 2000; Kettle, 2002]. Both COS and CS₂ are also emitted as a result of industrial activities linked to synthetic fiber manufacturing [Sturges *et al.*, 2001; Montzka *et al.*, 2004]. Additional sources include biomass burning and minor emissions from anoxic soils, wetlands, and volcanism [Watts, 2000; Kettle, 2002]. The primary loss mechanism for atmospheric COS is uptake by terrestrial vegetation. Other loss mechanisms include microbial consumption in oxic soils, uptake and hydrolysis in the surface ocean, removal in the troposphere through oxidation and direct photolysis, and loss to the stratosphere [Chin and Davis, 1993]. Based on recent top down estimates of the atmospheric COS fluxes [Suntharalingam *et al.*, 2008; Berry *et al.*, 2013], the COS levels in the preindustrial atmosphere would largely reflect a balance between the net oceanic source and the terrestrial uptake.

Atmospheric COS exhibits strong seasonal variability in the northern hemisphere, with a late summer minimum that follows the peak in terrestrial productivity [Montzka *et al.*, 2007]. This atmospheric drawdown and laboratory studies suggest a link to primary production [Goldan *et al.*, 1988; Kesselmeier and Merk, 1993]. During photosynthesis, COS is taken up by plant leaves, where the carbonic anhydrase enzyme acts as a catalyst in the hydrolysis of COS to H₂S. This enzyme is also responsible for the conversion of CO₂ to HCO₃[−] during the first stage of photosynthesis [Protoschill-Krebs *et al.*, 1996; Notni *et al.*, 2007]. Unlike CO₂, plants do not emit COS during respiration. Consequently, the uptake of COS by terrestrial plants is expected to scale with gross primary productivity (GPP) [Kuhn *et al.*, 1999; Sandoval-Soto *et al.*, 2005; Stimler *et al.*, 2010, 2011]. However, there is not yet a widely applicable quantitative relationship between the COS flux and the GPP at the ecosystem level [Xu *et al.*, 2002; Montzka *et al.*, 2007; Campbell *et al.*, 2008; Seibt *et al.*, 2010; Blonquist *et al.*, 2011; Asaf *et al.*, 2013].

Atmospheric COS has a role in the global climate system as a precursor of stratospheric sulfate aerosols and a tropospheric greenhouse gas. Crutzen [1976] proposed background COS as the major precursor for

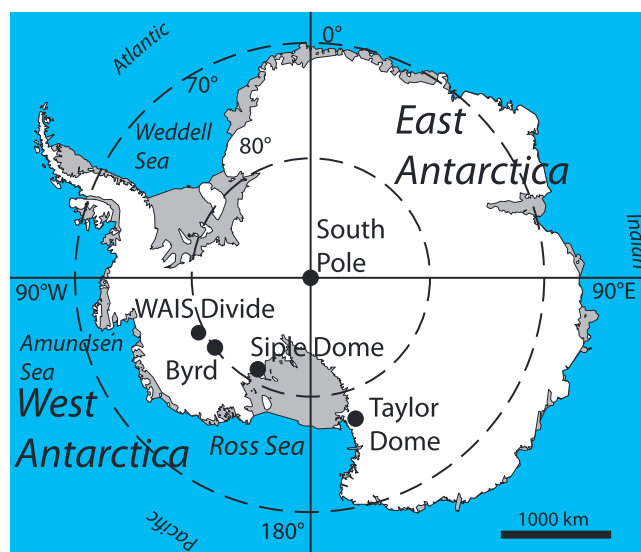


Figure 1. Antarctic map displaying the study sites.

natural variability and the impact of human activities on atmospheric COS levels. Firn air studies showed that there had been large increases in atmospheric COS during the early part of the twentieth century, constraining the anthropogenic component in the present-day budget to about 30% of the total sources [Sturges et al., 2001; Montzka, 2004]. Previous measurements in dry-drilled, shallow Antarctic ice cores from Siple Dome and South Pole showed that preindustrial COS mixing ratios ranged from 300 to 400 ppt over the last two millennia [Aydin et al., 2008].

Here we present new COS measurements in Antarctic ice cores from Byrd, Siple Dome, Taylor Dome, and West Antarctic Ice Sheet (WAIS) Divide (Figure 1 and Table 1), covering a wide range of surface temperatures, accumulation rates, and gas ages ranging up to 8 kyr (thousand years before 1950 Common Era (C.E.)). The results suggest that there is significant COS loss in ice cores on millennial time scales due to in situ chemistry. We examine the kinetics of this in situ COS loss using a one-dimensional (1-D) ice flow and heat flux model and suggest a method to correct for the COS loss that allows reconstruction of a COS atmospheric history based on ice core measurements.

2. Methods

Air is extracted from the bubbles in 400–600 g ice core samples in a dry extraction system that involves mechanical shredding at -50°C under vacuum [Aydin et al., 2007, 2008]. Four different extraction chambers were used in this study. Each chamber is a closed-end stainless steel tube (20 cm long, 15 cm in diameter, electron beam welds, made from 316L stainless steel) sealed with a copper gasket conflat flange. A flat cheese grater welded inside the chamber allows the ice core sample to shred under its own weight as the vessel is oscillated in a linear motion at 1 Hz and with a 15 cm throw. It takes 15–20 min of shredding to liberate 60–70% of the air trapped in an ice core sample. Pumping and gas extraction is done through a

stratospheric sulfate aerosols during volcanically quiescent periods. There is debate about the relative importance of background COS compared to other sources like anthropogenic SO_2 , COS from episodic tropical biomass burning events, and SO_2 from small volcanic eruptions [Crutzen, 1976; Chin and Davis, 1995; Notholt et al., 2003; Myhre et al., 2004; Solomon et al., 2011; Vernier et al., 2011]. A recent assessment suggests that the net climate impact of COS is minimal, because the cooling effect due to COS-derived stratospheric aerosols is largely offset by the greenhouse warming effect of COS in the troposphere [Brühl et al., 2012].

COS measurements in polar firn and ice have been used to assess the range of

Table 1. Site Characteristic of Various Antarctic Ice Cores

Ice Core Site	Location (Latitude–Longitude)	Temperature ^a (°C)	Accumulation ^b (cm y^{-1})	Elevation (m)	Thickness ^c (m)
Byrd	80.0°S–119.5°W	–28	17	1530	2191
Siple Dome	81.7°S–148.8°W	–25	11	615	1003
South Pole	89.9°S–144.4°W	–51	8	2800	2800
Taylor Dome	77.8°S–158.7°E	–42	7	2440	554
WAIS Divide	79.5°S–112.1°W	–30	22	1806	3450

^aAnnual mean surface temperature at present.

^bMean ice equivalent accumulation rate at present.

^cPresent thickness of the ice sheet.

