Methyl chloride in a deep ice core from Siple Dome, Antarctica

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[1] Methyl chloride (CH_3Cl) is a naturally occurring ozone-depleting substance and a significant component of the atmospheric chlorine burden. In this study CH_3Cl was analyzed in air bubbles from the West Antarctic Siple Dome deep ice core with gas ages ranging from about 65 kyr BP to the Late Holocene. CH_3Cl levels were below the modern Antarctic atmospheric level of 530 ppt in glacial ice (456 ± 46 ppt, 33–65 kyr BP) and above it during the early Holocene (650–700 ppt, 10–11 kyr BP). For most of the Holocene, CH_3Cl levels were 500–550 ppt, with good agreement between CH_3Cl levels in this core and in the Dome Fuji ice core (Saito et al., 2007). Several late Holocene ice core samples (<2 kyr BP), show evidence of enrichment in CH_3Cl relative to South Pole ice core samples of overlapping gas age. The Siple Dome record suggests that CH_3Cl levels in the glacial Southern Hemisphere atmosphere were about 16% lower than those during the mid-late Holocene. **Citation:** Saltzman, E. S., M. Aydin, M. B. Williams, K. R. Verhulst, and B. Gun (2009), Methyl chloride in a deep ice core from Siple Dome, Antarctica, *Geophys. Res. Lett.*, *36*, L03822, doi:10.1029/2008GL036266.

1. Introduction

[2] Methyl chloride (CH_3Cl) is one of most abundant halocarbons in the atmosphere with a global mean mixing ratio of about 550 ± 30 ppt (pmol mol^{-1}). It is a significant contributor to ozone depletion as the transport and subsequent photolysis of CH_3Cl of tropospheric origin is responsible for about 16% of the total stratospheric chlorine burden [*Montzka et al.*, 2003; *Clerbaux et al.*, 2007]. The sources of CH_3Cl are predominantly natural and include tropical plants [*Yokouchi et al.*, 2000], oceans [*Moore et al.*, 1996], salt marshes [*Rhew et al.*, 2000], biomass burning [*Andreae and Merlet*, 2001], wood-rotting fungi [*Harper*, 1985], and soils [*Keppler et al.*, 2000]. The major sinks of atmospheric CH_3Cl include reaction with OH, uptake by soils [*Keppler et al.*, 2005], and microbial degradation in the oceans [*Tokarczyk et al.*, 2003]. The atmospheric lifetime is 1.3 years [*Montzka et al.*, 2003]. Although pollutant sources of CH_3Cl appear to be minor, human activities can have an impact on its atmospheric abundance and cycling through changes in land use, climate, and atmospheric reactivity.

[3] Studies of CH_3Cl in air extracted from polar firn and ice cores potentially provide a way to examine the natural variability of atmospheric CH_3Cl and its relationship to climate change and human activities. Analysis of Antarctic firn air from South Pole and Siple Dome suggests that the mixing ratio of CH_3Cl in the overlying atmosphere is not altered in the firn column [*Butler et al.*, 1999]. Studies of air extracted from dry-drilled, shallow ice cores at South Pole and Siple Dome suggest that ambient CH_3Cl is also preserved during the process of pore close-off and burial, at least on time scales of 100–2,000 years [*Aydin et al.*, 2004; *Williams et al.*, 2007]. *Saito et al.* [2007] recently reported the first CH_3Cl measurements in a deep ice core from Dome Fuji. They found near-modern CH_3Cl mixing ratios in Holocene ice and elevated levels in glacial ice. They attributed elevated CH_3Cl levels in glacial ice partly to in situ production resulting from chemical reactions involving Cl^- and continentally-derived dust in the ice. Correcting for the effects of in situ production, they found the glacial CH_3Cl levels to be 700 ppt, about 30% higher than the mean levels measured in Holocene ice.

