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**Key Points:**
- First ice core COS measurements from the last glacial period
- In situ COS hydrolysis in ice cores stops in clathrate ice
- Evidence for large gross primary productivity during the last glacial/interglacial transition

**Supporting Information:**
- Table S1
- Figure S1
- Figure S2
- Texts S1–S3, Figures S1 and S2, and Table S1

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# Changes in atmospheric carbonyl sulfide over the last 54,000 years inferred from measurements in Antarctic ice cores

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**Abstract** We measured carbonyl sulfide (COS) in air extracted from ice core samples from the West Antarctic Ice Sheet (WAIS) Divide, Antarctica, with the deepest sample dated to 54,300 years before present. These are the first ice core COS measurements spanning the Last Glacial Maximum (LGM), the last glacial/interglacial transition, and the early Holocene. The WAIS Divide measurements from the LGM and the last transition are the first COS measurements in air extracted from full clathrate (bubble-free) ice. This study also includes new COS measurements from Taylor Dome, Antarctica, including some in bubbly glacial ice that are concurrent with the WAIS Divide data from clathrate glacial ice. COS hydrolyzes in ice core air bubbles, and the recovery of an atmospheric record requires correcting for this loss. The data presented here suggest that the in situ hydrolysis of COS is significantly slower in clathrate ice than in bubbly ice. The clathrate ice measurements are corrected for the hydrolysis loss during the time spent as bubbly ice only. The corrected WAIS Divide record indicates that atmospheric COS was 250–300 parts per trillion (ppt) during the LGM and declined by 80–100 ppt during the last glacial/interglacial transition to a minimum of 160–210 ppt at the beginning of the Holocene. This decline was likely caused by an increase in the gross primary productivity of terrestrial plants, with a possible contribution from a reduction in ocean sources. COS levels were above 300 ppt in the late Holocene, indicating that large changes in the COS biogeochemical cycle occurred during the Holocene.

## 1. Introduction

Carbonyl sulfide (COS) is the most abundant sulfur gas in the troposphere. The current global tropospheric mean is 480–490 parts per trillion (ppt), and the atmospheric lifetime is 2–3 years [*Montzka et al.*, 2007; *Suntharalingam et al.*, 2008]. Terrestrial vegetation plays an important role in the removal of COS from the atmosphere [*Chin and Davis*, 1993; *Watts*, 2000; *Kettle et al.*, 2002; *Berry et al.*, 2013]. During photosynthesis, COS is taken up by plant leaves and irreversibly hydrolyzed, linking atmospheric COS levels with terrestrial gross primary productivity [*Montzka et al.*, 2007; *Campbell et al.*, 2008]. This process accounts for 60–70% of the total COS removal from the atmosphere. COS is also taken up by soils (20–30%) and destroyed by direct photolysis and reaction with OH (<10%) [*Suntharalingam et al.*, 2008; *Berry et al.*, 2013].

The ocean has long been considered the most important natural source of atmospheric COS, accounting for more than half of the total burden [*Chin and Davis*, 1993; *Watts*, 2000; *Kettle et al.*, 2002; *Suntharalingam et al.*, 2008]. Oceanic emissions occur directly in the form of COS, and indirectly in the form of carbon disulfide ($CS_2$) and dimethyl sulfide (DMS), which oxidize to produce COS. In the most recent COS budget, oceanic emissions account for 80–90% of the natural sources, most of which may be occurring as direct emissions [*Berry et al.*, 2013; *Launois et al.*, 2015]. Biomass burning (10–20%) and a small contribution from volcanic activity comprise the remainder of the natural emissions [*Watts*, 2000; *Kettle et al.*, 2002; *Suntharalingam et al.*, 2008; *Berry et al.*, 2013].

Previous analyses of ice cores from several Antarctic sites show that atmospheric COS generally remained in the 330–350 ppt range over the few hundred years preceding the industrial era [*Aydin et al.*, 2008, 2014]. In contrast, there have been significant changes in atmospheric COS levels during the past century. Firn air measurements show COS increasing from 350 to 400 ppt at the beginning of the twentieth century to a peak of ~550 ppt in the late twentieth century, then falling below 500 ppt at the beginning of the 21st century

[*Sturges et al*., 2001; *Montzka et al*., 2004]. The firn air and ice core records indicate that the current COS levels in the atmosphere are about 35% higher than the preindustrial background. However, anthropogenic emissions are only about 20% of the natural emissions in the most recent COS budget [*Berry et al*., 2013; *Campbell et al*., 2015]. It is possible that changes in the terrestrial plant uptake of COS also contributed to the trends in atmospheric COS levels during the twentieth century [*Campbell et al*., 2015].

On timescales longer than a few thousand years, ice core COS measurements from different Antarctic sites exhibit systematic differences related to the thermal history of the ice cores [*Aydin et al*., 2014]. COS in ice from warmer sites is increasingly more depleted with depth (and age) relative to the measurements from colder sites. This suggests temperature-dependent COS loss to hydrolysis in ice core air bubbles. *Aydin et al*. [2014] estimated the Arrhenius parameters for the loss kinetics and corrected the measurements from different Antarctic sites using model-based temperature histories specific to each site (see supporting information). The corrected records from different sites displayed much better agreement than the original uncorrected records, allowing the reconstruction of an 8000 year COS atmospheric history.

Here we present 128 new measurements from the recently drilled deep West Antarctic Ice Sheet (WAIS) Divide ice core 06A (WDC-06A) from Antarctica [*WAIS Divide Project Members*, 2013] along with 82 new measurements from the Taylor Dome M3C1 ice core. Previously, COS was measured in 84 WDC-06A samples from the last 3000 years of the Holocene. These measurements were used in the development of the in situ hydrolysis correction method and the recovery of the 8000 year COS atmospheric history [*Aydin et al*., 2014]. The new measurements extend the WAIS Divide COS record to 54,300 years before present (calendar year 1950), providing the first comprehensive data set covering the Last Glacial Maximum (LGM) and the last glacial/interglacial transition. The majority of the new Taylor Dome measurements are from the Holocene, but this data set also includes 22 measurements from the last glacial period. Contemporaneous measurements from the WAIS Divide and the Taylor Dome sites are compared. The implications of the ice core record on the COS biogeochemical cycle are discussed.

## 2. Methods

The measurements were conducted at the University of California, Irvine (UCI) ice core trace gas laboratory using previously described instrumentation and methods [*Aydin et al*., 2007, 2008, 2014]. COS measurements are conducted with 10–30 $cm^3$ STP of air extracted from ice core samples selected specifically for gas analysis. The ice core air is dry extracted by mechanical shredding of the ice core samples in an isolated vacuum chamber at −50 °C. All components of the extraction system contacting the sample are stainless steel, except for the copper gaskets used for the vacuum seals of the extraction chambers. Four identical extraction chambers were used in this study. They were constructed using low-carbon 316 L steel and electron beam welds.

