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## 2,000-year record of atmospheric methyl bromide from a South Pole ice core

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[1] This study reports measurements of methyl bromide (CH<sub>3</sub>Br) in air bubbles from a South Pole ice core, with gas ages covering the past two millennia. The air was extracted by mechanical shredding of the core under vacuum and the evolved gases were analyzed by gas chromatography with high resolution mass spectrometry and isotope dilution. These samples had estimated mean gas ages ranging from 160 BCE to 1860 CE. The mean CH<sub>3</sub>Br mixing ratio in the ice core samples was 5.39 ± 0.06 ppt (1 s.e., n = 113). The CH<sub>3</sub>Br measurements from this core agree with those from a Siple Dome ice core for mean gas ages between 1671 and 1860 CE, where there is overlap between the cores. The data show no linear trend over the 2000 year period prior to industrialization. Together, Antarctic ice core and firn air measurements clearly demonstrate that the increase in atmospheric CH<sub>3</sub>Br during the twentieth century exceeds natural variability during the past 2000 years. There is evidence of centennial-scale variability in CH<sub>3</sub>Br on the order of ±10–20% that may indicate a natural climate sensitivity of the atmospheric levels of this ozone depleting substance. The analysis of CH<sub>3</sub>Br in additional Antarctic ice cores will be needed to confirm that the centennial-scale variability observed in this core represents a southern hemisphere atmospheric history.

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### 1. Introduction

[2] Methyl bromide, CH<sub>3</sub>Br, is present in the modern troposphere at a global mean mixing ratio of about 8 parts per trillion, and has an atmospheric lifetime of about 0.7 years [Montzka *et al.*, 2003b]. CH<sub>3</sub>Br is of considerable environmental importance as an ozone depleting substance, contributing an estimated 50% of the stratospheric bromine burden [Pfeilsticker *et al.*, 2000]. The principle anthropogenic use of CH<sub>3</sub>Br is as a fumigant for agricultural soils, and for durable goods, produce, and structures. In 1998, phase-out of CH<sub>3</sub>Br production began under the Montreal Protocol and its Amendments. Since that time, the atmospheric abundance of CH<sub>3</sub>Br has decreased by several parts per trillion [Yokouchi *et al.*, 2002; Montzka *et al.*, 2003a, 2003b].

[3] The natural biogeochemical cycle of CH<sub>3</sub>Br is complex, with emissions from both oceanic and terrestrial ecosystems, and from biomass burning. Removal from the atmosphere occurs primarily via reaction with OH, uptake by the oceans and by soils. As noted in several reviews, there remains considerable uncertainty in the atmospheric budget of CH<sub>3</sub>Br [Clerbaux *et al.*, 2006; Kurylo *et al.*, 1999; Montzka *et al.*, 2003a]. For example, a best estimate “bottom-up” inventory of the 1996 atmospheric CH<sub>3</sub>Br

budget yielded total sources of 141 Gg, and total sinks of 173 Gg [Montzka *et al.*, 2003a]. This imbalance reflects uncertainty in the magnitude of both natural sources and anthropogenic emissions. Terrestrial plant emissions probably represent the most uncertain term in the global budget, because relatively few plant species or biomes have been studied to date, and because of the challenges associated with differentiating between net and gross fluxes [Rhew *et al.*, 2003; Varner *et al.*, 2003; Redeker *et al.*, 2004; White *et al.*, 2005].

[4] Several studies have used air trapped in polar firn and ice to determine preindustrial atmospheric levels of CH<sub>3</sub>Br and to reconstruct its atmospheric history. Antarctic firn air from South Pole, Siple Dome, and Law Dome yielded early twentieth century levels of roughly 5–6 ppt in reasonable agreement with the known pattern of CH<sub>3</sub>Br production and usage [Butler *et al.*, 1999; Reeves, 2003; Trudinger *et al.*, 2004]. To date, only one study of CH<sub>3</sub>Br from an Antarctic ice core has been published [Saltzman *et al.*, 2004]. CH<sub>3</sub>Br in air extracted from bubbles in a Siple Dome ice core covering the years 1671–1942 CE yielded a mean level of 5–6 ppt, in good agreement with the content of basal firn air at South Pole.