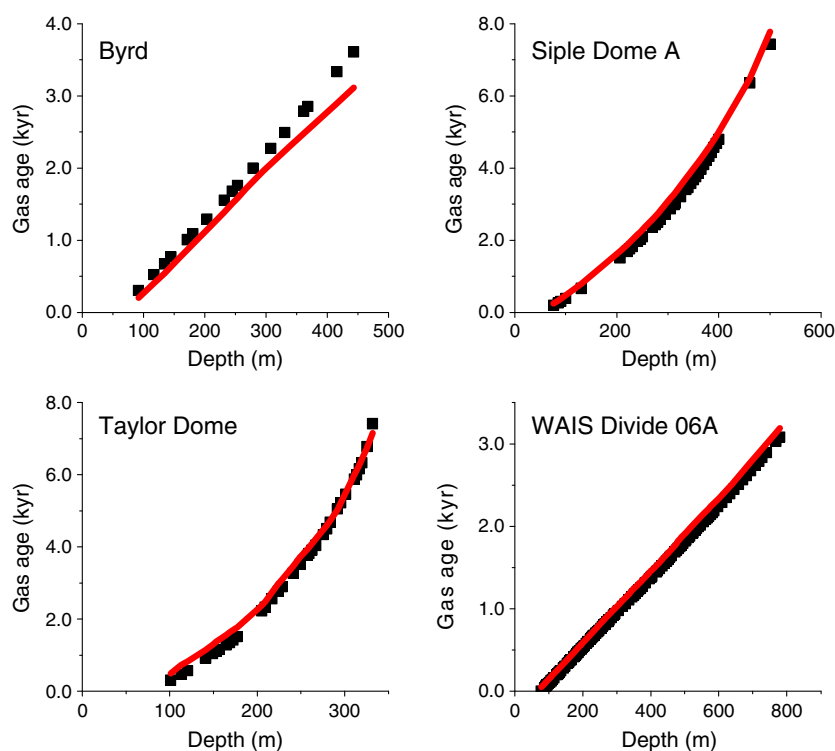


Figure 2. The depth versus gas age relationships for the Byrd, Siple Dome, Taylor Dome, and WAIS Divide 06A ice cores (black squares). Model-derived gas ages (red lines) are used in the COS hydrolysis corrections in section 8.

1.27 cm (1/2") ID stainless steel vacuum line that includes stainless steel bellows valves with alloy tips. The extracted air is frozen in a stainless steel tube immersed in liquid helium (4 K) and transferred to an automated preconcentration inlet system. The condensable constituents of air are trapped on glass beads at liquid nitrogen temperatures (77 K at 1 atm), transferred onto a fused silica capillary tube (0.25 mm ID) also at 77 K, then thermally injected into an HP-5890 gas chromatograph. Chromatographic separation is achieved on a 60 m long DB-1 column with a temperature program that starts at -50°C and ramps to a final temperature of 150°C in 20 min. The analytes are quantified with a magnetic sector mass spectrometer (Waters Autospec Ultra) running at a mass resolution of ~ 8000 ($m/\Delta m$). An isotope-labeled internal standard (^{13}C OS) is added to each sample during the first trapping phase on glass beads, and the COS abundance is quantified from the ratio of signals from the labeled and unlabeled isotopomers. The system is calibrated using COS gas standards prepared in our laboratory at parts per billion levels in high-pressure Al cylinders and diluted to parts per trillion levels in humid N_2 in electropolished stainless steel flasks.

3. Ice Core Samples and Chronologies

This study includes COS measurements from seven Antarctic ice cores collected at five different sites. The gas age scales used for each of the ice cores are based on previous publications as described below. All chronologies are given in thousand years before 1950 C.E., expressed as kiloyear (Figure 2).

Byrd: We measured COS in 17 samples from the upper 450 m of the Byrd ice core drilled at the Byrd station site in 1967–1968, using a mixture of diesel and trichloroethylene as the drill fluid. We detected drill fluid in most of the Byrd samples; however, there was no discernable drill fluid impact on measured COS levels. All samples from the Byrd ice core lie above the depth at which clathrates start to form [Price, 1995]. There is no methane-based gas age scale for the late Holocene portion of the Byrd ice core. The chronology for the samples from the Byrd ice core was determined using the published ice age scale [Blunier and Brook, 2001] and applying a delta age (difference between ice age and gas age) as described by Blunier et al. [1998].

Siple Dome A: We measured COS in 50 samples from the Siple Dome A ice core, which was drilled in 1996–1997 using n-butyl acetate as the drill fluid. We found that the presence of n-butyl acetate was associated with elevated levels of COS. Nine samples were left out of the current analysis because of drill fluid contamination. No clathrates were observed in the Siple Dome ice core. The gas ages are calculated from ice ages using an appropriate delta age from a firn model [Taylor et al., 2004a; Brook et al., 2005].

Siple Dome C: This is a shallow ice core dry drilled to a depth of 92 m in 1996. We measured COS in 33 samples, 4 of which were previously designated as outliers [Montzka et al., 2004]. The measurements from the Siple Dome C ice core are presented with the previously published COS chronology derived from ice ages based on visual stratigraphy and a constant delta age of 273 years based on firn modeling [Aydin et al., 2002; Montzka et al., 2004].

South Pole: The South Pole Remote Earth Science and Seismological Observatory (SPRESSO) ice core from the South Pole was dry drilled to a depth of 291 m in 2001–2002. We measured COS in a total of 106 samples, including 6 outliers [Aydin et al., 2008]. The measurements from the SPRESSO ice core are presented with the previously published COS chronology derived from ice ages based on visual stratigraphy and a constant delta age of 1028 years based on firn modeling [Aydin et al., 2008].

Taylor Dome M3C1: The Taylor Dome M3C1 ice core was drilled to a depth of 555 m using n-butyl acetate as the drill fluid in 1993–1994. We analyzed 61 samples from the upper 340 m. Twenty-two samples are not included in the analysis here, because the integrity of the ice core air sample was compromised due to the presence of excessive drill fluid, contamination of the extraction vessels, and leaks during the extraction process [Verhulst et al., 2013]. The Taylor Dome chronology during the Holocene is based on the synchronization of CO₂ measurements from the Taylor Dome and Dome C ice cores [Monnin et al., 2004].

WAIS Divide 05A: The 05A ice core was dry drilled to a depth of 295 m at the WAIS Divide in 2004–2005. Eight out of 56 samples are designated outliers. The COS chronology for the WAIS-D 05A measurements is based on the ice age scale “WDC05A-2” [Mitchell et al., 2011] and a constant delta age of 208 years. The calculation of the COS delta age is based on the CO₂ delta age of 205 years for the WAIS-D 05A ice core [Ahn et al., 2012]. The 3 year difference between the COS and the CO₂ gas ages is due to a small difference in the free air diffusivities of the two gases that causes COS mean age to be slightly older than CO₂ at the same depth.

WAIS Divide 06A: The 06A ice core was drilled during 2006–2012 to a depth of 3405 m using Isopar-K as the drill fluid. Isopar-K is a synthetic hydrocarbon solvent (ExxonMobil Chemicals) that consists primarily of higher isoalkanes. We analyzed a total of 84 samples from the upper 764 m of the ice core (the last 3000 years of the Holocene), which lies above the depth at which clathrates are commonly detected by microscopic examination (J. J. Fitzpatrick et al., Physical properties of the WAIS Divide ice core, *Journal of Glaciology*, manuscript in review, 2014). Four samples were lost due to analytical problems related to the presence of excessive drill fluid, and 1 sample was designated as an outlier. Drill fluid was detected in 38 of the remaining 79 samples; however, the presence of drill fluid had no apparent effect on the COS measurements. The gas age scale for the COS measurements is based on the ice age scale “WDC06A-7” [West Antarctic Ice Sheet (WAIS) Divide Project Members, 2013] and a constant delta age of 208 years.