[4] In this study, CH_3Cl was measured in 46 ice core samples from Siple Dome, West Antarctica. This was a pilot study carried out to assess the feasibility of analyzing CH_3Cl in ice from a deep West Antarctic ice core. Gas ages for the samples ranged from about 65 kyr BP to the Late Holocene. The analytical techniques used in this study involve dry extraction of air from ice core bubbles, followed by analysis using GC/MS with isotope dilution. The procedures and instrumentation used are identical to those used in several previous studies [*Aydin et al.*, 2007, *Williams et al.*, 2007; *Saltzman et al.*, 2004, 2008]. *Aydin et al.* [2007] examined CH_3Cl in the dry- and fluid-drilled ice cores from GISP2 and concluded that there was no evidence of contamination of CH_3Cl from the use of n-butyl acetate as the drill fluid. The same drilling fluid was used for the Siple Dome A core.

2. Siple Dome Site and Ice Core Characteristics

[5] The Siple Dome deep ice core was drilled as part of the West Antarctic Ice Sheet drilling program (WAISCORES; http://nsidc.org/data/nsidc-0120.html). The site is at an elevation of 621 masl, with an annual mean temperature of 24.5°C and a mean annual accumulation rate of 13.2 cm weq/yr [*Taylor et al.*, 2004]. The total depth of the Siple Dome ice core was 1004 m. Dating of the Siple Dome ice core is based on annual layer counting and correlation of Siple Dome methane variations to those in the GISP2 ice core [*Taylor et al.*, 2004; *Brook et al.*, 2005]. The Siple Dome ice core is 5″ in diameter, and was drilled using n-butyl acetate as the drilling fluid.

[6] Firn air studies at Siple Dome suggest that the width of the gas age distribution (at half-height) is approximately 25 years [*Aydin et al.*, 2004]. The spacing of samples

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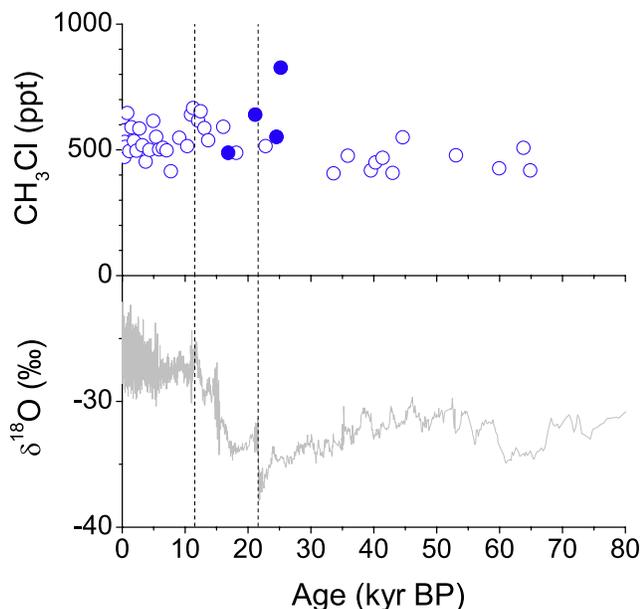[1]Department of Earth System Science, University of California, Irvine, California, USA.

Figure 1. Methyl chloride (CH_3Cl) and $\delta^{18}O$ in the Siple Dome deep ice core. Oxygen isotope data from *Brook et al.* [2005]. The filled circles denote the samples with highest Ca^{+2} levels measured in ice from the same depth. Vertical dashed lines denote the beginning and end of the glacial/ interglacial transition.

analyzed in this study is such that there is no overlap in terms of gas age between any of the neighboring samples.

3. Ice Core Sampling and Analysis

[7] The sampling strategy for this study was to select samples roughly equally spaced in time, over the length of the core. However, the analysis required relatively large volume, crack-free ice core samples, and sampling depths were adjusted for maximum core quality. The sampling effort yielded 46 samples, unevenly spaced in time, and with a bias towards the end of the glacial/interglacial transition and Holocene.

[8] In total, 58 ice core samples were analyzed for CH_3Cl in this study. Of these, 8 samples were lost during analysis. This occurred when excessive amounts of n-butyl acetate were released from fractured samples during extraction, plugging the GC column during the cryogenic phase of the chromatography. One sample was lost during the extraction because of a vacuum leak into the extraction chamber. Another sample, with an estimated gas age of 8.5 kyr BP, was excluded from this discussion because it contained 17 ppt of CFC-12. This indicates contamination by modern air which was probably trapped in invisible, healed fractures. Two additional samples were from the deep section of disturbed ice at Siple Dome (988 m and 991 m) and could not be assigned gas ages. The remaining 46 samples had a mean analytical uncertainty of 16 ± 8 ppt or $3 \pm 2\%$ of the measured CH_3Cl levels. Four of these samples (710.44, 833.84, 929.42, and 944.00 m) released just enough n-butyl acetate during extraction to partially plug the column and delay the elution of the analytes. CH_3Cl mixing ratios from these four samples are not excluded because they were not

anomalous with respect to the rest of the data set. All uncertainties are reported as $\pm 1\sigma$.