[5] The Antarctic ice and firn air results contrast markedly with results from Greenland. Firn air at both Summit and Tunu exhibit evidence of subsurface CH<sub>3</sub>Br production [Sturges *et al.*, 2001; Swanson *et al.*, 2002]. Elevated levels of CH<sub>3</sub>Br were also observed in GISP2 ice core samples from Summit, demonstrating that CH<sub>3</sub>Br-enriched firn air is incorporated into the ice [Aydin *et al.*, 2007]. Interestingly,

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CH<sub>3</sub>Br in Summit ice does not appear to increase down core, suggesting that production of CH<sub>3</sub>Br occurs prior to close-off.

[6] In this study, we report measurements of CH<sub>3</sub>Br from a South Pole ice core, covering the past two millennia. Gas samples from the uppermost portion of this core overlap in time with the Siple Dome ice core measurements, and greatly extend the time span of preindustrial CH<sub>3</sub>Br measurements. Together with firn air measurement, the two records provide a stronger basis for assessing the natural variability of CH<sub>3</sub>Br and the magnitude of the anthropogenic impact.

## 2. Methods

### 2.1. Drilling Site and Ice Core Characteristics

[7] The South Pole ice core used in this study was drilled in 2002 as part of the International Trans-Antarctic Scientific Expedition project [ITASE, 1990]. The 10 cm diameter ice core was dry-drilled to a depth of 295 m. The core was located at 89.93°S, 144.39°W, at the South Pole Remote Earth Science and Seismic Observatory (SPRESSO). For this study, 112 samples were analyzed, at depth intervals of approximately 1 m. The samples analyzed were longitudinal 1/2 core sections, approximately 15 cm in length, and ranging in mass from 400–600 g.

### 2.2. Ice Core Gas Dating

[8] The age of air in the ice core bubbles was estimated by determining the age of the enclosing ice, then applying an ice age/gas age difference. Ice ages for the SPRESSO core were based on visual layer counting to a depth of 208 m (D. Meese and T. Gow, personal communication), and linear extrapolation below that depth. The resulting age/depth curve suggests a mean ice accumulation rate of 8.3 cm/a water equivalent over the depth range of the samples used in this study (124–290 m). The mean age of air trapped in firn at pore close-off is not known for this exact site because firn air studies were not conducted. For the purposes of this study, we assumed the mean age of CH<sub>3</sub>Br in air to be 128 years at 121 m depth. This estimate is based on the observed mean gas age of CO<sub>2</sub> (92 years) at pore close-off at another South Pole site where firn air studies have previously been carried out [Battle *et al.*, 1996; Butler *et al.*, 1999]. Adjustment was made for the difference in diffusivity between CO<sub>2</sub> and CH<sub>3</sub>Br, giving an ice age-gas age difference of 1014 years for CH<sub>3</sub>Br.

[9] Firn air at pore close-off is composed of a mixture of ages, determined by the diffusive properties of the overlying firn column. Depth profiles of CO<sub>2</sub> and CFC-12 from the earlier South Pole firn air studies were used to tune the diffusivity profile of a 1-dimensional firn air diffusion model [Aydin *et al.*, 2004; Trudinger *et al.*, 2004]. This model provides an estimate of the age distribution of air at close-off. The 1-D model yields an age distribution with a full width at half maximum of 20–40 years. The ice core sampling interval of 1 m used in this study corresponds to an interval of approximately 12 years in mean gas age. Thus there should be considerable overlap in age distributions between adjacent ice core samples.

[10] Uncertainty in the absolute dating of mean gas ages for this core is not well quantified, but is estimated to be on

the order of a few decades. Sources of potential error include the uncertainty in layer-counted ice ages and firn air dating, and the fact that the firn age model is based on data from a different South Pole site.