Following the extraction, COS in the ice core air is preconcentrated using a glass bead trap at liquid nitrogen temperatures (−196 °C) and analyzed by gas chromatography (GC) with high-resolution mass spectrometry (MS). We implement an isotope dilution method for the calibration of the instrument and sample analysis. The calibration of the instrument is based on ppb level primary standards (unlabeled), which are diluted in nitrogen to prepare ppt level working standards. Varying levels of ppt level working standards are mixed with a fixed amount of ppt level $^{13}$C-labeled COS internal standard and analyzed with the GC/MS to determine the unlabeled/labeled standard response ratio. The mixing of the labeled and unlabeled standards is achieved on the glass bead trap at −196 °C during the preconcentration step. Both the primary and working standards as well as the isotope labeled standard are prepared at the UCI ice core laboratory. All samples are mixed with a known amount of ppt level $^{13}$C-labeled COS internal standard using exactly the same method as the calibration runs. The COS abundance in the sample is determined from the ratio of instrument response to unlabeled ($^{12}$COS) and labeled ($^{13}$COS) isotopomers. Our routine analysis involves measurement of this ratio, which allows us to account for sensitivity drifts in the mass spectrometer.

The calibration scale for the COS measurements presented in this study are consistent with earlier measurements from the UCI ice core laboratory [*Aydin et al*., 2007, 2008, 2014; *Montzka et al*., 2004]. An unofficial intercalibration effort with NOAA prior to publication of a short ice core COS record from Greenland displayed consistency between the NOAA and UCI calibration scales to within 2–3% [*Aydin et al*., 2007].

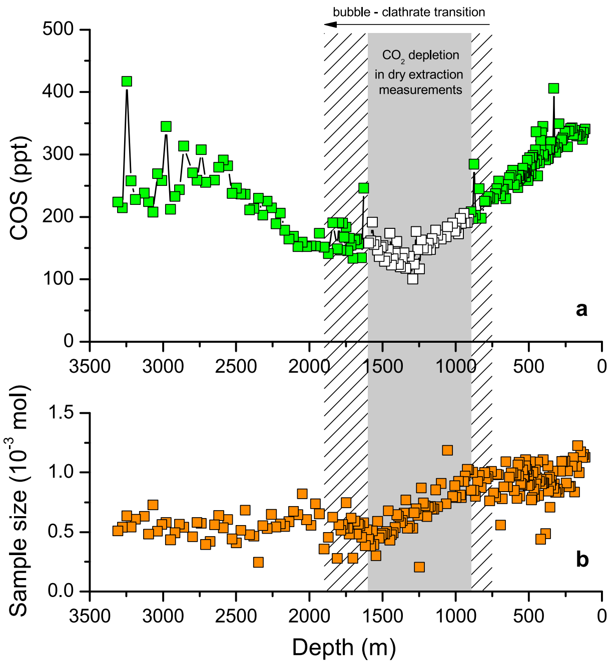


**Figure 1.** (a) The COS mixing ratio measured in 202 samples from the WDC-06A. The gray shaded area represents the depth range over which the dry extraction-based $CO_2$ measurements are anomalously low. The dashed areas mark the full extent of the bubble-clathrate transition in the WDC-06A based on microscopic inspection and laser borehole logging studies [*Fitzpatrick et al.*, 2014; R. C. Bay, personal communication, 2015]. The COS measurements that coincide with depleted $CO_2$ measurements are denoted with white squares. (b) The size of the ice core air samples used in COS analysis. We interpret the decline in sample size between 900 and 1600 m as a decline in the efficiency of our dry extraction system due to clathrate formation. Other factors can impact the sample size: (1) sample size is about 2% less than the amount of air actually extracted from the ice cores, but this difference is small and does not vary from sample to sample, and (2) total air content of the ice can change with depth due to environmental factors. However, the long-term variability in the total air content of the WAIS Divide ice is on the order of 10% and does not correlate with the change we see in sample size from 900 to 1600 m (R. B. Alley, E. J. Brook, and T. Sowers, personal communication, 2015).

## 3. Ice Cores and Chronologies

The drilling of the WDC-06A was completed in 2011 at a depth of 3405 m. The drill fluid was a hydrocarbon-based solvent Isopar-K (ExxonMobil Chemicals). The drilling site is located in West Antarctica (79.5°S, 112.1° W), 1.8 km above sea level. The current annual mean temperature at the WAIS Divide is −30 °C, and the ice equivalent accumulation rate is 22 cm yr$^{-1}$. COS measurements from the shallower sections (<767 m) of the WDC-06A were previously published using the "WDC06A-7" ice age scale, applying a constant delta age of 208 years to develop a gas chronology [*Aydin et al.*, 2014]. Here we use the newer WD2014 chronology [*Buizert et al.*, 2015; *Sigl et al.*, 2015]. The difference between the two chronologies is less than 20 years over the depth range of overlap (<767 m). The WD2014-based gas chronology is substantially better dated than the gas chronologies for any other deep Antarctic ice core drilled to date. It extends back through the LGM at equal or better accuracy than the deep ice cores drilled in central Greenland. In this paper, ice core gas ages are specified in kyr, defined as thousands of years before calendar year 1950.

The Taylor Dome site is located in East Antarctica (77.8°S, 158.7°E), 2.4 km above sea level. The current annual mean temperature is −42 °C, and the ice equivalent accumulation rate is 7 cm yr$^{-1}$. The M3C1 ice core was drilled to bedrock, which is only 554 m below the surface of the ice sheet at Taylor Dome. Drilling was completed in 1994 using *n*-butyl acetate as the drill fluid. The Taylor Dome measurements presented here are from the Holocene and last glacial period. We use a hybrid of three previously published chronologies [*Brook et al.*, 2000; *Monnin et al.*, 2004; *Ahn and Brook*, 2007] for dating the new COS measurements (see supporting information). The Taylor Dome chronology has considerably larger uncertainty than that for WAIS Divide.

The COS mixing ratios measured in the ice core samples are reported without correction for gravitational enrichment in the firn. The correction is in the order of 1% at both sites, and it is applied only to the hydrolysis-corrected records, which represent atmospheric COS levels inferred from the ice core measurements. The magnitude of the gravitational correction is dependent on the thickness of the diffusive firn layer, which varies in response to temperature and accumulation rate at the site. The change in gravitational correction is largest when transitioning from glacial to interglacial conditions; however, the magnitude of the correction remains close to 1% at all times.

