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Preindustrial atmospheric carbonyl sulfide (OCS) from an Antarctic ice core

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[1] The concentration of carbonyl sulfide (OCS) has been determined in several preindustrial air samples extracted from a shallow ice core from Siple Dome, West Antarctica. The extraction of the air was carried out by shredding the core under vacuum, followed by analysis by gas chromatography with mass spectrometric detection. 11 ice core samples were analyzed, ranging in depth from 82.3 to 90.7 m. The ages assigned to OCS in the ice core samples range from 1616 to 1694 AD. The observed OCS mixing ratios range from 322.6 pptv to 442.3 pptv with a mean of 372.8 ± 37.2 pptv. These levels are significantly lower than the present day atmospheric mixing ratio of 500 pptv and suggest that the anthropogenic sources comprise approximately 25% of the present day OCS budget. *INDEX TERMS*: 0394 Atmospheric Composition and Structure: Instruments and techniques; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 1610 Global Change: Atmosphere (0315, 0325); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry

1. Introduction

[2] Carbonyl sulfide (OCS) is the most abundant tropospheric sulfur gas, with an average mixing ratio of approximately 500 pptv and an atmospheric lifetime of 4.3 years [Chin and Davis, 1995]. OCS has a complex biogeochemical cycle, with natural sources and sinks involving both the oceans and terrestrial biosphere [Andreae and Crutzen, 1997]. OCS is also formed in the atmosphere from the photochemical oxidation of carbon disulfide (CS_2) [Khalil and Rasmussen, 1984; Chin and Davis, 1993] and dimethylsulfide (DMS) [Barnes et al., 1994, 1996; Arsene et al., 2001]. DMS and CS_2 are both produced by natural (primarily oceanic) sources. CS_2 is also produced in a variety of industrial processes.

[3] Attention has focused on OCS largely because of the suggestion that the transport to and the photolysis of this compound in the stratosphere can be the source of the stratospheric sulfate layer during periods of volcanic quiescence [Crutzen, 1976; Turco et al., 1980]. The increases observed in the background stratospheric aerosol layer during the 1970's and 80's have drawn attention to anthropogenic OCS and possibly sulfur dioxide (SO_2) emissions as likely sources [Sedlacek et al., 1983; Hofmann, 1990; Golombek and Prinn, 1993]. The existing database of tropospheric OCS measurements does not exhibit a significant trend and the global budget calculations suggest that OCS cannot solely account for the variability in the stratospheric aerosols [Hofmann, 1991; Chin and Davis, 1995]. Results from recent modeling efforts support the view that OCS cannot be the primary source of variability in sulfate aerosols in the stratosphere [Weissenstein et al., 1997; Kjellström, 1998].

[4] Large uncertainties remain in estimates of the source and sink terms in the atmospheric budgets of OCS, CS_2 , and DMS [Chin

and Davis, 1993; Kjellström, 1998; Watts, 2000]. Such uncertainties place limits on our ability to assess the impact of anthropogenic activities on the atmospheric burden, and to assess the potential for future changes. Polar ice cores contain an archive of preindustrial air that can provide a baseline against which the current budget estimates of anthropogenic OCS sources can be compared. The ice core data can also provide an invaluable record of natural variability and the influence of climate on biogeochemical cycles.

[5] Measurements of OCS in Arctic firm air suggest a slight decrease in atmospheric OCS levels in the northern hemisphere during the past decade while the results from Antarctic firm air seem to suggest OCS concentrations were lower early in the twentieth century [Sturges et al., 2001]. Recent measurements of OCS in Antarctic firm air indicate that southern hemisphere OCS levels have increased by approximately 21% during the past century [Stephen A. Montzka, personal communication]. In this study, we present the first results from an effort to extract and analyze OCS in preindustrial air from a shallow Antarctic ice core, from Siple Dome, West Antarctica. The results from ice core and firm air measurements agree in that they indicate preindustrial OCS levels to be lower than present day levels, and suggest that it is possible to develop a long-term paleoatmospheric record for this gas.

2. Siple Dome Ice Core

[6] The Siple Dome C core used for this study was drilled in December 1995 at Siple Dome, West Antarctica, as part of the West Antarctic Ice Sheet program (WAISCORES). The site is located at 81.65°S and 148.81°W and an elevation of 620 m near the edge of the Ross Ice Shelf. The core is 10 cm in diameter, and was drilled to a depth of 91.945 m. The pore close-off at Siple Dome occurs in the range of 48–52 m.