4. Results

COS has been previously measured in two shallow ice cores from Siple Dome and South Pole [Aydin et al., 2002, 2008; Montzka et al., 2004]. The South Pole record dates back to about 2 kyr, displaying a 331 ± 18 ppt average and an overall increasing trend (forward in time) of 1.8 ppt/100 yr. The Siple Dome C record covers the last 300 years and display a mean of 350 ± 31 ppt. The mean COS levels are similar in the two data sets, but the period of overlap is not long enough for a comprehensive site-to-site comparison. In this study, we present new ice core COS measurements from the previously unsampled Byrd, Taylor Dome, and WAIS Divide sites in Antarctica and from the deep Siple Dome A ice core (Figure 1 and Table 1). The COS measurements from the WAIS Divide 05A (dry drilled) and 06A (fluid drilled) ice cores compare well with each other and with the previously published data from the South Pole during the last 1 kyr (Figure 3a). On time scales longer than 1 kyr, the South Pole and WAIS Divide records diverge with the WAIS Divide 06A measurements, displaying a steeper downcore decline (Figure 3a). Similarly, mean COS levels at the Byrd, Siple Dome, and Taylor Dome sites agree with the South Pole measurements during 1–0 kyr but display diverging trends during 3–1.5 kyr (Figure 3b).

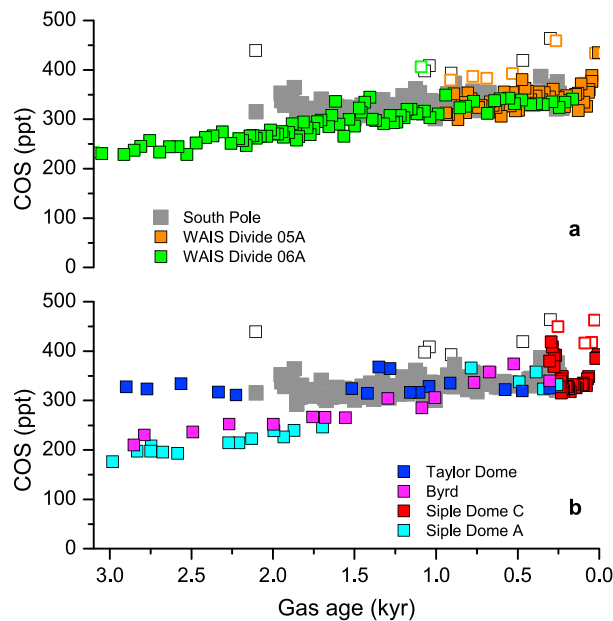


Figure 3. (a) COS measurements in the South Pole (gray squares), WAIS Divide 05A (orange squares), and WAIS Divide 06A (green squares) ice cores for the last 3 kyr. (b) COS measurements in the Byrd (magenta squares), Siple Dome A (cyan squares), Siple Dome C (red squares), South Pole (gray squares), and Taylor Dome (blue squares) ice cores for the last 3 kyr. The open squares denote outliers for the ice cores with the same color markers.

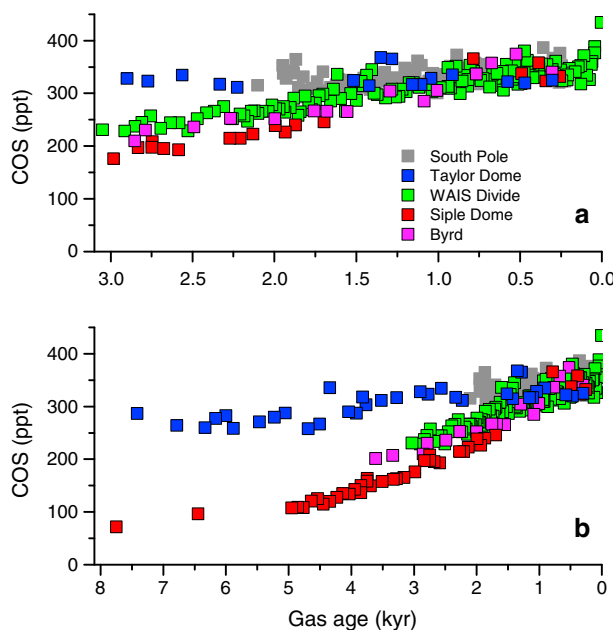


Figure 4. (a) COS measurements in the Byrd (magenta squares), Siple Dome A (red squares), South Pole (gray squares), WAIS Divide 05A and 06A (green squares), and Taylor Dome (blues squares) ice cores for the last 3 kyr. For clarity, the Siple Dome C data are not shown. (b) The same data sets as in Figure 4a but for the last 8 kyr.

The agreement between all the measurements during 1–0 kyr (Figure 4a) demonstrates reproducibility in fluid- and dry-drilled ice cores from a variety of Antarctic sites. All ice core records considered here appear to preserve the same initial atmospheric COS signal regardless of the location and without significant changes to the COS composition in the firm or during bubble close off. The results also confirm our previous finding that preindustrial mean COS levels were 30–35% below the modern value of 500 ppt. However, with increasing depth and age, there is divergence between the COS measurements from different sites. Siple Dome results exhibit the steepest downcore trend and the lowest COS levels, measuring less than 200 ppt at 3 kyr, about 100 ppt at 5 kyr, and with two more measurements between 8 and 6 kyr in 60–70 ppt range (Figure 4b). The COS in the WAIS Divide 06A and Byrd ice cores follows a similar, steep downcore trend but at somewhat higher levels than Siple Dome, with the lowest COS levels measuring 200–230 ppt at 3 kyr. In contrast, the Taylor Dome data display more moderate changes, with the downcore decrease starting after 3 kyr and the COS mixing ratio reaching a minimum of only 250 ppt around 5–6 kyr (Figure 4b).

The site-to-site differences in COS measurements cannot be attributed to atmospheric gradients. COS gradients across the high-latitude southern hemisphere are negligible in the modern atmosphere [Montzka *et al.*, 2007], and there is no reason to expect large spatial gradients over Antarctica in the preindustrial atmosphere given the nature of COS sources and the tropospheric lifetime of 2–3 years. The degree of diffusive smoothing in the firm is different at each site, and this could impact how high-frequency atmospheric variations are preserved at different sites; however, the long-term COS trend should not be impacted. Furthermore, the time-dependent

nature of the site-to-site differences in COS levels (i.e., increasing divergence over longer time scales) indicates that they are not due to analytical biases or contamination during the extraction and analyses of the ice cores.

There is an apparent relationship between the magnitude of the downcore COS trends and the mean annual temperatures at different sites. The colder South Pole and Taylor Dome sites exhibit higher COS levels than the warmer sites (Figure 4 and Table 1). We propose that COS is continually destroyed in situ via a temperature-dependent hydrolysis reaction. It follows that the total COS loss in a given ice core sample would reflect the integrated effect of its entire postentrapment temperature history and not quantitatively correlate with the modern surface temperature at the site. The thermal history of an ice core sample from a specific depth depends on spatially and temporally varying quantities like the surface temperature, the accumulation rate, and the ice sheet thickness. In the following sections, we first utilize simple ice sheet models to reconstruct temperature histories for the ice core samples and then use these thermal histories to examine the kinetics of in situ COS loss.