## 4. WAIS Divide Results

A total of 212 ice core samples from the WDC-06A were analyzed for COS, ranging in depth from 115.2 to 3308.0 m, including the 84 measurements from 3 to 0 kyr that were previously published [*Aydin et al.*, 2014].

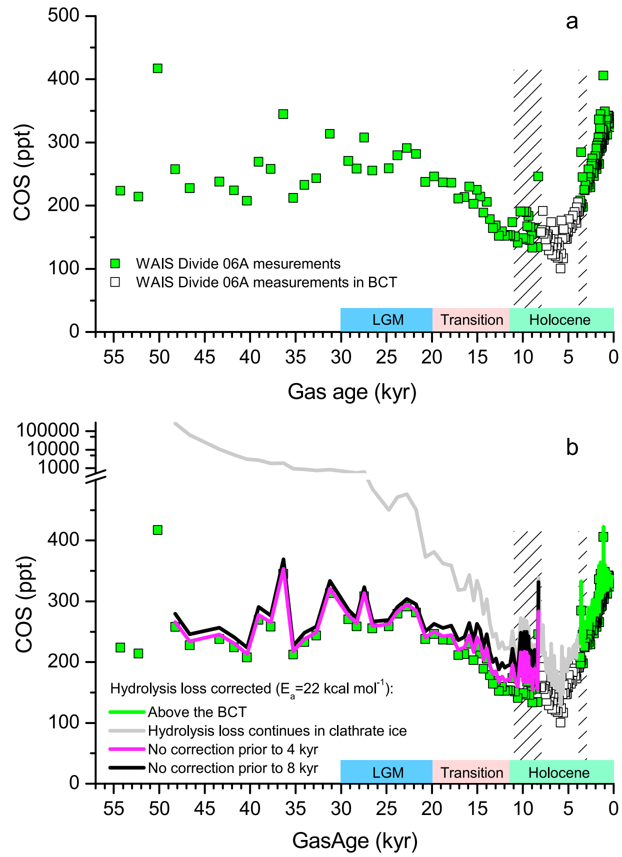


**Figure 2.** (a) The WDC-06A COS measurements on the WDC2014 age scale [*Buizert et al.*, 2015; *Sigl et al.*, 2015]. The measurements from the bubble-clathrate transition are denoted with white squares. The dashed areas mark the full range of measurements that may have been impacted by the clathrate formation. The approximate timings of the Last Glacial Maximum (LGM), the last transition, and the Holocene are marked on the *x* axis. Globally, the ice sheets reached their maximum positions sometime between 33 and 26.5 kyr and stayed unchanged until 20–19 kyr [*Clark et al.*, 2009], marking the beginning and the end of the LGM. The $CO_2$ maximum that marks the beginning of the Holocene occurs at 11.5 kyr [*Marcott et al.*, 2014]. The transition from the LGM conditions to the Holocene, which involves large-scale deglaciation, occurs between 20 and 11.5 kyr. (b) The COS measurements are corrected for loss to hydrolysis under three different conditions: (1) no hydrolysis loss correction prior to 4 kyr (magenta line) due to clathrates, (2) no hydrolysis loss prior to 8 kyr (black line) due to clathrates, and (3) hydrolysis loss continues through clathrate ice (gray line). All corrections are carried out with an activation energy ($E_a$) of 22 kcal mol$^{-1}$. The 4 kyr (magenta line) and 8 kyr (black line) corrections are shown in clathrate ice only (older than 8.3 kyr). There is a break on the *y* axis at 500 ppt, with values higher than 500 ppt shown on a logarithmic scale.

Ten of the 212 samples were lost during processing: five due to presence of excessive drill fluid in the sample that plugs a trap during preconcentration, three due to air leaks during extraction (determined by CFC-12 measurements), and two due to mass spectrometer malfunction during analysis. The remaining 202 measurements are shown in Figure 1a. The measurements range from 100 to 417 ppt, and the average $1\sigma$ uncertainty for the 202 measurements is $18 \pm 6$ ppt ($\pm 1\sigma$). This uncertainty reflects the cumulative effect of the analytical uncertainty and the uncertainty arising from the variability in background COS levels in the extraction and analytical systems [*Aydin et al.*, 2007].

The gas extraction efficiency of most dry extraction systems is less than 100%, and a considerable amount of air can be left behind in intact bubbles [*Schmitt et al.*, 2011]. The extraction efficiency of our system is roughly 60% for the bubbly upper sections of the WDC-06A. At greater depth, ice core air transitions from bubbles to clathrates due to increasing hydrostatic pressure. This can further reduce extraction efficiency because of the smaller size of the clathrates. We observed a steady decline in the quantity of air extracted from the ice core samples from 900 to 1600 m (Figure 1b). The onset of the clathrate formation was visually observed in the WDC-06A near 760 m [*Fitzpatrick et al.*, 2014]. Inspection of the WDC-06A borehole with a laser dust logger showed that the air bubbles disappear at around 1900 m (R. C. Bay, personal communication, 2015). These observations suggest that the full range of the bubble-clathrate transition in the WDC-06A extends from 760 to 1900 m (Figure 1).

In the bubble-clathrate transition zone, trace gases can display a preference for the clathrate phase compared to bulk air, and this often causes a bias in the measurements if the gas extraction efficiency is less than 100% [*Ikeda et al.*, 1999; *Sowers et al.*, 2003]. The dry extraction-based $CO_2$ measurements in the WDC-06A are anomalously depleted from 900 to 1600 m (J. Ahn and E. J. Brook, personal communication, 2015) where we observe the decline in the sample size, suggesting $CO_2$ depletion in the ice core air bubbles in the WDC-06A bubble-clathrate transition zone. It is highly likely that the COS measurements from 900 to 1600 m in the WDC-06A are similarly impacted. The discontinuity and the sharp minimum observed in COS near 1250 m suggest that the measurement bias may be largest in the middle of this depth range (Figure 1a). The measurements from 760 to 900 m and from

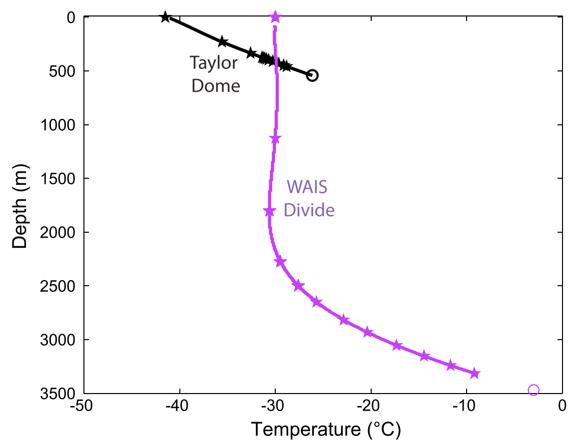


**Figure 3.** The borehole temperatures for the WDC-06A (purple) [*WAIS Divide project members*, 2013] and the Taylor Dome M3C1 (black) (G. D. Clow, personal communication, 2013) ice cores. Stars are placed at 5000 year intervals to 50,000 years ago. Circles denote the bottom of the ice sheet. WAIS Divide measurements end at 3330 m (120 m above the bed).