### 2.3. Ice Core Gas Extraction

[11] A dry extraction technique was used to sample the air bubbles in the ice core samples [Aydin *et al.*, 2007]. This was done by mechanically shredding the ice core sample across a stainless steel grater in a stainless steel vacuum chamber. Prior to use, the chamber was heated overnight to 120°C and repeatedly humidified and evacuated. Ice core samples were mechanically scraped to remove several mm of surface ice before being sealed in the chamber. The ice and chamber were repeatedly evacuated and flushed with clean N<sub>2</sub>, then precooled to -50°C. The chamber was maintained at this temperature during extraction. After final pumping, the sample was shredded for approximately 15 min, and the evolved air was cryogenically condensed into a stainless steel tube immersed in liquid helium (4 K) for subsequent analysis. N<sub>2</sub> “blanks” were collected from the chamber before and after the sample was shredded, as discussed below.

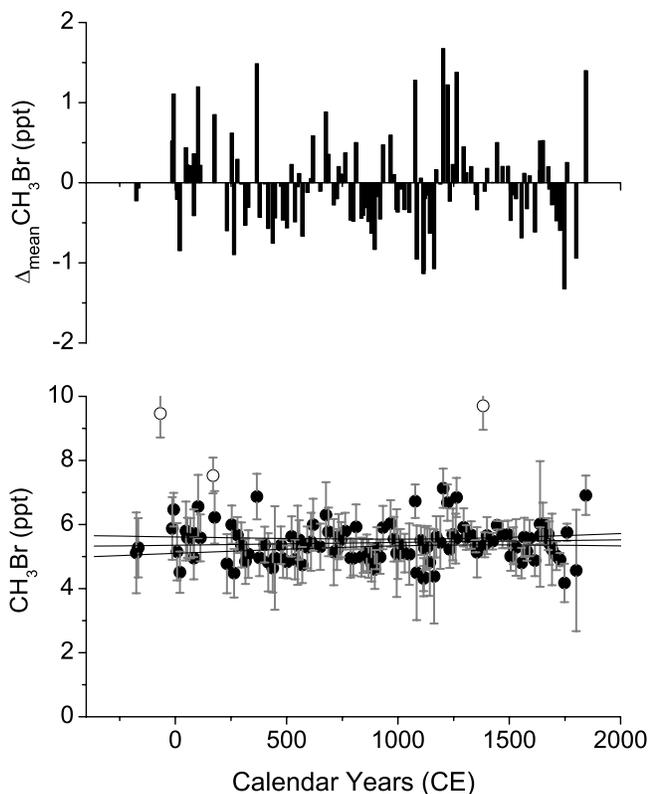
### 2.4. Gas Analysis

[12] Ice core gas samples were analyzed by gas chromatography with high resolution mass spectrometric analysis and quantification was based on isotope-labeled internal standards [Aydin *et al.*, 2007]. The analytical instrumentation and techniques are different from those used for our earlier ice core Siple Dome CH<sub>3</sub>Br measurements [Saltzman *et al.*, 2004], and have significantly reduced the analytical uncertainties. The ice core gas sample was allowed to flow through a stainless steel u-trap containing glass beads, immersed in liquid nitrogen. During this process, the non-condensable gases were expanded into an evacuated 300 cm<sup>3</sup> calibrated volume held at constant temperature. The sample size was determined by measuring the pressure increase in the calibrated volume. An aliquot of internal standard containing CD<sub>3</sub>Br was added to the u-trap containing the ice core sample, using the same procedure. This gas standard typically consisted of 30 cm<sup>3</sup> of 80 ppt CD<sub>3</sub>Br in humidified N<sub>2</sub>. The combined sample and standard was thermally transferred into a He carrier stream into a liquid nitrogen-cooled 0.32 mm ID fused silica trap, and thermally injected onto the gas chromatographic column.