4. Results and Discussion

[9] The CH_3Cl levels measured in the Siple Dome ice core are shown in Figure 1. The 11 oldest ice core samples analyzed in this study range in age from 33–65 kyr BP. These samples exhibited CH_3Cl levels ranging from 407 to 550 ppt, with a mean of 456 ± 46 ppt. Four samples were analyzed from the time period between 21–25 kyr BP, during the Last Glacial Maximum (LGM). Three of the LGM samples ranged in CH_3Cl mixing ratio from 515 to 640 ppt CH_3Cl. The other was 826 ppt, which appears to be anomalous relative to the entire Siple Dome CH_3Cl data set. Seven samples were analyzed from the glacial/interglacial transition. These samples range in age from 12–18 kyr BP with mixing ratios from 488–653 ppt. The remaining 24 samples were from the Holocene, with ages from 0.13–11.5 kyr BP. These samples had CH_3Cl levels ranging from 415–666 ppt with a mean of 542 ± 65 ppt. Overall, the CH_3Cl data appears to consist of two populations, one covering the glacial period prior to the LGM with a mean of 456 ± 46 ppt CH_3Cl (n = 11), and another from the LGM to the late Holocene, with a larger variance and higher mean of 549 ± 64 ppt (n = 34, excluding the outlier at 826 ppt).

[10] The youngest samples from the Siple Dome deep core overlap in gas age with previously published measurements on dry-drilled Siple Dome and South Pole ice cores [*Aydin et al.*, 2004; *Williams et al.*, 2007] (Figure 2). The two earlier studies show reasonable agreement, where there is age overlap between the two cores. Of the 9 overlapping samples in this study, 3 show reasonable agreement with the earlier measurements, and 6 exhibit CH_3Cl levels elevated by 50–150 ppt. This is a small basis for comparison of the two sites, but the provisional conclusion is that there is some evidence for enrichment of CH_3Cl in these late Holocene samples from the Siple Dome deep core. This enrichment does not increase systematically with increasing depth or age, and thus does not appear to be caused by ongoing in situ production of CH_3Cl in ice. The apparent
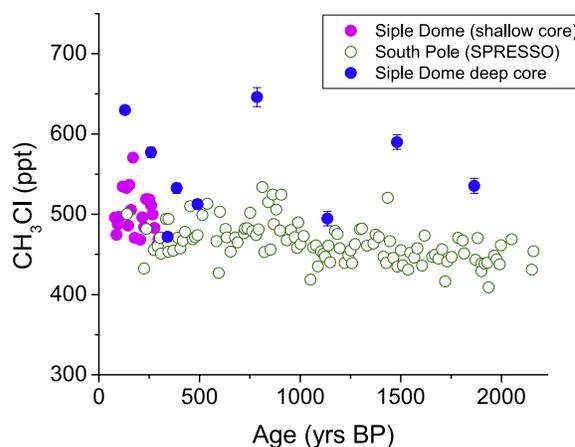