1600 to 1900 m display higher scatter than the sections immediately above and below, suggesting that the quality of COS measurements are impacted by the coexistence of bubbles and clathrates over the full depth range of the bubble-clathrate transition. The dry extraction-based $CO_2$ measurements in full clathrate ice from WDC-06A are not anomalous [*Marcott et al.*, 2014]. We assume that the COS measurements in full clathrate ice below 1900 m to also be devoid of artifacts caused by the dry extraction technique that occur when bubbles and clathrates coexist.

The deepest WDC-06A COS sample from 3308 m is dated to 54.3 kyr and the shallowest from 115 m to 0.2 kyr (Figure 2a). The COS measurements prior to 25 kyr exhibit high variability, with positive spikes near 50, 36, 31, and 27 kyr. The measurement resolution during the last glacial period is only 1–2 thousand years, so there is no overlap between the air extracted from neighboring samples. Two out of the four positive spikes (31 and 27 kyr) are within $2\sigma$ (±36 ppt) of the baseline that can be depicted from closest measurements and similar positive spikes have been identified in younger bubbly ice both from WAIS Divide and other sites in Antarctica [*Aydin et al.*, 2008, 2014]. The spikes observed in the WDC-06A glacial ice may represent real atmospheric changes or may be caused by an unidentified source of contamination that occasionally impacts the measurements. They require validation by increased resolution and measurements from another ice core.

Excluding the four positive spikes, the measurements range from 207 to 269 ppt during 54 to 33 kyr, with no discernable trend. The measurements from 31 to 23 kyr range from 291 to 314 ppt, representing a maximum that coincides with the LGM. COS declines from 22 kyr onward to just over 150 ppt by 12–11 kyr. Above the bubble-clathrate transition zone, there is a steady increase until about 1 kyr when COS levels stabilize in 310 to 350 ppt range.

## 5. In Situ COS Hydrolysis in Clathrate Ice

COS hydrolysis in ice core air bubbles can be described as a temperature-dependent first-order loss process. The lifetime ($k^{-1}$) of the reaction is longer than 10,000 years at the current surface temperature (−30 °C) at WAIS Divide but shorter than 1000 years at −10 °C [*Aydin et al.*, 2014]. If the same reaction kinetics applied to the measurements in clathrate ice, there would be dramatic COS losses in glacial ice from WDC-06A because of the rapidly increasing ice temperature below 2300 m (~15 kyr) (Figure 3). The COS loss can be quantified and the measurements can be corrected by using model-based Lagrangian temperature histories developed for the WDC-06A samples (Figure 4) and temperature-dependent first-order loss rates (see supporting information).

We first apply a hydrolysis loss correction to all the WDC-06A samples from the depth they were recovered to the bubble lock-in zone. The hydrolysis correction is less than 100 ppt from 15 to 8 kyr but increases rapidly for the measurements older than 15 kyr (Figure 2b). By 25 kyr, the correction is about a factor of 2. By 50 kyr, the hydrolysis loss correction implies inferred atmospheric COS levels in excess of 300 parts per billion, roughly 1000 times the measured levels. This is clearly unrealistic, especially given that the COS change during the last glacial/interglacial transition, a period of significant global environmental change, barely exceeds 100 ppt even with the correction.

It is evident that the COS loss kinetics inferred from bubbly ice measurements do not apply to clathrate ice. Most of the bubble-clathrate transition occurs between 4 kyr (900 m) and 8 kyr (1600 m) in WDC-06A. We repeated the hydrolysis loss corrections assuming that the COS hydrolysis ceases at 4 kyr or 8 kyr

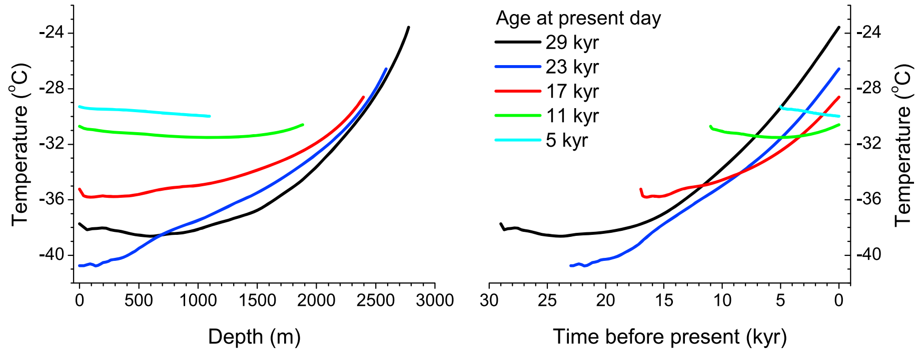


**Figure 4.** WAIS Divide temperature histories from the 1-D ice sheet model versus (left) depth and (right) time before present (see supporting information). The temperature histories are shown every 6000 years: 29 kyr (black), 23 kyr (blue), 17 kyr (red), 11 kyr (green), and 5 kyr (cyan). The correction for COS loss to hydrolysis is calculated by tracking the modeled temperature history of a sample from the depth it was recovered to the bubble lock-in depth. For example, the sample with a gas age of 29 kyr (black) is recovered from near 2800 m depth where the in situ ice temperature is −23.6 °C. When it was at the surface 29,000 years ago, the temperature was −37.7 °C. To simulate the termination of COS hydrolysis in clathrate ice, we carry out the correction only for the last 4000 or 8000 years before the ice reaches the lock-in depth.

(Figure 2b). As expected, the calculated corrections are much smaller in both cases. The most notable differences are for the glacial ice measurements, with the correction remaining less than 10 ppt for the 4 kyr scenario, and less than 25 ppt for the 8 kyr scenario. This is due to the colder surface temperatures during the glacial period resulting in colder temperature histories, especially when the ice is relatively close to the surface (i.e., younger than 4 or 8 kyr) (Figure 4). The difference between the 4 kyr and 8 kyr scenarios increases somewhat after 20 kyr. The largest difference coincides with the beginning of the Holocene (Figure 2b) as a consequence of the warmer temperature histories (Figure 4).