5. Physical Model: Obtaining Temperature Histories for Ice Cores

Thermal histories for the ice core samples were calculated with a 1-D ice flow and heat flux model [WAIS Divide Project Members, 2013]. The vertical ice flow is approximated following the *Dansgaard and Johnsen's* [1969] model, with modification to incorporate basal melting and sliding [Dahl-Jensen et al., 2003]. The heat flow is an advection-diffusion problem [Cuffey and Paterson, 2010] solved with a finite-volume scheme [Patankar, 1980]. The model incorporates a firn layer near the surface and bedrock below the base of the ice sheet. An accumulation rate history is specified for each site so that the modeled depth-age scale matches the data within uncertainty for suitable ice flow parameters at each site (see supporting information for details). The surface temperature history is calculated from the water stable isotope values ($\delta^{18}\text{O}$) assuming a constant calibration factor for each site. Geothermal flux is prescribed in bedrock at 10 km below the base of the ice sheet.

Thermal histories were calculated for four of the five ice core sites. The thermal history at the South Pole was assumed to have been constant at the modern mean annual temperature (-50.5°C) because of the thick ice sheet and the young age (shallow depth) of the oldest samples analyzed. For WAIS Divide, Siple Dome, and Taylor Dome, the isotope calibrations for the surface temperature histories and the geothermal fluxes were constrained by the measured borehole temperature profiles. We used the suggested isotope calibration factors of $0.5\text{‰}/^\circ\text{C}$ for Taylor Dome [Steig et al., 1998] and $0.7\text{‰}/^\circ\text{C}$ for Siple Dome [Taylor et al., 2004b] and the geothermal flux values that gave the best match to the modern borehole temperature profiles (see supporting information for details). For WAIS Divide, we use a calibration factor of $1.0\text{‰}/^\circ\text{C}$, which yields a temperature history similar to the middle estimate of *WAIS Divide Project Members* [2013]. Two measurements of the borehole temperature profile at Byrd disagree in the upper 500 m [Budd and Young, 1969; Gow et al., 1968]. We did not use the borehole temperature measurements as a constraint at Byrd, using instead the WAIS Divide isotope scaling.

We calculate the thermal histories by tracking the ice temperature from the sample depth back through time until the sample reaches the firn lock-in depth. The COS loss above the lock-in depth is ignored because firn air mixes with the overlying atmosphere relatively quickly via diffusion through the permeable firn layer. The gas age at the top of the lock-in zone is on the order of 10 years at most ice core sites. The temporal variations in the firn lock-in depth is calculated following *Herron and Langway* [1980], using the same accumulation rate and surface temperature histories that were used in the ice flow and heat flux modeling.

At WAIS Divide, the sample thermal histories remain nearly constant at the surface temperature of -30°C because the high accumulation rate (22 cm yr^{-1} ice equivalent) results in a temperature profile that is nearly isothermal in the upper half of the ice sheet (Figure S1 in the supporting information). The ice younger than 4 kyr remains within 0.6°C of the modern site temperature (Figure 5). The temperature gradients are steeper at Siple Dome and Taylor Dome (Figure S1 in the supporting information) due to the lower accumulation rates and the thinner ice sheets (Table 1) providing less insulation from the geothermal flux at the bed. Consequently, the ice at Siple Dome warms by 6°C (5°C at Taylor Dome) as it moves from the surface of the ice sheet to a depth of 330 m (230 m at Taylor Dome) over 4000 years (Figure 5).

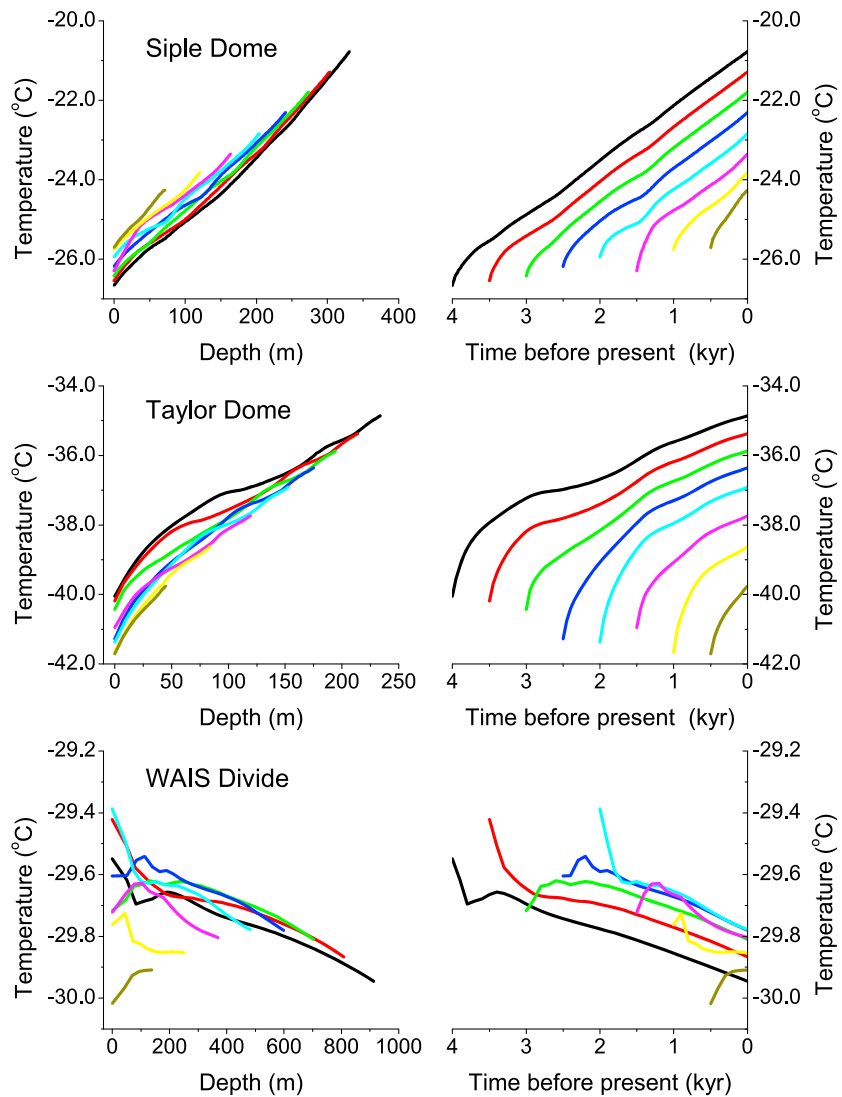
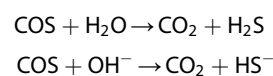


Figure 5. Temperature histories from the 1-D ice sheet models with respect to (left) depth and (right) time before present for (top) the Siple Dome, (middle) Taylor Dome, and (bottom) WAIS Divide sites. Temperature histories for the ice core samples are shown every 500 years: 4 kyr (black), 3.5 kyr (red), 3.0 kyr (green), 2.5 kyr (blue), 2.0 kyr (cyan), 1.5 kyr (magenta), 1.0 kyr (yellow), and 0.5 kyr (dark yellow). The COS hydrolysis correction for a sample is calculated by tracking its temperature history from the depth it was recovered back to the surface. For example, the Siple Dome model predicts that an ice sample from 330 m that is presently at -20.9°C was at the surface 4000 years ago when the mean annual surface temperature was -26.8°C .

