

## ***Interactive comment on “Post-coring entrapment of modern air in polar ice cores collected near the firn-ice transition: evidence from CFC-12 measurements in Antarctic firn air and shallow ice cores” by M. Aydin et al.***

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### Response to Referee #2 Comments

We thank referee #2 for many valuable comments and suggestions, many of which we have incorporated into a revised version of the manuscript. However, we also wish to note a bit of self-contradiction in this review. This is instructive because we believe it reflects confusion on this issue in the community as a whole and highlights some shortcomings in the text that contributed to the misinterpretation of our results.

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The review starts out by agreeing with our major findings, stating that the manuscript “provides evidence of the shallow sample problem in a more systematic and complete way than the scattering of evidence that exists in the literature” and that “it has been known for a while by ice core researchers that measurement of enclosed gases can be problematic near close off.” The rest of the comments argue that it is well established that gas measurements near close-off are not problematic as implied by Law Dome ice core records. Resolving this conflict requires careful reading of the original literature, which we have attempted to do (see below). The major point of this manuscript is that there are challenges associated with trace gas measurements in shallow ice cores near the close-off region at most locations. We feel strongly that this information should be available to interested researchers from all disciplines, not only to ice core researchers. This does not pose a challenge to the integrity of the global ice core archive. In reality, it is quite the contrary. The present work puts ice cores from a variety of Antarctic sites to a highly stringent test, and outside of a narrow depth range near the close-off, we find no evidence of modern air contamination. One important implication of this manuscript is that, at many ice core sites, it may not be possible to confirm the integrity of the ice core air with respect to a trace gas by testing continuity through the firn-ice transition. This is particularly important for ongoing efforts to expand the suite of trace gases measured in ice cores.

The referee lists several publications as relevant for the current work. In the responses below, we changed the order they were brought up by the referee for organizational reasons.

Etheridge et al. (1996 and 1998) and MacFarling Meure et al. (2006): These publications include measurements of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O in ice cores and firn air from Law Dome, Antarctica. Etheridge et al. (1996 and 1998) indeed compared CO<sub>2</sub> and CH<sub>4</sub> data in overlapping firn air and ice cores and observed agreement. In our responses to RC #1, we stated that the Law Dome data fit the pattern we observe in that the extent of post-coring entrapment appears to correlate inversely with the accumulation rate

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(see responses to RC#1 for details). We do not and have never intended to challenge the integrity of the Law Dome records. In the revised version of the manuscript, we tried to clarify this point. Based on the suggestions of referee #2, we further modified this section and included references to the CH<sub>4</sub> results of Etheridge et al. (1998) and CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O measurements of MacFarling Meure et al. (2006) (see suggested changes to the manuscript below).

MacFarling Meure et al. (2006) rejected some data “when there was evidence of post coring melting (4 samples), leaks (5), insufficient air sample for a reliable measurement of N<sub>2</sub>O (7), significant open pore spaces in shallow cores (3) and equipment failures (3)”. The phrase significant open pore spaces in shallow cores suggests that they may have observed the process we describe in our manuscript. However, this phrase is not sufficient for us to suggest that post-coring entrapment is observed even at sites with very fast accumulation—such as within shallower horizons in the firn where there is a higher percentage of open porosity at the time of collection. As a result we have limited our discussion of this work.

Ferretti et al. (2005), and Francey et al. (1999): These publications include stable isotope data for CO<sub>2</sub> and CH<sub>4</sub>. Since we are not refuting the validity of trace gas records from Law Dome, within the context of our manuscript, these publications add no additional information to the CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O measurements (Etheridge et al., 1996 and 1998; MacFarling Meure et al., 2006).

Martinerie et al. (1992) and Etheridge et al. (1992): The referee raises an important point. Martinerie et al. (1992) showed that the bubbles in the winter layers close-off at shallower depths than the summer layers. Etheridge et al. (1992, 1996) mention selecting samples that contain winter layers only so as to avoid ones that contain open porosity, which again suggests that they probably suspect the open pores may close after collection, trapping modern air. The samples used in our study were typically ~15 cm pieces that were trimmed down before the extraction to eliminate potentially contaminated outer layers. Our fastest accumulation rate site is WAIS-D at 22 cm/y

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(ice equivalent), followed by Siple Dome at 11 cm/y, and South Pole at 8 cm/y. Given the amount of ice required to make an analysis, we were not able to separate winter and summer layers during sample selection and it is likely that all our samples contain at least one summer layer. Unfortunately, we have no way to test whether it was just the summer that caused the modern air entrapment problem. We made a note of this fact in the revised version of the manuscript and included the suggested references in the manuscript (see suggested changes to conclusions below). It should be noted that the sample requirement of our measurements is not unusual for ice core trace gas analysis and the study sites reflect a rather wide range of accumulation rates. In contrast, the accumulation rate at Law Dome is very fast at 1.2 m/y, which makes it possible to selectively pick winter layers.