[7] The difference between the ice age and the OCS gas age is determined by simulating the propagation of an OCS spike through the firm using a one-dimensional model that simulates diffusion and gravitational settling of gases in firm air [Trudinger et al., 1997; Schwander et al., 1988; Schwander, 1989]. The model is initialized with a mean annual snow accumulation rate of $100 \text{ kg m}^{-2} \text{ y}^{-1}$ and a mean annual temperature of -25.4°C . The diffusion coefficient of OCS in air is calculated to be $1.1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ [Wilke and Lee, 1955] for a mean annual atmospheric pressure of 898.5 mbar [Antarctic Meteorological Research Center, Space Science and Engineering Center, University of Wisconsin-Madison, <http://uwamrc.ssec.wisc.edu/aws/awsproj.html>]. The density profile used is a polynomial fit to experimental observations [Gregg W. Lamorey, personal communication]. The OCS spike is incorporated into the ice with a mean ice age-gas age difference of approximately 289 years. The age distribution of an ice core sample of OCS is about ± 5 years (1σ).

[8] The OCS gas ages are assigned by subtracting the ice age-gas age difference from the ice ages of each ice core sample. Ice ages were determined by visual layer counting with an uncertainty of $\pm 5\%$ [Richard B. Alley, personal communication]. A small negative correction of 0.7% is applied to the final OCS

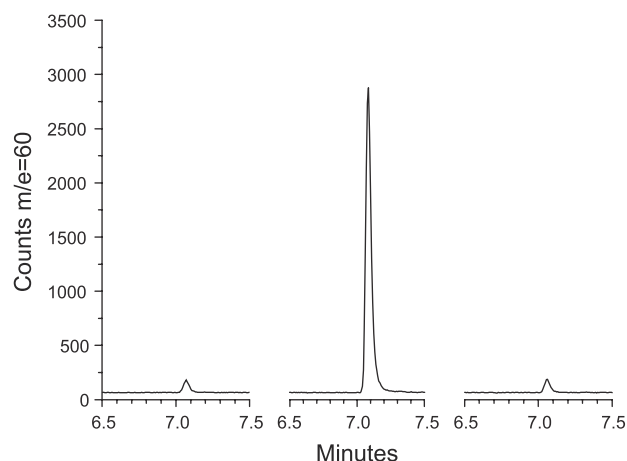


Figure 1. Selected ion-monitoring signal from the OCS parent ion ($m/e = 60$) during analysis of a Siple Dome ice core sample (~ 400 g from 83 m). Left panel: N_2 introduced over ice core sample prior to extraction, Middle panel: 33 ml STP air extracted from the ice core sample, Right panel: N_2 introduced over shredded ice core sample after extraction.

mixing ratios to correct for the effects of gravitational enrichment in firm air.

3. Ice Core Gas Extraction and Analysis

[9] The samples extracted ranged in size from 300–600 g. Air trapped in the ice cores was released using a dry extraction technique and analyzed by gas chromatography with mass selective detection. The extraction system is similar in design and function to those developed by *Etheridge et al.* [1988] and *Sowers and Jubenville* [2000] for analysis of CO_2 , CH_4 , and N_2O . The system consists of a cylindrical stainless steel vacuum chamber, which is 20 cm in diameter, 22 cm in length, and has a volume of approximately 7 L. The chamber is electropolished and has conflat end flanges with copper gaskets. Mounted concentrically inside the vacuum chamber is a grater, which is constructed by perforating a stainless steel tube that is 10 cm in diameter. The extraction chamber is mounted in a commercial chest freezer and connected by shafts and bearings to a paint shaker outside the freezer. The paint shaker provides linear and rotary motion (about 2 cm and 10° at 5 Hz). The extraction chamber is connected to a stainless steel vacuum line via a valve, bellows, and tubing. All valves on the chamber and vacuum line are stainless steel bellows valves with alloy or copper valve tips. The chamber is disconnected from the vacuum line while the can is in motion.

[10] The extraction process is as follows. The ice core sample and the extraction chamber are precooled to $-50^\circ C$, and the sample is placed inside the grater in the chamber. The chamber is evacuated, filled with nitrogen, and evacuated again several times to remove residual air. The chamber is then disconnected from the vacuum line, and the shaker is operated for 25–30 minutes. This shredding process liberates 70–80% of the air trapped in the ice core.