6. Hydrolysis of COS in Aqueous Solution and Implications for Loss Rates in Polar Ice Cores

COS undergoes hydrolysis in aqueous solution via neutral and base-catalyzed reaction mechanisms [Thompson *et al.*, 1935].



It is believed that these reactions proceed through a monothiocarbonate intermediate, analogous to H_2CO_3 formed in the hydrolysis of CO_2 [Philipp and Dautzenberg, 1965]. At 294 K, the hydrolysis lifetime (*e*-folding time) of COS in aqueous solution at $\text{pH} < 6$ is 22–23 h. At higher pH, the reaction rate becomes strongly pH-dependent and increases dramatically: At pH values of 7, 8, and 9, and at 294 K, the reaction lifetimes are

19 h, 12 h, and 2 h, respectively [Elliott *et al.*, 1989]. The rate constants (k) for the hydrolysis of COS in acidic and basic solutions have different activation energies (E_a) and can be expressed in the Arrhenius form as follows [Elliott *et al.*, 1989]:

$$k_{\text{pH}<6} = 3.6 \times 10^{10} e^{-(10450/T)} (\text{s}^{-1}) \quad \text{for } E_a = 21 \text{ kcal mol}^{-1} \quad (1)$$

$$k_{\text{pH}>9} = 8.0 \times 10^9 e^{-(6040/T)} (\text{M}^{-1} \text{s}^{-1}) \quad \text{for } E_a = 12 \text{ kcal mol}^{-1} \quad (2)$$

Extrapolating these aqueous phase rate constants to the conditions in polar ice is not straightforward, because the potential impacts of factors like the presence of a solid-gas interface, the mobility of reactants through the ice matrix, and the presence of impurities have not been explored. Assonov *et al.* [2005] measured the ^{18}O isotope exchange rate between firn air CO_2 and the surrounding ice matrix at three Antarctic sites and inferred that the isotopic exchange rate between CO_2 and $\text{H}_2\text{O}_{\text{ice}}$ is about 5 orders of magnitude slower than the rate in aqueous solution at 0°C . They also found a lower E_a for CO_2 hydration in ice compared to that in water (7.8 versus 16–19 kcal mol^{-1}). Because COS and CO_2 hydrolysis are believed to occur via similar intermediates, Assonov *et al.* [2005] assumed that COS hydrolysis might exhibit a similar relationship between the values of k and E_a in polar ice and in aqueous solutions. However, the hydration rates they estimated for COS appear to be too slow to account for the diverging downcore trends in ice core COS measurements. For example, they predict a lifetime close to 70,000 years for COS hydrolysis at the WAIS Divide surface temperature (-30°C). The physical model results show that the ice at WAIS Divide was essentially isothermal during the last 4000 years at temperatures similar to the present-day surface temperatures (Figure 5). The ice core measurements indicate that the COS in the WAIS Divide ice core is 10–15% lower than what is measured in the much colder South Pole ice core at 2 kyr (Figure 3a). Assuming that the loss to hydrolysis is negligibly small in the South Pole ice core and attributing the WAIS Divide—the South Pole difference entirely to in situ hydrolysis, we can infer a lifetime of about 10,000 years at -30°C . This is roughly sevenfold faster than predicted by the isotopic equilibration of CO_2 in the firn, suggesting that this is not a good quantitative model for COS hydrolysis in ice cores.

7. Empirical Chemical Model: COS Loss Kinetics in Polar Ice

If COS loss in ice cores is due to a temperature-dependent chemical process like hydrolysis, it should be possible to infer the loss kinetics from the ice core data. As previously noted, one of the requirements is the knowledge of the ice core temperature histories. In addition, we will assume that the air trapped in contemporaneous ice core samples from different Antarctic sites had the same COS mixing ratio at the time of bubble lock in. This assumption is well supported by both the ice core and the modern surface air measurements, and what we know about the atmospheric COS fluxes.

We further assume that the kinetics of COS hydrolysis is pseudofirst order, as described by the expression:

$$-\frac{d[\text{COS}]}{dt} = k \cdot [\text{COS}] \quad (3)$$

where the rate constant k is a function of temperature only and described by the Arrhenius equation:

$$k(T) = A \cdot e^{-\frac{E_a}{RT}} \quad (4)$$

In equation (4), the preexponential constant A (y^{-1}) and the activation energy E_a (kcal mol^{-1}) are unknown parameters, T is the temperature (K), and R ($\text{kcal mol}^{-1} \text{K}^{-1}$) is the universal gas constant.

The model calculation starts with the measured COS mixing ratio. It steps backward in time, from the present day to the time of bubble lock in, using the analytical solution to equation (3):

$$[\text{COS}]_{t_n} = [\text{COS}]_{t_{n-1}} \cdot e^{k(T) \cdot \Delta t} \quad (5)$$

where t_{n-1} and t_n represent the sequential times separated by the interval Δt . A new k is calculated at each time step, using the temperature histories from the physical model and prescribed values for the two unknown parameters (A and E_a) in equation (4). The result of this calculation is an estimate of the initial COS content in each ice core sample at the time of lock in. In theory, there should exist unique values of A and E_a , which yield the same initial COS level for all the ice core samples of the same gas age.

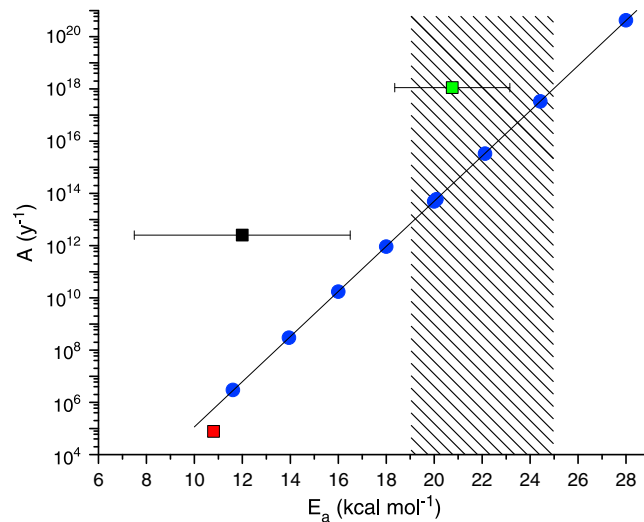


Figure 6. The E_a and A pairs found during the search with MATLAB function *fminsearch* (blue circles). A logarithmic scale is used for the y axis. The parameters of the linear relationship between E_a and $\log(A)$ (black line) are given in equation (6). The dashed region indicates the E_a values that best minimize (95% confidence) the difference between the data pairs used in the minimization (see also Figure 7). Measured values for the acidic (pH < 6, green square) and basic (pH = 9, black square) aqueous phases [Elliott *et al.*, 1989], and the estimate of Assonov *et al.* [2005] for hydrolysis in ice cores (red square) are also shown.

A MATLAB objective minimization algorithm (*fmincon*) was used to search for A and E_a values that minimize the difference between COS levels in different ice cores after applying a correction for loss to hydrolysis. Overlapping measurements from different ice cores were used in pairs (e.g., Siple Dome–WAIS Divide). The difference between the mean COS levels in the ice cores that make up a pair is treated as a “cost,” which the search algorithm seeks to minimize (see supporting information for details). Six ice core pairs with overlapping age ranges were used in the minimization: Siple Dome–WAIS Divide, Siple Dome–Byrd, Siple Dome–Taylor Dome, WAIS Divide–South Pole, WAIS Divide–Byrd, and WAIS Divide–Taylor Dome. The Siple Dome–South Pole pair was not used because there were only a few overlapping data points. Each pair was evaluated over a time period of overlap specific to that pair. For the Siple Dome–Taylor Dome pair, measurements that date older than 5 kyr were not used.