[13] Chromatographic separation was carried out on a DB-1 column, thermally programmed from -50 to 120°C. CH<sub>3</sub>Br and CD<sub>3</sub>Br were monitored at m/z 93.94 and 96.96, respectively, using an Autospec dual focusing mass spectrometer (Waters, Bedford MA) in electron impact ionization mode. The instrument was tuned to a resolution (m/Δm at 5% peak height) of approximately 6000. At this resolution, the mass deficit of bromine causes the CH<sub>3</sub>Br peaks to be completely separated from isobaric hydrocarbons. To provide a “lock mass” for mass calibration of the instrument, deuterated dodecane was bled continuously into the ion source.

### 2.5. Standardization

[14] The calibration of CH<sub>3</sub>Br in this study was ultimately based on primary gas standards containing 10 ppb CH<sub>3</sub>Br.



**Figure 1.**  $\text{CH}_3\text{Br}$  measurements on South Pole ice core samples. Lower panel: Data shown with  $1\sigma$  analytical uncertainties and the linear least squares fit to the data ( $\bullet$ ), excluding outliers ( $\circ$ ), defined as  $\pm 2\sigma$  from the overall mean. The regression line is shown with 95% confidence intervals. Upper panel: Data expressed as a deviation from the mean (black bars).

These are prepared in our laboratory in high pressure aluminum cylinders by volumetric addition of pure  $\text{CH}_3\text{Br}$  to a gravimetrically determined amount of  $\text{N}_2$ . The ppb-level standards are diluted into humidified, electropolished canisters to generate ppt-level working standards. The  $\text{CD}_3\text{Br}$  internal standards are prepared in the same manner. The isotope-labeled standards are regularly calibrated against freshly prepared unlabeled working standards. Several cylinders in our laboratory with unlabeled  $\text{CH}_3\text{Br}$  standards are periodically monitored and the calibration scale used in this laboratory is periodically intercompared with standards used by NOAA GMD.

## 2.6. Extraction Blanks

[15] A critical aspect of the analysis is the estimation of the procedural “blank” associated with contact between the gas sample and 1) the stainless steel surfaces of the extraction chamber, 2) the ice core and snow surfaces, and 3) the tubing and valves used to handle the gas sample during the extraction and analysis. Pre- and post-extraction blanks were obtained by adding a volume of clean  $\text{N}_2$ , roughly equivalent to the air content of the sample, to the chamber containing the ice core sample. The  $\text{N}_2$  is left in the chamber for the same amount of time it takes to shred an ice core sample (15 m). Typically, two pre- and one post-extraction blanks are run for each ice core sample. This

$\text{N}_2$  is collected and analyzed in the same manner as the air extracted from the ice core sample. The average of pre- and post-extraction blanks is assumed to apply to the ice core sample. The magnitude of the blanks appears to be related to how recently the extraction chamber was baked out prior to use, and to the rigor of the chamber bake-out procedures. The ratio of signal to blank for these samples ranged from 7 to 70.

## 2.7. Uncertainty Analysis

[16] The total uncertainty in an ice core  $\text{CH}_3\text{Br}$  analysis is estimated by propagating the individual uncertainties derived from the precision of the calibration runs and the variability of the ice core  $\text{N}_2$  blanks. For the measurements reported in this study, the mean overall relative uncertainty (reported as  $1\sigma$ ) was  $15 \pm 7\%$ , calculated as the square root of the sum of the squares of the calibration and  $\text{N}_2$  blank uncertainties. The magnitude of the uncertainty is highly dependent on the ice core sample size.

[17] No correction was made for possible loss of analyte to the chamber or ice/snow surfaces during extraction. Experiments were carried out in which air and gas standards with known  $\text{CH}_3\text{Br}$  mixing ratios (8–40 ppt) were added to the chamber with no ice, intact ice core sample, and shredded ice core sample, then extracted and analyzed. No loss of  $\text{CH}_3\text{Br}$  was detectable in these experiments, within the uncertainty of the analysis.