These results show that in situ reactive loss of COS either does not occur in clathrate ice or occurs at much slower rates than in bubbly ice. The treatment of the bubble-clathrate transition in our hydrolysis corrections is unrealistic. For example, we ignore the fact that the bubble-clathrate transition takes a few thousand years to complete. However, the relatively minor differences between the 4 kyr and 8 kyr scenarios suggest that the corrections applied to the WDC-06A measurements in full clathrate ice are not highly sensitive to the details of the clathrate formation process at this site. In both the 4 kyr and 8 kyr scenarios, the corrected COS records based on full clathrate ice measurements display what appears to be a robust atmospheric signal associated with the last glacial/interglacial transition. The atmospheric COS levels drop 80–100 ppt in an apparent inverse correlation with the warming climate (Figure 2b).

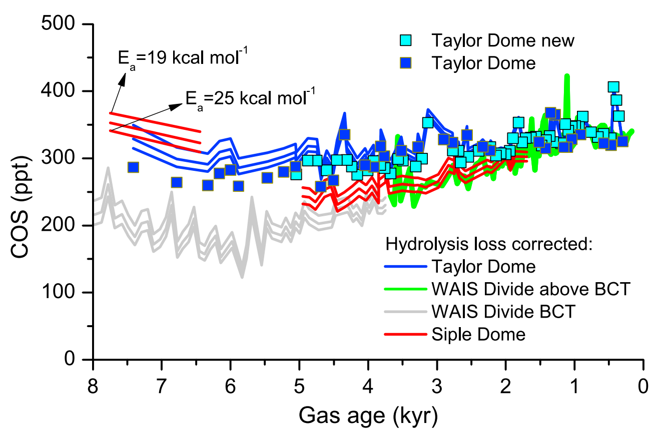


**Figure 5.** The previous published Taylor Dome measurements from the last 8000 years (blue squares) *Aydin et al.* [2014] were replicated from 5 to 0 kyr with new measurements from the same Taylor Dome M3C1 ice core (cyan squares). The new corrected record based on all Taylor Dome measurements (blue lines) does not significantly differ from what was published. The corrected WAIS Divide records from bubbly ice (green lines), and the corrected Siple Dome records (red lines) were also previously shown [*Aydin et al.*, 2014]. The corrected WAIS Divide records from the bubble-clathrate transition (gray lines) are based on new measurements. The three lines for the corrected records at all sites represent three hydrolysis loss corrections for three different activation energies ($E_a$ = 19, 22, and 25 kcal mol$^{-1}$), which cover the range of possible $E_a$ values that characterize the hydrolysis of COS in ice cores (see supporting information). The lowest $E_a$ results in the largest correction at all sites.

## 6. Taylor Dome Results

This study includes 82 new COS measurements from the Taylor Dome M3C1 ice core from Antarctica. The Taylor Dome ice sheet is only 554 m deep and does not allow clathrate formation. The measurements range from 59 to

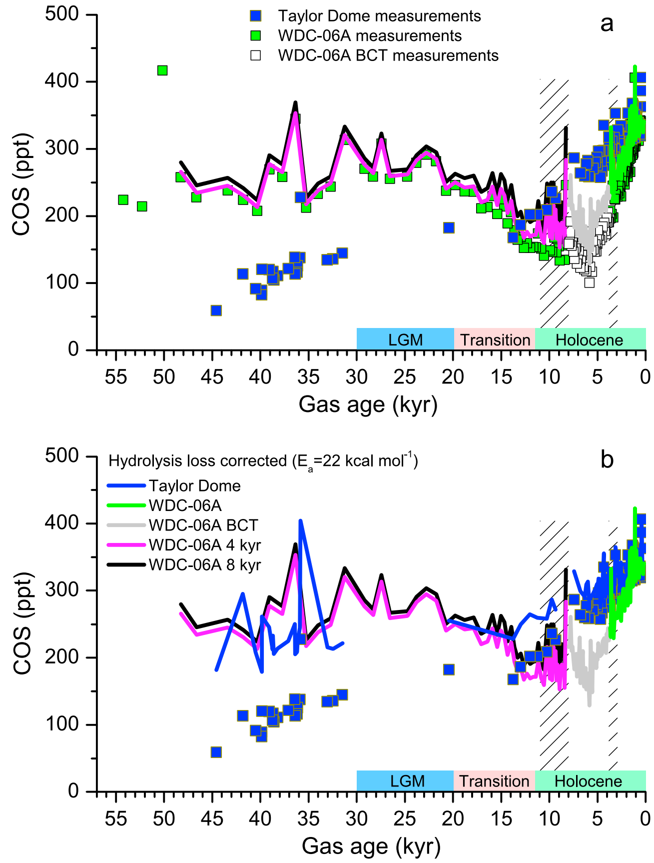


**Figure 6.** (a) Taylor Dome measurements (blue squares) are shown with the WAIS Divide measurements (green and white squares) and the corrected WAIS Divide records (green, gray, black, and magenta lines). All Taylor Dome measurements older than 9 kyr are new. (b) The corrected Taylor Dome (blue lines) record is shown with the corrected WAIS Divide records. All corrections shown in this figure are with $E_a = 22$ kcal mol$^{-1}$.

406 ppt, and the average $1\sigma$ uncertainty for the 82 measurements is $12 \pm 7$ ppt ($\pm 1\sigma$). Fifty-three of the new measurements are from the top 291 m of the ice core, covering the last 5000 years of the Holocene and providing overlap with prior measurements from the same Taylor Dome ice core (Figure 5). Previously published Taylor Dome measurements displayed higher COS levels than the corrected records from WAIS Divide and Siple Dome from 4 to 2 kyr [*Aydin et al.*, 2014]. With the new measurements, there is now a better agreement between the records from different sites although the Taylor Dome measurements still remain somewhat higher than the corrected WAIS Divide and Siple Dome records prior to 2.5 kyr.

The hydrolysis loss-corrected WAIS Divide records display lower COS levels than both the Taylor Dome and Siple Dome records for ages older than 3.5 kyr (Figure 5). This is not surprising given that at 3.7 kyr (900 m), the clathrate formation is well underway in the WDC-06A, which is expected to cause a negative bias that we do not correct for. The uncertainty that arises from the value of the activation energy ($E_a$) used in the corrections is considerably smaller than the difference between the WAIS Divide records from the bubble-clathrate transition and the other ice cores. The apparent low bias due to the biasing in the bubble-clathrate transition notwithstanding, the WAIS Divide records qualitatively support previous findings based solely on the Taylor Dome and Siple Dome records that there was a COS minimum in the atmosphere near 6–5 kyr [*Aydin et al.*, 2014].