The A and E_a values found by the minimization routine were sensitive to the chosen starting values and the parameter space allowed for the search, indicating that the search algorithm was not finding a global minimum. However, the solutions did exhibit a linear relationship between E_a and the logarithm of A (Figure 6) as follows:

$$\log A = 0.864E_a - 3.580 \tag{6}$$

We tested the sensitivity of the parameters in equation (6) with respect to the choice of measurement pairs used in the minimization and found them to be robust (see supporting information for details). Subsequently, a second search was conducted over a wide E_a range (5 kcal mol⁻¹ through 45 kcal mol⁻¹), with the corresponding A values calculated from equation (6) to explore the agreement between ice core pairs in a paired *t* test (Figure 7).

The South Pole–WAIS Divide pair provides the most stringent constraints on the minimization, excluding solutions for values of E_a lower than 17 kcal mol⁻¹ and higher than 25 kcal mol⁻¹. In contrast, the pairings that include Taylor Dome never yield agreement, implying that the search algorithm cannot find solutions that make both the Siple Dome–Taylor Dome and the WAIS Divide–Taylor Dome pairs agree (Figure 7). When all the pairings are considered, the E_a values that best satisfy the minimization requirements lie in 19–25 kcal mol⁻¹ range, with corresponding A values of $6.90 \times 10^{12} - 1.06 \times 10^{18}$ year⁻¹. The measured E_a for COS hydrolysis in acidic water [Elliott *et al.*, 1989] falls within this range (Figure 6). Our estimates of the COS hydrolysis lifetime in ice cores are generally shorter than what was predicted by Assonov *et al.* [2005], most notably for temperatures above 240 K (Figure 8). A steeper temperature dependence (i.e., higher E_a) results in longer lifetimes than the Assonov *et al.*'s [2005] estimates at temperatures below 230 K. Our estimates also imply a smaller stepwise change in the COS hydrolysis lifetime at the water ice phase boundary (Figure 8).

There is no a priori guarantee that a single rate expression (i.e., one set of Arrhenius parameters) governs the COS loss kinetics in these ice cores. For example, if COS hydrolysis takes place on ice surfaces, variations in impurity levels and crystal structure between ice cores from different sites, or between ice core samples from the same site but different depths, may influence the reaction rates. The fact that the data from multiple ice

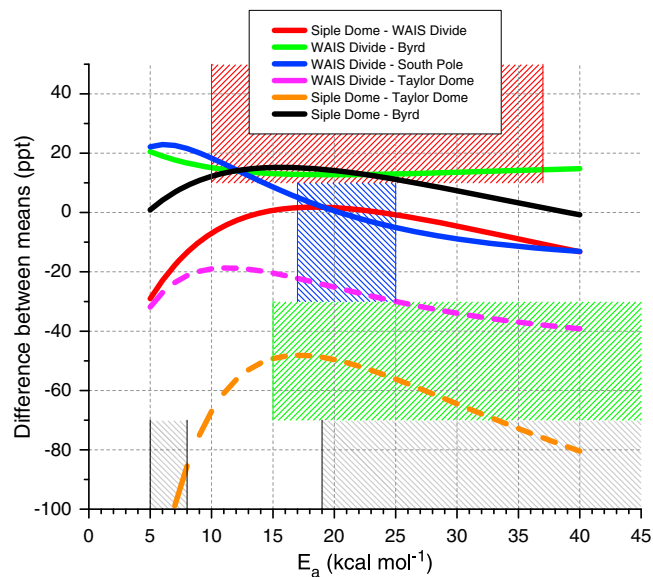


Figure 7. The change in the difference between the means of overlapping measurement pairs based on equation (6): Siple Dome–WAIS Divide (red line), Siple Dome–Byrd (black line), Siple Dome–Taylor Dome (orange dashed line), WAIS Divide–Byrd (green line), WAIS Divide–South Pole (blue line), and WAIS Divide–Taylor Dome (magenta dashed line). The stacked shaded boxes indicate the range of E_a values that yields equality (t test, 95% confidence) between different pairings used in the minimization (same color code as the lines). The pairings of Taylor Dome with Siple Dome and WAIS Divide never yield agreement (i.e., the difference between the means is always different than zero with 95% confidence) along the specified search space. Based on these results, the hydrolysis corrections to the COS measurements from all the sites are conducted in $E_a = 19\text{--}25 \text{ kcal mol}^{-1}$ range, which satisfies the equality criteria for all the pairings except the ones that include Taylor Dome.

to 25 kcal mol^{-1} at 1 kcal mol^{-1} increments. The corresponding A values were calculated using equation (6). As expected, the corrections are larger for older samples, and in the case of similar gas ages, for ice cores that have warmer temperature histories (Figure 9). The magnitudes of the corrections also depend on the choice of A and E_a used in the correction, with larger values for these parameters resulting in longer lifetimes (Table 2) and smaller corrections.

The corrected records display a considerably better agreement than the original, uncorrected measurements, especially between the Byrd, Siple Dome, and WAIS Divide ice cores from West Antarctica (Figure 10). The hydrolysis correction significantly increases the COS levels in the relatively warm Siple Dome ice core, resulting in agreement with the corrected records from the Byrd and the WAIS Divide ice cores (Figures 9 and 10). However, the COS levels calculated for the three West Antarctic ice cores remain lower than those from the Taylor Dome ice core during 4–2 kyr. This is the period during which the Taylor Dome data cannot be reconciled with the Siple Dome and WAIS Divide measurements in the minimization search for A and E_a . The difference between the corrected records from Taylor Dome and Siple Dome does not systematically increase with time as there is better agreement between the corrected records from these two ice cores during 5–4 kyr and 8–6 kyr, except for one anomalously high Taylor Dome measurement at 4.3 kyr (Figure 10).

Assuming that the first-order kinetic model is adequate, the correction method involves three sources of uncertainty that may contribute to the observed discrepancies between the corrected records during 4–2 kyr:

1. Model-derived thermal histories: Simple 1-D models are used to simulate the thermal evolution of the various ice core samples. In addition to the potential shortcomings of using a 1-D model to describe a 3-D flow field, there are uncertainties in the age–depth relationship, the surface temperature histories, and the geothermal flux prescribed in the model.

cores yield a systematic relationship between A and E_a empirically supports the assumption that COS hydrolysis occurs by a common process at various sites with a single governing rate expression. The Taylor Dome ice core is an exception to this, given the fact that we cannot find a solution that makes Taylor Dome agree with both the Siple Dome and the WAIS Divide results. However, we consider it unlikely that this particular problem is due to the influence of impurities on reaction rates. The impurity levels in Antarctic ice cores are low during the Holocene, and the problem with the Taylor Dome ice core appears to be most pronounced during a particular time period. We discuss the possible causes for the anomalous behavior of COS in the Taylor Dome ice core in the following section.