Figure 2. CH_3Cl in the Siple Dome deep ice core (black circles (this study)), Siple Dome shallow core (gray circles [*Aydin et al.*, 2004]), and South Pole shallow ice core (open circles [*Williams et al.*, 2007]) for the past 2 kyr BP.
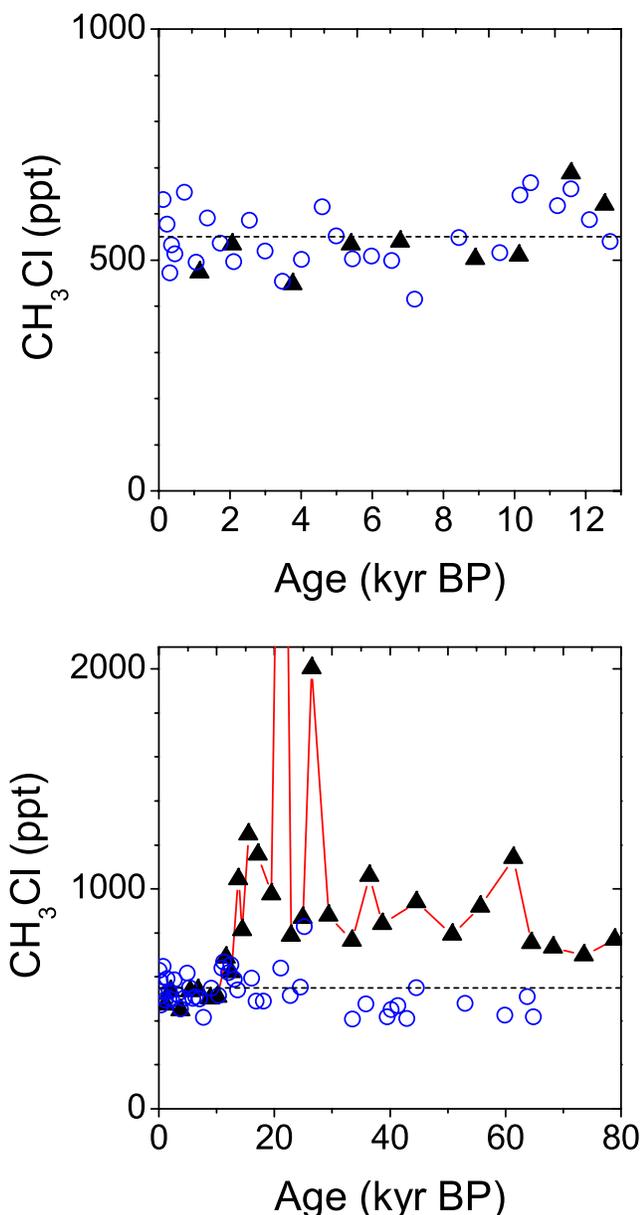
Figure 3. CH_3Cl in the Siple Dome (open circles) and Dome Fuji (black triangles) ice cores. (left) Holocene and (right) entire record. The dashed line denotes modern atmospheric CH_3Cl levels.

disagreement could be an artifact related to intermittent in situ production in firn, which may also explain subtle discrepancies between firn records from different sites [*Trudinger et al.*, 2004]. It may also be possible that CH_3Cl levels in the samples could be altered during sample handling or storage. The general consistency between CH_3Cl in firn air and shallow, dry drilled ice at Siple Dome, and agreement between shallow ice core samples from Siple Dome and South Pole suggests that atmospheric CH_3Cl is faithfully incorporated into ice core bubbles at this site. It should be noted that the age distributions of air in bubbles at South Pole is much broader than at Siple Dome (about 50 vs. 25 years wide at half height), so one would expect a more heavily smoothed record of atmospheric variations in South Pole ice compared to Siple Dome.

[11] The only other published deep ice core CH_3Cl record is from Dome Fuji, East Antarctica [*Saito et al.*, 2007]. Dome Fuji is a colder site at a higher elevation (3810 m), than Siple Dome, with a mean annual temperature of $-58°C$ and an accumulation rate of 32 kg m^{-2} y^{-1} weq. Like Siple Dome, the Dome Fuji core was drilled using n-butyl acetate drilling fluid. The Dome Fuji gas record is highly smoothed compared to Siple Dome. The gas age distribution has a width at half height of roughly 350 years for the Late Holocene [*Sugawara et al.*, 2003]. In Holocene ice, there is fairly good agreement between the CH_3Cl records from the two cores (Figure 3). The Dome Fuji mean CH_3Cl level for 0–11 kyr BP is 504 ± 37 ppt, which is not significantly different from Siple Dome. Both records exhibit slightly elevated CH_3Cl levels of 600–700 ppt around 11–13 kyr BP, near the end of the glacial/interglacial transition. The agreement between the two cores is quite good even on an individual sample basis. This is surprising given analytical uncertainties, the uncertainty in gas dating, and the differences in the width of the age distributions at the two sites. It should be noted that only the two shallowest samples from Dome Fuji overlap in time with the records shown in Figure 2. The 1150 BP sample is in agreement with both Siple Dome and South Pole cores. The 1900BP sample is agreement with the Siple Dome data from that period, but 50–100 ppt higher than the South Pole data. The general agreement between Dome Fuji and SDM-A records suggests that the cores are capturing paleoatmospheric variations during the Early and Mid Holocene.