The remaining 29 Taylor Dome measurements analyzed in this study are spread out unevenly over a broad age range covering 45 kyr through 9 kyr (Figure 6a). The 21 measurements from 45 to 31 kyr display an increase over time, measuring less than 60 ppt at 45 kyr and about 150 ppt at 30 kyr. The one measurement from 20.4 kyr is just below 200 ppt, which is higher than the measurements at either ends of the large data gap between 31 kyr and 14 kyr. The seven Taylor Dome measurements from 14 to 9 kyr display another increasing trend from about 180 ppt to 250 ppt. These Taylor Dome data allow a comparison with the WAIS Divide measurements in full clathrate ice from 45 to 31 kyr and from 14 to 11 kyr. Neither one of the increasing trends observed in the Taylor Dome measurements is evident in the WAIS Divide records (Figure 6a).

When the Taylor Dome measurements from 45 to 9 kyr are corrected for loss to hydrolysis, the agreement between the Taylor Dome and the WAIS Divide records improves markedly for the Taylor Dome measurements from 45 to 31 kyr and also for the two measurements from 20.4 kyr and 13.8 kyr (Figure 6b). The improved agreement is due to the Taylor Dome measurements requiring larger corrections on older time horizons as a result of the steadily increasing temperature of the ice sheet with depth (Figure 3). The hydrolysis loss correction is applied over the whole depth of the Taylor Dome ice core because no clathrates were observed in this core. The apparent agreement between the corrected Taylor Dome and WAIS Divide records during the last glacial period provides further evidence that COS hydrolysis does not occur in WAIS Divide clathrate ice.

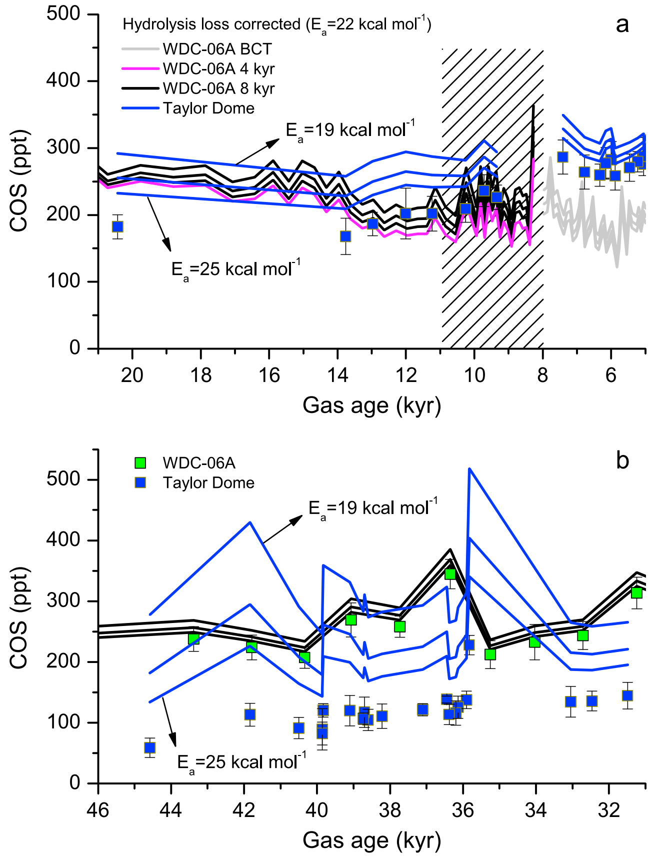


**Figure 7.** The hydrolysis corrections for all sites are carried out for three different $E_a$'s (19, 22, and 25 kcal mol$^{-1}$) to display the impact of using different Arrhenius parameters on the correction applied to the WAIS Divide and Taylor Dome measurements. The markers and lines are color coded as in Figures 2 and 6. At both sites, the smaller $E_a$ value results in larger corrections, and the difference between the corrections carried out with different $E_a$ values gets larger as the correction magnitude increases. (a) From 21 to 5 kyr. The WAIS Divide correction with no hydrolysis loss correction prior to 4 kyr (magenta line) is shown for $E_a = 22$ kcal mol$^{-1}$ only. (b) From 46 to 31 kyr. For WAIS Divide, only one set of hydrolysis corrections (black lines, no correction prior to 8 kyr) are shown. The Taylor Dome corrections are more sensitive to the value of $E_a$ than the WAIS Divide.

The two data sets do not compare as favorably during the glacial/interglacial transition and the early Holocene. Six of the seven corrected Taylor Dome measurements from 14 to 9 kyr are elevated with respect to WAIS Divide, with the only exception being the oldest sample from 13.8 kyr (Figure 6b). Additionally, both the measurements and the corrected records from Taylor Dome suggest that COS increased from 14 to 9 kyr, while the WAIS Divide records show a decline from 14 to 12 kyr, with a possible increase starting only after 11 kyr.

The discrepancy between the two ice cores during 14 and 9 kyr may be due to the uncertainties in the measurements and the uncertainty in the Taylor Dome gas age chronology during the glacial/interglacial transition. The sampling resolution of the Taylor Dome data from the last glacial/interglacial transition is not high enough to capture the measurement variability evident at this site during the late Holocene (Figure 5). There has not yet been a formal effort to synchronize any of the Taylor Dome chronologies with the WAIS Divide chronology, which further complicates the comparison of relatively short-lived features. We also cannot rule out the possibility that WAIS Divide measurements from full clathrate ice may still be biased by an experimental artifact that has not been previously observed in other trace gas measurements, particularly during the time period that immediately follows the end of the bubble-clathrate transition when Taylor Dome and WAIS Divide measurements do not agree. However, with better agreement between the WAIS Divide and the Taylor Dome records at 13.8 kyr (full clathrate WAIS Divide ice) and near 10 kyr (almost full clathrate WAIS Divide ice), it is not evident why the bias would peak at 12–11 kyr such that the records from the two sites display apparently opposing trends and disappear in older full clathrate ice. New measurements from different sites are needed for better assessment of the apparent discrepancy between the Taylor Dome and WAIS Divide measurements during 14 through 9 kyr.