8. Corrected Ice Core COS Records

Ice core COS measurements were corrected for in situ COS loss to hydrolysis using equations (4) and (5) and the modeled temperature histories for each site. Each data set was corrected using seven different E_a s starting at 19 kcal mol^{-1} and increasing

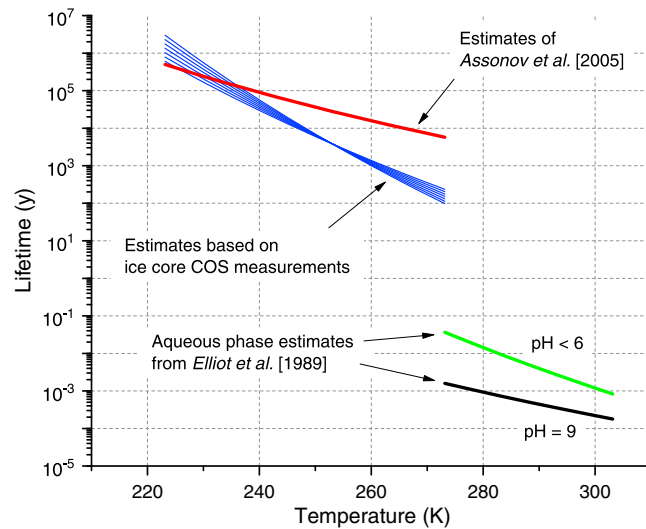


Figure 8. The change in COS hydrolysis lifetime (k^{-1}) with temperature. A logarithmic scale is used for the y axis. The lifetime estimates based on ice core COS measurements (blue lines for $E_a = 19\text{--}25 \text{ kcal mol}^{-1}$) display a steeper temperature dependence than prior estimates (red line from Assonov et al. [2005]). The temperature dependences of the reaction lifetime in the acidic (green line) and basic (black line) aqueous phases are also shown. The reaction lifetime in basic aqueous phase was calculated for pH = 9. The reaction rate becomes pH dependent for pH > 6 [Elliott et al., 1989].

2. Ice core COS measurements: The current data set has relatively narrow age intervals, where high-quality data are available from multiple cores. There are no known calibration-based biases between the Taylor Dome measurements and the other data sets. However, we cannot rule out the possibility that the Taylor Dome measurements from this period are elevated due to some unaccounted for positive bias due, for example, to the presence of drill fluid-related contaminants.
3. Chronologies: Uncertainty in the gas ages assigned to various ice core samples means that COS measurements in samples of identical age from different cores may not actually represent synchronous samples of the atmosphere. There is an additional complication that arises from the fact that model chronologies are not the same as the chronologies used for the gas measurements. However, the differences between

the model-based chronologies and the measurement gas ages are not large enough to introduce a significant bias in any of the corrected records, with the possible exception being the Byrd measurements from below 300 m (2 kyr) (Figure 2).

We explored the sensitivity of the results to uncertainties in the thermal histories by tuning the physical models for the Siple Dome and Taylor Dome ice cores with a range of values for the geothermal flux and the isotope calibration factor. During mid-to-late Holocene, the uncertainties in the geothermal flux and the isotope calibrations do not result in large variations in thermal histories and the resulting corrections applied to the COS measurements for in situ loss to hydrolysis (see supporting information for details). It is also evident from our results that the corrected records from the Byrd, Siple Dome, and WAIS Divide ice cores are lower than even the uncorrected measurements from Taylor Dome during 4–2 kyr (Figures 9 and 10). We conclude that the discrepancy between Taylor Dome and the other records during the 4–2 kyr time period cannot be attributed to the uncertainties in temperature histories alone. It appears that inaccuracies in the COS measurements and the chronologies contribute to the discrepancy observed during 4–2 kyr.

We have more confidence in the most recently measured WAIS Divide data set than any of the other deep ice cores because of the high density of the measurements and the fact that we found no evidence of drill fluid impact on COS measurements in this ice core. There is also high confidence in the WAIS Divide chronology, given the high accumulation rate at this site and the high time resolution of chemical measurements used for developing a chronology for this ice core [WAIS Divide Project Members, 2013]. The chronology of the Siple Dome ice core during the Holocene is also considered reasonably accurate [Taylor et al., 2004a]. In contrast, the uncertainties in the Taylor Dome and the Byrd chronologies are fairly large even during the Holocene [Blunier et al., 1998; Blunier and Brook, 2001; Monnin et al., 2004]. We suggest that the corrected records from the Siple Dome and the WAIS Divide sites likely represent real variations in atmospheric COS during the mid-to-late Holocene, with the recognition that more work is needed to address the potential shortcomings due to the simple chemical model adopted here.

Collectively, the Siple Dome, the South Pole, and the WAIS Divide records suggest a 60–80 ppt rise in atmospheric COS over the 2000 years between 3 and 1 kyr. Based on the Siple Dome results alone, it is

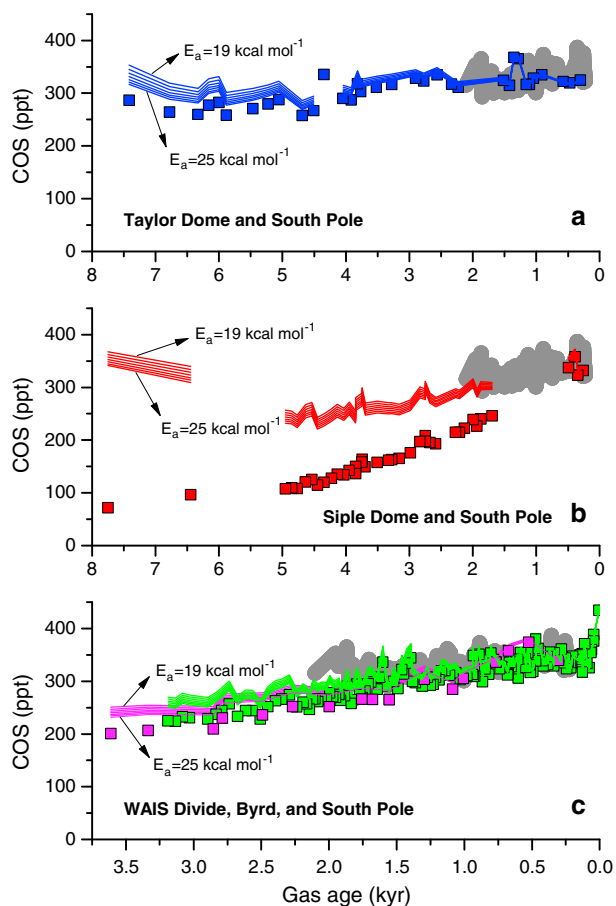


Figure 9. The ice core COS measurements (square markers) and the COS records corrected for in situ hydrolysis (lines): (a) Taylor Dome (blue), (b) Siple Dome (red), and (c) Byrd (magenta) and WAIS Divide (green). For the South Pole, only the corrected records (gray lines) are shown in all three panels. We show seven different corrected records for each site, calculated for $E_a = 19\text{--}25 \text{ kcal mol}^{-1}$. For all the ice cores, the magnitude of the correction is smaller for higher E_a values.