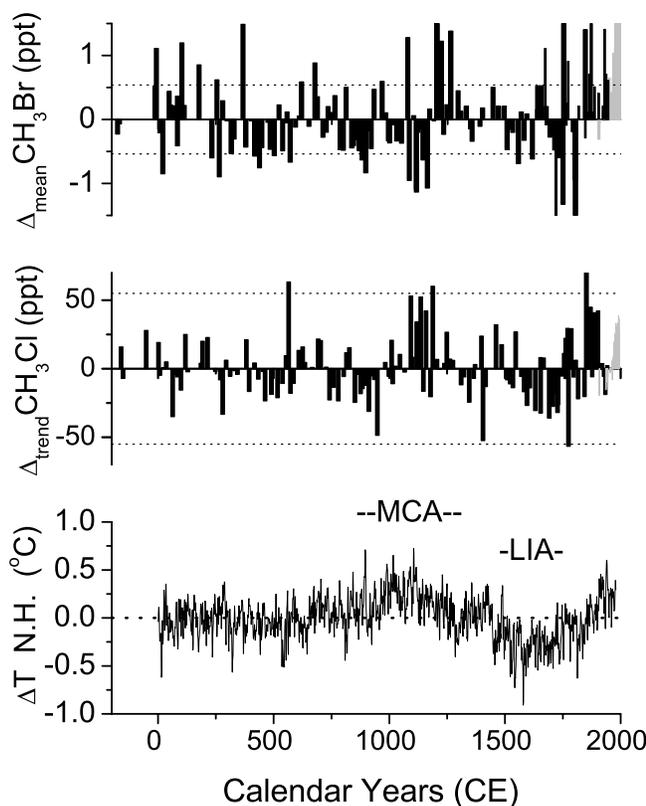
## 2.8. Quality Control Criteria

[18] Samples with CFC-12 levels greater than 5 ppt or  $\text{CH}_3\text{Br}$  blanks greater than 20% of the ice core signal were eliminated from the data set. These criteria eliminated 10 measurements. The cut-off limit of 5 ppt is roughly twice the CFC-12 detection limit for the smallest samples. Most of the samples rejected on the basis of CFC-12 were from the shallowest section of the core (<133 m). This likely reflects the existence of a small amount of open porosity near the close-off depth, which closes during storage, trapping modern air.

## 3. Results and Discussion

[19]  $\text{CH}_3\text{Br}$  measurements from the South Pole ice core samples are shown as a function of mean gas age in Figure 1. Of the 116 samples, three outliers were identified as lying outside  $\pm 2\sigma$  ( $\pm 1.6$  ppt) of the overall mean of  $5.48 \pm 0.076$  ppt (1 s.e.). These outliers most likely reflect artifacts, such as undetected cracks in the ice or contamination during storage and handling. There was no objective reason to discard these points based on our quality control criteria of elevated CFC-12 or analytical blanks. The remaining data gave a mean of  $5.39 \pm 0.06$  ppt (1 s.e.,  $n = 113$ ). For most of the data points, there is overlap between the  $\text{CH}_3\text{Br}$  levels in adjacent samples, within the measurement uncertainty. This is expected, given the broad age distribution at South Pole, and the close spacing of the samples in terms of mean age.

[20] There is no linear trend with age in the  $\text{CH}_3\text{Br}$  data set. A linear regression of the  $\text{CH}_3\text{Br}$  measurements (weighted by analytical uncertainty) against mean gas age yields a slope of  $0.008 \pm 0.009$  ppt per 100 years which is not statistically different from zero. One robust conclusion from this result is that there is no evidence in the data for