We also examine the impacts of the uncertainties in the hydrolysis corrections on the comparison between the WAIS Divide and Taylor Dome COS records from 45 kyr to the early Holocene (Figures 7a and 7b). It is clear that the differences between the Taylor Dome measurements from 11.2, 12.0, and 13.0 kyr and the WAIS Divide record persist regardless of the $E_a$ chosen for the hydrolysis loss correction (Figure 7a). From 45 to 31 kyr, a wide range of atmospheric histories can be inferred from the Taylor Dome COS measurements for the full range of applicable $E_a$ values (Figure 7b). In contrast, the WAIS Divide records corrected with different $E_a$'s do not significantly differ from each other. The best agreement between the two data sets is achieved when $E_a = 22$ kcal mol$^{-1}$. Despite the general agreement between the mean atmospheric COS levels inferred from both data sets during 45 through 31 kyr, there are disagreements between individual data points that cannot be explained by uncertainties in the measurements or the hydrolysis loss corrections. Further discussion of these data requires higher-resolution measurements and synchronized chronologies for the two ice cores.

## 7. Implications

The 80–100 ppt decline during the last glacial/interglacial transition is one of the most prominent features of the ice core COS record from WAIS Divide (Figures 2 and 6). This decline indicates a shift in the biogeochemical cycling of COS associated with the change in global climate from glacial to interglacial conditions. COS does not remain stable at the low levels observed at the beginning of the Holocene. Measurements from multiple ice cores display higher COS during the late Holocene than the LGM. In this section, we explore possible changes in the major COS sources and sinks that could have driven such variability in atmospheric COS levels.

The removal of COS from the atmosphere is dominated by terrestrial plant uptake. This sink is closely related to the gross primary production by terrestrial plants (GPP) [*Hilton et al.*, 2015; *Campbell et al.*, 2008; *Montzka et al.*, 2007]. Chamber experiments suggest that the plant uptake of COS can be estimated from GPP as follows [*Stimler et al.*, 2010]:

$$\text{Uptake} = \text{GPP} \times \text{LRU} \times X_{\text{COS}}/X_{\text{CO2}} \quad (1)$$

where Uptake (molCOS.yr$^{-1}$) is the land plant uptake of COS, GPP (molC.yr$^{-1}$) is the gross primary production by land plants, leaf relative uptake (LRU) is the normalized leaf-scale relative uptake of COS to $CO_2$, and $X_{\text{COS}}$ and $X_{\text{CO2}}$ are the ambient mixing ratios of COS and $CO_2$, respectively. At steady state, COS sources will be balanced by the plant uptake from equation (1), assuming other COS removal processes are negligible. Atmospheric COS levels reach steady state quickly because of the relatively short lifetime (2–3 years). If the observed COS decline during the last glacial/interglacial transition was driven solely by changes in GPP (i.e., no COS source changes), we can write

$$\text{GPP}_{\text{HL}} \times \text{LRU}_{\text{HL}} \times \frac{(X_{\text{COS}})_{\text{HL}}}{(X_{\text{CO2}})_{\text{HL}}} = \text{GPP}_{\text{LGM}} \times \text{LRU}_{\text{LGM}} \times \frac{(X_{\text{COS}})_{\text{LGM}}}{(X_{\text{CO2}})_{\text{LGM}}}, \quad (2)$$

where the subscripts HL and LGM designate the Holocene and the Last Glacial Maximum. Equation (2) can be rearranged to examine the change in GPP required to explain the observed COS variability in the ice core data:

$$\frac{\text{GPP}_{\text{HL}}}{\text{GPP}_{\text{LGM}}} = \frac{(X_{\text{COS}})_{\text{LGM}}}{(X_{\text{COS}})_{\text{HL}}} \times \frac{(X_{\text{CO2}})_{\text{HL}}}{(X_{\text{CO2}})_{\text{LGM}}} \times \frac{\text{LRU}_{\text{LGM}}}{\text{LRU}_{\text{HL}}}. \quad (3)$$

Measurements in Antarctic ice cores indicate that the atmospheric $CO_2$ mixing ratio increased by a factor of ~1.4, from ~190 ppm during the LGM to ~265 ppm at 11.6 kyr at the beginning of the Holocene [*Monnin et al.*, 2001; *Fluckiger et al.*, 2002; *Ahn et al.*, 2004; *Elsig et al.*, 2009; *Marcott et al.*, 2014]. During the same time period, the ice core COS record from WAIS Divide displays a decline from about 270 ppt to 170–190 ppt (a factor of ~1.5). The LRU is also expected to change during the glacial/interglacial transition because increasing $CO_2$ favors the growth of C3 over C4 plants. Plant chamber experiments suggest that the LRU for C4 species is 60% of that for C3 species [*Stimler et al.*, 2011]. Dynamic vegetation models estimate that the fraction of forest GPP (C3 plants) relative to global GPP (C3 + C4 plants) increases from 0.4 during the LGM to 0.6 during the late Holocene [*Prentice et al.*, 2011]. This suggests about a 10% increase in the global average LRU during the glacial/interglacial transition or $\text{LRU}_{\text{LGM}}/\text{LRU}_{\text{HL}}$ of ~0.9. Inserting the ice core data and the model-based LRU change into equation (3) ($1.4 \times 1.5 \times 0.9$ on the right side of the equation) gives $\text{GPP}_{\text{HL}}/\text{GPP}_{\text{LGM}} = 1.9$, indicating roughly a doubling of GPP during the last glacial/interglacial transition. Uptake by terrestrial plants does not account for 100% of the COS removal from the troposphere. This calculation is accurate only if there is a similar magnitude increase in the soil uptake of COS, which accounts for ~30% of COS removal from the atmosphere. Larger (smaller) percent change in soil uptake would imply a smaller (larger) GPP increase than what this calculation suggests.

The GPP change during the last glacial/interglacial transition has been previously estimated using dynamic global vegetation models (DGVMs). In simulations driven by $CO_2$ histories and climate data from the Paleoclimate Modeling Intercomparison Projects (PMIP2 and PMIP3), the terrestrial GPP increases by a factor of 1.44 between the LGM and the late (preindustrial) Holocene [*Prentice et al.*, 2011]. Although in the right direction, this is a smaller GPP increase than what we calculate for the glacial/interglacial transition assuming constant COS sources.

The WAIS Divide ice core measurements display roughly a doubling of COS levels from 170 to 190 ppt in the beginning of the Holocene to 330–350 ppt in the late Holocene. This suggests that significant changes in GPP may have occurred during the Holocene. By contrast, the DGVM simulations indicate steady GPP during the Holocene. GPP variations in these models are primarily driven by variability in global average temperature and atmospheric $CO_2$. The relative stability of the global climate and the atmospheric $CO_2$ during the middle-to-late Holocene results in only a 1% GPP change in the models between the middle (6 kyr) and the late Holocene [*Braconnot et al.*, 2012].