COS, CS_2 , and DMS and loss to hydrolysis [Kettle et al., 2001, 2002]. It is likely that a large source-driven rise in atmospheric COS would necessitate an increase in the oceanic emissions of all the three sulfur gases. The COS rise can also be driven by a decline in the GPP of terrestrial plants and a resultant reduction in the COS removal rate. Concurrent with the COS rise during 5–1 kyr, there was an increase in atmospheric CO_2 coupled with a decline in the $\delta^{13}\text{C}$ of atmospheric CO_2 [Monnin et al., 2004; Elsig et al., 2009], which may be partially explained by changes in GPP. It is interesting to note that the atmospheric levels of methane and methyl chloride also increased during mid-to-late Holocene when COS was rising [Brook et al., 2000; Flückiger et al., 2002; Verhulst et al., 2013]. Although these trace gases have very different biogeochemical cycles, the concurrent trends may be driven by a common underlying reason such as changes in tropical hydrology [Verhulst et al., 2013].

Table 2. COS Lifetime (k^{-1}) Estimates for Ice Core Hydrolysis at Selected Temperatures

Temperature (K)	Lifetime ^a (year)	Lifetime ^b (year)
223.15	603,109	2,988,084
233.15	95,896	265,834
243.15	17,738	28,858
253.15	3,749	3,733
263.15	892	564
273.15	236	98

^a $E_a = 19 \text{ kcal mol}^{-1}$ and $A = 6.90 \times 10^{12} \text{ year}^{-1}$.
^b $E_a = 25 \text{ kcal mol}^{-1}$ and $A = 1.06 \times 10^{18} \text{ year}^{-1}$.

possible that the atmospheric levels of COS started to rise as early as 5 kyr and increased by about 100 ppt. During the time periods that precede 5 kyr, the Taylor Dome measurements remain stable in 250–300 ppt range (Figure 4b). As is the case for the entire Taylor Dome ice core, the older samples are also warmer. Consequently, the corrected Taylor Dome records show that COS was about 50 ppt higher at 7 kyr than at 5 kyr (Figure 10). When corrected, the two Siple Dome measurements from 6.4 kyr and 7.7 kyr (Figures 4b and 10) also suggest higher atmospheric COS levels in the early Holocene. Due to limited data and larger uncertainties, the timing and the magnitude of the COS changes during the early stages of the Holocene cannot be accurately determined. However, we consider these trends to be robust and conclude that there was likely a COS minimum in the atmosphere centered around 5 kyr.

The corrected ice core records excluding the Taylor Dome suggest a rise in atmospheric COS during 5–1 kyr of 70–100 ppt or 23–33% ($\Delta\text{COS}/\text{mean COS} = 70\text{--}100 \text{ ppt}/300 \text{ ppt}$). An increase of this magnitude can be driven by changes in the two dominant terms in the COS budget: the ocean source and the terrestrial uptake. The ocean source of COS reflects the net effect of direct and indirect emissions in the form of

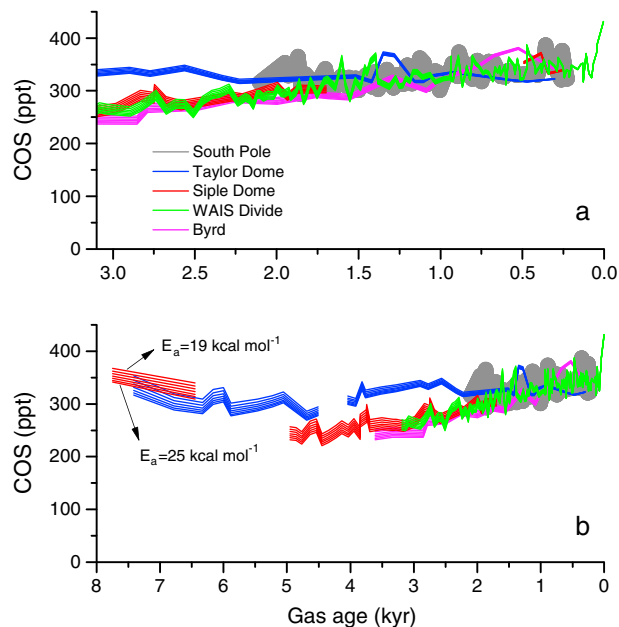


Figure 10. The corrected COS records from all the five sites for (a) the last 3000 years and for (b) the last 8000 years. The Byrd (magenta lines), the Siple Dome (red lines), the South Pole (gray lines), the Taylor Dome (blue lines), and the WAIS Divide (green lines) records are shown in both panels. We show seven different corrected records for each site, calculated for $E_a = 19\text{--}25 \text{ kcal mol}^{-1}$. For all the ice cores, the magnitude of the correction is smaller for higher E_a values.

the kinetic parameters of a pseudofirst-order rate equation to minimize the difference between contemporaneous samples from various ice cores. These kinetics are used in conjunction with a simulation of the thermal history of each ice core sample to estimate the loss of COS since lock in. The accuracy of such corrections depends on the quality of the data used to infer the kinetic parameters of the COS hydrolysis, the accuracy of the ice core thermal histories for various sites, and the validity of the assumption that the same kinetics apply at all sites. Better estimates of COS loss kinetics will require additional measurements on well-dated ice cores in varying thermal regimes.

Thick ice sheets with low surface temperatures are better suited for ice core COS measurements since little or no correction will be required for in situ losses to hydrolysis. The kinetic parameters of the COS loss determined in this study are obtained using only clathrate-free Holocene ice. It remains to be seen whether the same COS hydrolysis kinetics apply to glacial ice, which has higher concentrations of impurities derived from terrestrial dust and sea salt aerosols. Similarly, the impact of air clathrates on COS hydrolysis has not yet been studied. Further measurements on deep ice cores from multiple sites with different characteristics will be required to investigate these issues.

The current measurements suggest that there have been significant changes in atmospheric COS levels during the Holocene. The corrected records display a COS minimum during the mid-Holocene, followed by a steady rise over a period of time while atmospheric CO_2 was also increasing. The uptake of COS by terrestrial plants is the major atmospheric loss mechanism and the single largest term in the COS budget. The long-term COS increase during mid-to-late Holocene could indicate a possible concurrent decrease in terrestrial productivity. The results demonstrate how paleoatmospheric COS records may provide new constraints on the carbon cycle associated with past environmental change.

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9. Conclusions

The Antarctic ice core records measured to date all appear to record the same atmospheric COS level of 330–350 ppt during a few hundred years preceding the industrial era. However, on longer time scales, there are significant and systematic differences between COS measurements from different sites. COS levels tend to decrease with increasing depth and age in late Holocene ice, and this effect is larger in warmer ice cores. We interpret these observations as being indicative of COS loss due to in situ hydrolysis and present a method to correct for such loss. We find no evidence of in situ production systematically altering COS levels in Antarctic ice. It appears more likely that the occasional outliers are linked to sample contamination introduced during the drilling, handling, or gas extraction.

The kinetics of COS loss are estimated by modeling the thermal history of the ice core samples and optimizing

Acknowledgments

We thank Gary Clow for borehole temperature measurements at Taylor Dome and Siple Dome and Gary Clow and Kurt Cuffey for measurements at WAIS Divide. We thank the scientists, the drillers, and the support personnel that participated in the drilling of the Byrd, Siple Dome, Taylor Dome, and WAIS Divide ice cores. This work was supported by the NSF Division of Polar Programs grants PLR-1043780; PLR-0636953; PLR-0839122 for M.A., M.R.N., K.R.V., and E.S.S.; and PLR-0944197 for T.J.F. and E.D.W. T.J.F. also received support from the NASA Earth and Space Science Fellowship.

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