**Figure 2.** Comparison of variability in ice core and firm air  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  with a Northern hemisphere multiproxy temperature reconstruction [Moberg *et al.*, 2005]. Black bars—ice core measurements from the SPRESSO South Pole (this study) and Siple Dome cores [Aydin *et al.*, 2004; Saltzman *et al.*, 2004; Williams *et al.*, 2007]. Gray bars—South Pole and Siple Dome firm air measurements from [Butler *et al.*, 1999]. Ice and firm data are expressed as a deviation from the mean of the South Pole data for  $\text{CH}_3\text{Br}$ , and deviation from a linear trend for  $\text{CH}_3\text{Cl}$ . The dashed lines show  $\pm 10\%$  of the average preindustrial  $\text{CH}_3\text{Br}$  and modern  $\text{CH}_3\text{Cl}$  mixing ratios. Note: the  $\text{CH}_3\text{Br}$  firm air and Siple Dome ice core data are truncated by the  $y$  axis scale.

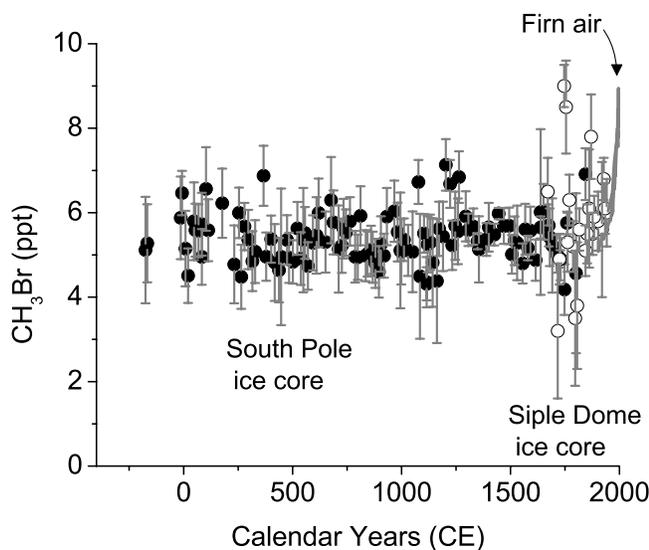
down core loss of  $\text{CH}_3\text{Br}$  due to *in situ* chemical reactions. The lack of linear trend in  $\text{CH}_3\text{Br}$  is notably different from the results for methyl chloride,  $\text{CH}_3\text{Cl}$ , in the same ice core. Over the past 2000 years,  $\text{CH}_3\text{Cl}$  exhibits a trend equivalent to  $3 \pm 0.3$  ppt per 100 years or roughly  $0.75\%/100$  years relative to the mean of 470 ppt [Williams *et al.*, 2007]. The striking difference in behavior of these two gases argues against *in situ* chemical or biological loss as the cause of the trend in  $\text{CH}_3\text{Cl}$ .  $\text{CH}_3\text{Br}$  is much more susceptible than  $\text{CH}_3\text{Cl}$  to *in situ* chemical loss via hydrolysis or nucleophilic substitution reactions. Much less is known about biological uptake of  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$ , but similar biological uptake rates have been observed in salt marshes and seawater [Rhow *et al.*, 2001; Tokarczyk *et al.*, 2003]. The lack of trend in  $\text{CH}_3\text{Br}$  also argues against the  $\text{CH}_3\text{Cl}$  trend being due to changes in atmospheric OH or biomass burning, as they would exert comparable effects on the atmospheric levels of both compounds.

[21] There is some evidence of centennial scale variability in the  $\text{CH}_3\text{Br}$  data. Figure 1 (upper panel) shows the residual  $\text{CH}_3\text{Br}$  after subtraction of the mean mixing ratio. These residuals are on the order of  $\pm 0.5$ –1 ppt. The data are not normally distributed about the mean, which is confirmed statistically at the 95% confidence level [Shapiro and Wilk, 1965]. The analytical uncertainties in the measurement technique are normally distributed and the samples were analyzed in random order, so the observed patterns of variability likely reflect actual variations in the ice chemistry. The periods from 250–550, 750–850, 1100–1200, and 1500–1750 CE are lower than mean for the record as a whole, while the period from 1200–1300 CE appears higher. If these variations prove to be real, then the late Holocene atmospheric variability of  $\text{CH}_3\text{Br}$  was on the order of  $\pm 10\%$ .  $\text{CH}_3\text{Cl}$  in the same core exhibited variability on the order of  $\pm 5\%$ , after removal of the linear trend [Williams *et al.*, 2007]. There are some similarities in the patterns of variability of the two methyl halides, but they are not identical.