The COS ice core records also provide some clues about the nature and the timing of possible GPP changes during the Holocene. It is possible that there was at least one COS maximum between 10 and 7 kyr (Figure 6b and 7a) and a minimum between 6 and 5 kyr (Figure 5). Given that most of the COS data from these age ranges are from WAIS Divide and these measurements are impacted by the bubble-clathrate transition at that site, determining the magnitude and exact timing of these events will require additional measurements in bubbly or full clathrate ice from different sites. The gradual increase in COS over the middle-to-late Holocene is a well-identified feature in the ice core COS records [*Aydin et al.*, 2014]. It is possible that changes in climate and land cover, such as large-scale desertification in Africa and Asia over the last 6000 years of the Holocene [e.g., *Wanner et al.*, 2008], resulted in global GPP changes during the Holocene that impacted atmospheric COS levels but is not captured by the PMIP simulations. The COS increase that starts at 6–5 kyr and ends at 1–0.5 kyr coincides with increasing atmospheric $CO_2$ and a depletion in $\delta^{13}CO_2$ [*Elsig et al.*, 2009], which suggests a gradual decline in GPP contributed to the $CO_2$ increase during middle-to-late Holocene [*Aydin et al.*, 2014].

We have so far assumed that the changes in atmospheric COS were due entirely to changes in terrestrial uptake. Changes in COS sources may also have occurred. Direct and indirect oceanic emissions constitute the most important natural source of COS [*Watts*, 2000; *Kettle et al.*, 2002; *Suntharalingam et al.*, 2008; *Berry et al.*, 2013]. The bulk of the direct oceanic source results from photochemical breakdown of colored dissolved organic compounds in the surface ocean where some of the newly produced COS is hydrolyzed and destroyed before it is emitted to the atmosphere. The indirect oceanic COS sources are linked to carbon disulfide ($CS_2$) and dimethyl sulfide (DMS) emissions from the oceans and their subsequent oxidation in the atmosphere. Recent studies suggest that the direct oceanic emissions may be 2–3 times larger than the indirect oceanic emissions [*Berry et al.*, 2013; *Launois et al.*, 2015], although this is yet to be confirmed by observations.

It is not easy to assess how the complex biogeochemistry of the COS ocean source would respond to changes in global climate. One might speculate that the surface ocean during the last glacial period contained more organic matter than today, given the considerably higher dust and aerosol loading in the glacial atmosphere [e.g., *Mayewski et al.*, 1994]. This could result in more COS and $CS_2$ production in the surface ocean and consequently lead to higher ocean-to-atmosphere COS flux. Warmer surface ocean temperatures during the Holocene would mean faster hydrolysis of COS compared to the glacial period (roughly 10% per °C) [*Elliott et al.*, 1989; *Launois et al.*, 2015] but also lower the solubility (roughly 10% per °C) [*Elliott et al.*, 1989], which results in a buffered system with respect to temperature changes in the surface ocean. If a decrease in oceanic COS sources contributed to the COS decline during the last glacial/interglacial transition, it was likely driven by changes in dissolved organic matter concentrations in the surface ocean. Without observational evidence on changes in dissolved organics in the surface ocean during the last glacial/interglacial transition, it is not possible to estimate how much the oceanic COS sources might have declined.

It is harder to invoke a role for the oceans with respect to the atmospheric COS changes during the Holocene. Large changes in organic matter content of the surface ocean seem less plausible, making it unlikely that the COS ocean sources could be the main driver of atmospheric COS variability during the Holocene.

Wildfires are another source of atmospheric COS but comprise only 10–20% of the total natural COS emissions today [*Berry et al.*, 2013; *Campbell et al.*, 2015]. Attributing the COS doubling during the Holocene solely to increased emissions from biomass burning would require at least a fivefold sustained increase in global wildfire emissions. Unless the contribution from biomass burning is severely underestimated in the COS inventories, it is unlikely that changes in biomass burning emissions played a prominent role in atmospheric COS variability during the Holocene or during the last glacial/interglacial transition.

## 8. Conclusions

This study presents the first ice core COS measurements from the last glacial period and the last glacial/interglacial transition, including the first measurements of COS in air extracted from full clathrate ice. It has been previously shown that COS is lost via hydrolysis in ice core air bubbles [*Aydin et al.*, 2014]. The results presented here suggest that the loss processes occurring in bubbly ice must either stop or occur at considerably slower rates in clathrate ice. WAIS Divide measurements from the last glacial period require little or no correction for loss to hydrolysis because the ice that forms during the glacial period experiences a colder temperature history, while in bubbly phase. Despite the cold surface temperatures, Taylor Dome is not an ideal site for studying COS in the glacial atmosphere. The shallow ice sheet at the Taylor Dome does not allow clathrate formation and results in considerable COS loss in glacial ice since hydrolysis continues for the age of the ice and most of the aging occurs at warmer temperatures than the surface. Ice cores from cold East Antarctic sites where the ice sheet is thicker may preserve an atmospheric COS record of the last several glacial/interglacial cycles, owing to the fact that the clathrate formation at such sites occurs relatively close to the surface while the ice is still very cold.

The ice core COS records presented in this study reveal several new findings: (1) Atmospheric COS varied in 200–300 ppt range for a major part of the last glacial period ($<$54 kyr), with peak levels of about 300 ppt during the LGM; (2) atmospheric COS declined during the last glacial/interglacial transition and was below 200 ppt in the beginning of the Holocene; and (3) the early-to-middle Holocene appears to be a period of high COS variability in the atmosphere, with levels ultimately stabilizing above 300 ppt in the late Holocene. Additional ice core measurements from different sites are needed to verify these findings. This is particularly necessary for confirming the magnitude of the COS decline during the last transition, which is based solely on WAIS Divide measurements, and to establish the atmospheric COS variability during the early Holocene when the only available data not impacted by the bubble-clathrate transition are the few sparse measurements from Taylor Dome. Future measurements in well-dated ice cores will also improve the understanding of ice core COS hydrolysis. For example, measurements in full clathrate ice from a site with different thermal history characteristics than WAIS Divide are necessary for a better assessment of COS hydrolysis in clathrate ice.

The magnitude of the COS decline during the last glacial/interglacial transition is larger than expected from the model-based estimates of the GPP increase. It is possible that decreases in the oceanic emissions also contributed to the COS decline during the last transition. COS variability during the Holocene is considerably greater than the model-based estimates of GPP variability during the Holocene. This perhaps indicates that the models are overly simplistic in their treatment of GPP.

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