[11] After the extraction, the chamber is reconnected to the vacuum line and the released gases are transferred into a 76 cm long, 1/4" O.D. stainless steel tube immersed in liquid helium. It takes about 10 min to cryogenically pump $\sim 95\%$ of the sample into the tube.

[12] The extracted air is analyzed immediately after recovery. The samples are drawn at a controlled rate through a glass bead trap at liquid nitrogen temperature ($79^\circ K$). Non-condensable constituents of the sample, including nitrogen, oxygen, and argon flow into a large, calibrated volume. The size of the sample is deter-

mined by measuring the pressure in this volume. More than 98% of the gas in the tube passes through the cryotrap.

[13] The trapped gases are thermally desorbed from the glass bead trap onto a 0.01" I.D. stainless steel tube in liquid nitrogen for refocusing before they are injected onto the GC column. Chromatographic separation is carried out using a 60 m long, 0.25 mm I.D. DB-VRX column with 1.4 μm film thickness (Agilent Technologies), using a helium flow of 2 ml min^{-1} as the carrier gas. The GC oven is programmed to run for 6 min at $28^\circ C$, then ramped at $35^\circ C min^{-1}$ to $100^\circ C$. The first 15 m of the column is configured as a precolumn and is switched out of line with the remainder of the column at 3 min. OCS is detected using an HP 5973 quadrupole mass spectrometer in electron impact mode by selected ion monitoring of the parent ion at $m/e = 60$.

[14] The calibration of the system is based on four high-pressure Aculife-treated aluminum cylinders (Scott Gases) with 200 to 500 ppbv OCS in nitrogen. These cylinders are prepared in our laboratory by volumetric addition of pure OCS and gravimetric addition of the balance nitrogen. The absolute accuracy of the cylinder concentration is estimated at 2%. An informal intercomparison with uncertified gravimetric standards provided by NOAA/CMDL yielded agreement to within 1%. Standards at pptv level are prepared by manometric dilution of the ppbv level standards with nitrogen in electropolished stainless steel flasks. Each flask is filled with approximately 10 torr water vapor before OCS is introduced. The final pressure in the flasks is nearly 1100 mbar and the mixing ratios range from 200 to 800 pptv. These flasks are analyzed on the GC/MS in the same manner as samples.

[15] The size of the samples used in this study ranged from 30 to 50 ml STP. The protocol for analyzing an ice core sample involves taking pre- and post-shredding blanks. This is done by adding 30–50 ml STP of N_2 to the extraction chamber containing the ice core sample prior to shredding, allowing it to sit for 25–30 min, and analyzing the resultant gas. A similar blank is collected over the shredded ice core after the sample is extracted and the extraction chamber is fully flushed and evacuated. These system blanks ranged from 4% to 12% of the signal from samples, with a mean of 7%. It is assumed that the gas extracted from the ice core contains a similar blank, and the mean of the pre to and post-shredding blanks for each sample is subtracted from the signal obtained from the ice core sample itself (Figure 1). The difference between pre- and post-shredding blanks for individual samples ranged from $\pm 0.1\%$ to $\pm 2.7\%$, with a mean of $\pm 1.1\%$.

[16] Following the blank determination, gas standards at pptv level are introduced over the crushed ice to check for losses of OCS during the extraction procedure. They are allowed to sit for

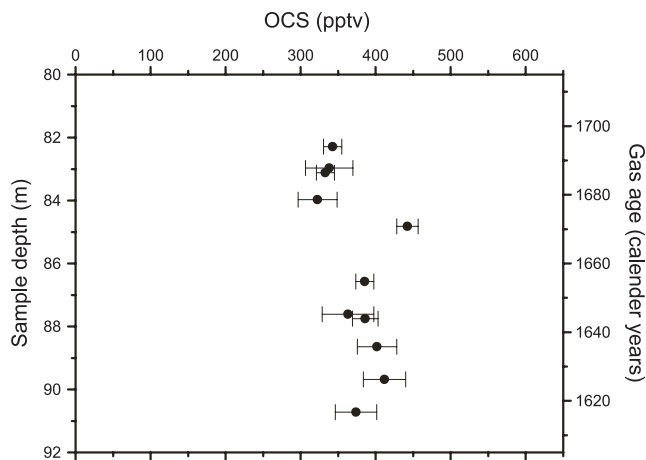


Figure 2. Mixing ratio of OCS in Siple Dome ice core samples plotted against the mean gas age.