[12] The Siple Dome and Dome Fuji CH_3Cl records are markedly different during the glacial period and for the glacial/interglacial transition prior to 13 kyr (Figure 3). The Dome Fuji data show glacial CH_3Cl levels that are considerably higher than Holocene levels with all the glacial data exceeding 700 ppt and much of it above 1 ppb. By contrast, the Siple Dome glacial data prior to the LGM and the glacial/interglacial transition (33–65 kyr BP) are comparable to, or slightly lower than Holocene levels, with a mean of 456 ± 46 ppt. *Saito et al.* [2007] demonstrated a strong positive correlation between the glacial CH_3Cl levels at Dome Fuji and the levels of Ca^{+2} in the enclosing ice. This is convincing evidence that there is "excess" CH_3Cl in the Dome Fuji core, resulting from in situ production, most likely related to chemical or biological reactions involving terrigenous dust and/or associated organic material. Such a correlation cannot be explained by changes in paleoatmospheric CH_3Cl levels, because the air in the glacial bubbles at Dome Fuji is roughly 2 kyr younger than the enclosing ice. *Saito et al.* [2007] used a linear regression of CH_3Cl against Ca^{+2} to infer that the "excess" CH_3Cl was superimposed on a background glacial level of 700 ppt. However, they noted that this did not rule out the possibility of "excess" CH_3Cl even in ice with low Ca^{+2}.

[13] A similar comparison between CH_3Cl and Ca^{+2} was carried out for the Siple Dome ice core using data from *Mayewski and Maasch* [2006] and unpublished data (P. A. Mayewski, personal communication, 2008; http://www.nsidc.org/data/waiscores/data.html). No correlation was found between CH_3Cl and Ca^{+2} for either the Holocene (0–11 kyr BP) or glacial samples (33–65 kyr BP (auxiliary

material).[1] Four samples from the LGM and glacial/ interglacial transition (ages 16.9, 21.1, 24.2, and 25.2 kyr BP) have the highest Ca^{+2} levels (>0.8 μmol l^{-1}) of the samples from Siple Dome and are indicated by filled circles in Figure 1. Of these, only the 826 ppt sample at 25.2 kyr BP exhibits a CH_3Cl level significantly larger than the rest of the Siple Dome record. Taken as a whole, the Siple Dome CH_3Cl record exhibits no correlation with Ca^{+2} (see auxiliary material). If the four high Ca^{+2} samples are removed, the data exhibits a negative correlation, caused by the difference between Holocene and glacial samples. Thus, there is no evidence for dust-related in situ production of CH_3Cl with the possible exception of the time periods when the Ca^{+2} levels exceed 0.8 μmol l^{-1}. Ca^{+2} concentrations in the Siple Dome core are lower than at Dome Fuji by roughly a factor of two. In addition, Ca^{+2} in Siple Dome ice includes a significant contribution from sea salt as well as terrestrial dust. Based on comparisons of Na^+/Ca^{+2} and Mg^{+2}/Ca^{+2} ratios, only about 15% of the Ca^{+2} at Siple Dome was derived from terrestrial sources during the Holocene ($0-11$ kyr BP). During last glacial period ($33-65$ kyr BP) about 50% of the Ca^{+2} was of terrestrial origin. *Saito et al.* [2007] did not observe a correlation between dust levels and CH_3Cl during the Holocene when Ca^{+2} levels were below 0.6 μmol l^{-1}. This may suggest a threshold in dust input above which in situ production of CH_3Cl becomes detectable above the atmospheric background.