[22] Figure 2 shows the variations in  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$ , along with the multiproxy Northern Hemisphere climate record of Moberg *et al.* [2005]. Both trace gas records exhibit minima centered around the years 500, 800, and 1700 CE. These records suggest that the cool period of the Little Ice Age ( $\sim 1400$ –1800 AD) was associated with lower levels of atmospheric methyl halides relative to the Late Holocene means for these gases. The behavior of the two gases is strikingly different around the warm period known as the Medieval Climate Anomaly ( $\sim 800$ –1200 AD).  $\text{CH}_3\text{Cl}$  exhibits a strong and sustained maximum, apparently lagging the onset of warming record by about 75 years. At the  $\text{CH}_3\text{Cl}$  maximum (1180 AD),  $\text{CH}_3\text{Br}$  has a strong minimum. By about 1220 A.D. the two reverse, with  $\text{CH}_3\text{Br}$  reaching its maximum of 7.2 ppt for the preindustrial record before decreasing into the Little Ice Age. Because these two gas records were measured on the same ice core, their dating relative to each other is quite precise, limited largely by the width of the gas age distributions. There are larger uncertainties associated with the relative dating of the ice core data and the multiproxy climate record, which have unrelated chronologies.

[23] The fact that  $\text{CH}_3\text{Br}$  exhibits greater short-term variability than  $\text{CH}_3\text{Cl}$  (on a relative basis), is likely due in part to differences in analytical precision. The mixing ratio of  $\text{CH}_3\text{Cl}$  in this ice core is approximately 80-fold larger than that of  $\text{CH}_3\text{Br}$ . However, the  $\text{CH}_3\text{Br}$  deviations are consistently larger than those of  $\text{CH}_3\text{Cl}$  even where numerous measurements confirm extreme values, such as during the Little Ice Age minimum. The different patterns of variability of the two gases are surprising, given that they share most of the major budget terms in their biogeochemical cycles. As in the case of the long term trend discussed above, these differences seem to rule out simple explanations for the variability such as changes in atmospheric OH levels or biomass burning.

[24] Figure 3 is a compilation of the data from this study and previously published measurements of  $\text{CH}_3\text{Br}$  from South Pole and Siple Dome ice cores and firm air archives, and from Law Dome firm air [Butler *et al.*, 1999; Saltzman *et al.*, 2004; Trudinger *et al.*, 2004]. There is some temporal overlap between the mean gas ages of the uppermost



**Figure 3.** Comparison of South Pole (SPRESSO) ice core  $\text{CH}_3\text{Br}$  measurements and previously published data from Siple Dome, West Antarctica [Saltzman *et al.*, 2004].

SPRESSO samples and those of the earlier published measurements on a Siple Dome ice core [Saltzman *et al.*, 2004]. For mean gas ages between 1671 and 1860 AD, the SPRESSO and Siple Dome ice cores are in reasonable agreement, with mean  $\text{CH}_3\text{Br}$  levels from the two cores of  $5.46 \pm 0.83$  and  $5.61 \pm 1.60$  ppt, respectively. The scatter in the SPRESSO data set is clearly smaller than that in the older Siple Dome data. This probably reflects a combination of improved analytical instrumentation and procedures, and perhaps differences in ice core quality.