Table 1. Global OCS Sources from *Watts* [2000]

	OCS (Tg y ⁻¹)
<i>Natural sources</i>	
Oceans	0.30 ± 0.25
Soil and wetlands	0.05 ± 0.04
Volcanism	0.05 ± 0.04
Precipitation	0.13 ± 0.08
DMS oxidation	0.17 ± 0.04
CS ₂ oxidation	0.20 ± 0.09
Total	0.90 ± 0.29
<i>Anthropogenic sources</i>	
CS ₂ oxidation	0.22 ± 0.11
OCS direct	0.12 ± 0.06
Total	0.34 ± 0.13
Biomass burning	0.07 ± 0.05

25–30 min in the chamber, and analyzed using the same procedure as ice core samples. The mixing ratio of OCS in standards is unaffected by this procedure. The overall precision of the OCS mixing ratio measurement for each ice core sample is determined by combining the uncertainties due to the system calibration and the system blank. The overall uncertainty for each sample is shown as error bars in Figure 2. The lowest and highest errors for the data set are ±3.1% and ±9.3% of the reported mixing ratio, respectively, while the average precision of the data set is ±5.9%.

4. Results and Discussion

[17] The Siple Dome ice cores analyzed in this study had OCS mixing ratios ranging from 322.6 to 442.3 pptv (Figure 2), with a mean of 372.8 ± 37.2 pptv (1σ). The dates estimated for OCS in the ice core samples range from 1616 to 1694. In two cases, a pair of samples was analyzed which were close enough in depth that the age distributions of the air in them should have significant overlap. In both cases, the samples gave mixing ratios that were identical within the analytical uncertainty.

[18] The data appear to cluster in two groups. The deepest six samples have a mean OCS mixing ratio of 387.1 ± 17.8 pptv. The shallowest four samples have slightly lower mixing ratio, with a mean of 334.1 ± 8.6 pptv. This difference is statistically significant at the 95% confidence interval. The one sample between the two groups has the highest mixing ratio observed, 442.3 pptv.

[19] One of the concerns associated with the analysis of ice core OCS is the question of hydrolysis. OCS undergoes base-catalyzed hydrolysis in aqueous solution via the reaction $\text{OCS} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{S}$. No data is available for the rate of this reaction in ice, although extrapolation of aqueous phase rates suggests that it could be significant in liquid-like surface layers at polar ice core temperatures [Elliott *et al.*, 1989]. If hydrolysis did occur, it would complicate the interpretation of ice core measurements in terms of paleoatmospheric levels. The results of this study argue against chemical loss, as there is clearly no decrease over the 78 year span represented by these ice core measurements.

[20] The observed OCS levels are significantly lower than those in the modern atmosphere. The global average OCS mixing ratio is approximately 500 pptv with a ±50 pptv spread around the mean [Chin and Davis, 1995]. More recent measurements are 3% lower [Stephen A. Montzka, personal communication], indicating annual mean mixing ratios for OCS of around 485 pptv in both hemispheres. The Siple Dome ice core data suggest that the preindustrial atmospheric OCS burden was approximately 25% less than modern atmospheric levels. The current emission inventory of OCS indicates a natural source strength of 0.90 ± 0.29 Tg y⁻¹, which is roughly three times the known anthropogenic sources of 0.34 ± 0.13 Tg y⁻¹ (Table 1). Thus, the best estimate of current source strengths is in agreement with the ice core data. Biomass burning, which consists of both anthropogenic and natural components, is only 5% of the total OCS budget.

[21] Recent measurements of OCS in South Pole firn air suggest that atmospheric levels of OCS were 400 pptv at around 1920 [Stephen A. Montzka, personal communication]. It is assumed that industrial emissions of OCS and CS₂ were small at that time relative to their current levels. The fact that the Siple Dome ice core shows even lower levels two to three hundred years earlier suggests that there was either an anthropogenic perturbation to the OCS budget at that time, perhaps via biomass burning, or there is variability in the natural biogeochemical cycle. It is possible that the 15% increase observed between the shallow and deep clusters of ice core data is due to such variability in the natural biogeochemical cycle of OCS.

5. Summary

[22] The results of this study indicate that preindustrial OCS levels were approximately 25% lower than current atmospheric levels. These results are in general agreement with current estimates of the anthropogenic contribution to the OCS budget. There is no evidence of chemical loss of OCS in the ice, suggesting that it should be possible to develop a long-term paleoatmospheric record for this gas through the analysis of deep ice cores.

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