[14] Ice temperatures at Siple Dome are considerably warmer than at Dome Fuji, particularly in glacial ice near the warm bedrock. As a result, the rates of in situ chemical or biological reactions should be many times faster at Siple Dome than at Dome Fuji [*Rohde et al.*, 2008]. The fact that CH_3Cl levels at Siple Dome are lower in glacial ice than Holocene ice raises the question of whether CH_3Cl is stable in polar ice over such long time periods. CH_3Cl can be lost from aqueous solution by hydrolysis and nucleophilic substitution [*Elliott and Rowland*, 1993]. Presumably, such reactions can occur in the quasi-liquid layer at ice crystal surfaces and grain boundaries where impurities are concentrated, but there is no experimental basis from which to estimate the rates of such reactions under the conditions in polar ice. *Williams et al.* [2007] reported an increasing trend in the South Pole ice core data of 3 ppt per hundred years over the past 2 kyr. Such a trend could reflect either increasing atmospheric CH_3Cl levels or in situ loss of CH_3Cl down core. If the South Pole trend was due to chemical loss, it would indicate a lifetime of roughly 16,000 years. An analogous loss at Siple Dome would likely be even faster, due to the warmer ice temperatures. While such losses cannot be ruled out, the lack of consistent down core trends within the Holocene and the apparent stability from $33-65$ kyr BP argue against such losses as a dominant factor controlling Siple Dome CH_3Cl levels.

5. Conclusions

[15] The Siple Dome CH_3Cl data suggest a glacial atmosphere with CH_3Cl levels of about 450 ppt, roughly 15% lower than the modern Antarctic atmospheric level of

530 ppt or 5% lower than preindustrial Late Holocene levels. This difference could reflect lower glacial CH_3Cl emissions from the oceans, terrestrial ecosystems, and biomass burning, and/or higher atmospheric OH levels. Both the surface sources and the atmospheric sinks of CH_3Cl are located predominantly in the tropics and subtropics, so changes in atmospheric CH_3Cl likely reflect changes in low latitude conditions [*Yokouchi et al.*, 2000; *Yoshida et al.*, 2004]. One of the surprising aspects of the data from Siple Dome is that the CH_3Cl variability in this deep ice core is not much larger than that measured in late Holocene samples from South Pole [*Williams et al.*, 2007]. This suggests that the various factors controlling atmospheric CH_3Cl levels either 1) are not directly linked to global mean temperature, or 2) have different temperature sensitivities which offset one another.

[16] During the early-mid Holocene, ($2-11$ kyr BP), there is good agreement between the Siple Dome and Dome Fuji CH_3Cl records. CH_3Cl mixing ratios were at their highest during the early Holocene, with levels exceeding 600 ppt or more than 10% above modern levels. Since about 10 kyr BP, the levels have remained very close to those in the modern atmosphere. However, the finding of lower CH_3Cl during the last glacial period at Siple Dome is opposite from that inferred from the Dome Fuji data. Considering that the atmospheric lifetime of CH_3Cl is comparable to the intrahemispheric mixing time, it is not likely that the paleoatmospheric levels over the Dome Fuji and Siple Dome were significantly different from one another. Differences in in situ ice chemistry and biology between the two sites likely account for this discrepancy.

[17] There is some evidence for "excess" CH_3Cl in Siple Dome ice of late Holocene age (<2 kyr BP). This is puzzling, considering that Siple Dome firn air and shallow ice agree with South Pole data, and Siple Dome deep core samples from the Early and Mid Holocene agree well with Dome Fuji. At Siple Dome, the CH_3Cl increase from glacial to Holocene appears to have started by 24 kyr BP. This would imply a change in tropical conditions well before the onset of the glacial/interglacial transition as recorded in isotope records from Antarctic ice cores. This seems unlikely, and we suspect that four LGM samples with elevated dust inputs ($Ca^{+2} > 0.8$ μmol l^{-1}) contain "excess" CH_3Cl.

[18] At present, it is not clear exactly which sections in the Siple Dome ice core contain a paleoatmospheric CH_3Cl signal and which may be affected by in situ processes. Consequently, it is premature to draw any conclusions regarding the paleoenvironmental conditions needed to explain the record in its entirety. Additional firn and ice core CH_3Cl measurements at these and other polar sites are needed to resolve these uncertainties and to understand the origin of CH_3Cl in polar ice.

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