#### 4. Conclusions

[25] The  $\text{CH}_3\text{Br}$  measurements on this South Pole ice core are generally consistent with Siple Dome ice core measurements, and with firn air measurements from South Pole and other Antarctic sites, lending support to the idea that the Antarctic ice core archive preserves a record of paleoatmospheric  $\text{CH}_3\text{Br}$ . The South Pole  $\text{CH}_3\text{Br}$  record shows no evidence of a trend over the past 2,000 years and exhibits less variability than the much shorter Siple Dome ice core record. This is due in part to improved analytical precision resulting from the use of more sensitive analytical instrumentation, isotope dilution, and improved sample handling techniques. The South Pole results suggest that centennial-scale variations in atmospheric  $\text{CH}_3\text{Br}$  over the past two millennia, excluding the past century, was on the order of  $\pm 10\text{--}20\%$  (Figure 2). The centennial-scale variability in the South Pole record is not likely to be due entirely to analytical uncertainty, and both  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  appear to exhibit climate-related variability. We do not consider it yet proven that the relatively small variations in either  $\text{CH}_3\text{Br}$  or  $\text{CH}_3\text{Cl}$  represent atmospheric signals. This will require measurements on additional ice cores covering the same time period, and demonstration of a consistent temporal pattern of variability.

[26] These ice core results establish a millennial-scale baseline for comparison with the variations in atmo-

spheric  $\text{CH}_3\text{Br}$  during the past century. It is clear that man's influence on the atmospheric  $\text{CH}_3\text{Br}$  burden during the last century far exceeded natural variability during the past two millennia. The difference in  $\text{CH}_3\text{Br}$  levels in the modern atmosphere and those prior to industrialization are generally consistent with current best estimates for the anthropogenic contribution to the atmospheric  $\text{CH}_3\text{Br}$  budget. However, there remains a significant imbalance in our inventories of  $\text{CH}_3\text{Br}$  sources and sinks. Balancing the modern  $\text{CH}_3\text{Br}$  budget using the best estimates for all the known sources and sinks requires invoking a "missing source", which is thought to be related to emissions from terrestrial ecosystems and which is roughly comparable in the northern and southern hemispheres [Saltzman *et al.*, 2004]. The "missing source", or at least the southern hemispheric portion of it, is needed in order to maintain preindustrial mean levels of 5.5 ppt, assuming that the other natural budget terms remain unchanged [Butler *et al.*, 1999; Reeves, 2003; Saltzman *et al.*, 2004].

[27] There are several surprising aspects to this study. First is the simple fact that there appears to be an ice core record of atmospheric  $\text{CH}_3\text{Br}$  at all, given the extremely low mixing ratio of this gas and its susceptibility to nucleophilic substitution reactions and hydrolysis. Second, atmospheric  $\text{CH}_3\text{Br}$  levels varied over a rather narrow range over the past two thousand years during a period in which human population and land use underwent major changes. Although historical and proxy climate records show detectable centennial scale climate variability over this period, climate was rather stable by comparison with glacial and earlier Holocene variability. The modest variability in the  $\text{CH}_3\text{Br}$  ice core record likely indicate that the major terms in the  $\text{CH}_3\text{Br}$  budget (oceanic production and consumption, terrestrial emissions, biomass burning, atmospheric OH, and soil uptake) remained relatively constant over this period. Or, it may indicate that the various  $\text{CH}_3\text{Br}$  sources and sinks varied in such a way that their changes offset one another, leading to an apparently stable atmospheric  $\text{CH}_3\text{Br}$  level. Finally, differences in behavior between  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  in this ice core are unexpected, and highlight the need for a better understanding of their biogeochemical budgets. Future measurements covering a wider range of climatic conditions may provide some insight into the extent of atmospheric variability, and mechanisms controlling it.

[28] **Acknowledgments.** The authors thank the ITASE project for drilling and making the SPRESSO ice core available for this study, Tony Gow and Debra Meese for layer counting stratigraphy of the core, the National Ice Core Laboratory for assistance with sampling, and Steve Montzka, Jim Butler, and Mark Battle for scientific discussion and firn air data. This research was supported by the National Science Foundation under grants OPP-0338359 and OPP-0440602. Margaret Williams was supported by a postdoctoral fellowship from the Gary Comer Foundation.

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