Fabre et al. (2000) and Trudinger et al. (2002): These papers estimate the diffusivity of gases in firn air and discuss methods to reconstruct atmospheric histories from firn air measurements. Judging by the context that they were brought up in, the referee is likely not referring to restructuring of pores within the ice cores after collection, which would be similar to the type process suggested in our conclusions: “The open pores must later close, possibly due to successional sublimation and recrystallization.” The referee might rather be talking about changes to the ice core samples that occur due to the physical impacts of the drilling process and the saw cuts during sampling. Such changes may complicate laboratory measurements of diffusivity or closed porosity. We would like to point out that these problems are not the main topic of these two studies and are merely mentioned without any observational support. It is also not clear to us that there is any direct relevance to our observations because the problems associated with sampling and drilling should impact the cores randomly. Our observations suggest a process that selectively impacts the samples collected near the firn-ice transition zone.

Responses to comments of the referee about the title, abstract, and the introduction

We changed the title of the manuscript to “Post-coring entrapment of modern air in

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some shallow ice cores collected near the firn-ice transition: Evidence from CFC-12 measurements in Antarctic firn air and ice cores.” The abstract has been revised (see suggested changes to abstract below).

The last sentence of the Introduction is “In this study, we focus on the compositional integrity of the air bubbles trapped in shallow ice cores using CFC-12 measurements as a tool to identify post-coring entrapment of modern air.” We think that this is a fair description of the research presented in this manuscript, and does not constitute a conclusive sentence.

The conclusions section has been modified to reiterate the reliability of deep ice core records. However, we disagree with the referee’s assertion that with careful drilling, storage, and sample preparation, one could get reliable gas records to within a few meters of close-off wherever the site may be. If such factors were determinant in our observations, CFC-12 containing samples would be randomly distributed through the sampled depth range. This is clearly not the case at any of the three sites.

Responses to specific questions of the referee in the order they were raised

How much of the observed contamination and its variation between samples and sites is simply due to sample storage time in different environments, the packaging of cores (sealed bags etc) and the amount of ice removed during cleaning and the duration of pumping on a prepared sample?

In conclusions (2nd paragraph, page 17), we state the time passed between collection and analysis for each site. They were 2 y, 3 y, and 7 y for WAIS-D, SPRESSO, and Siple Dome, respectively. We do not know whether this has any significance for our observations in terms of site to site differences. The duration of pumping is uniform for all samples. The samples are flushed with clean N<sub>2</sub> gas under vacuum to clean out the air that may reside in restricted open pores. The flushes are followed by clean N<sub>2</sub> blanks to determine whether the sample in the chamber is contaminant free and ready for shredding. These procedures are explained in this manuscript. Prior publications

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that explain the procedures in more detail are cited in the manuscript (Aydin et al., 2007, 2008; Saltzman et al., 2008; Williams et al., 2007).

All samples were packaged in bags, although in our opinion packaging should only be relied upon to avoid particulate and liquid contaminants. If there are pores that close off after recovery, trapping some amount of modern air, the composition of the ice core air will be compromised even if the samples were sealed in zero-air at the time of collection. It should be noted that contamination problems associated with sample collection, preparation, and analysis, including potential inconsistencies in the ice thickness shaved off from the outer surface, would impact the cores randomly. What we observe is not a random phenomenon.

Some deep drilling projects in the past used CFC’s as drilling fluid. What is the chance that some of the contamination found, particularly in the Siple Dome samples (which have levels higher than ambient modern air), was from cores, samples, equipment or storage environments used for those projects?

All samples in this study are from shallow, dry-drilled cores as noted in the Samples and site characteristics section of the manuscript (page 5). The only fluid-drilled cores analyzed before or during the analyses of these samples in our laboratory were drilled with n-butyl acetate, which was the drill fluid used for the deep Siple Dome core. The issue of elevated CFC-12 levels in the storage environment (freezers) is also discussed in the manuscript on pages 13 and 14.

It would be very useful if the concentrations of other gases were measured in the ice core samples. This would help confirm the estimates of percentage of the gas that was entrapped after drilling, perhaps with more certainty than for the CFC-12 approach, since this gas can have highly variable backgrounds in the environments where the cores are stored and handled. Is there information on this, or is it planned to be done?

We agree with the referee that a larger variety of synthetic compounds should be measured to develop a better understanding of this phenomenon, and to quantify and cor-

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rect for it, if possible. We addressed this question in our responses to referee #1 as well. We are working on adding more compounds to our analysis, although adding the purely anthropogenic ones to those we regularly analyze has not been our priority. It is very challenging to determine the mixing ratio of various compounds in the different environments ice cores are stored and handled, especially with respect to the particular cores used in this study because a considerable time has passed since the drilling date.

Sturrock et al., JGR, 2002, also produced a record of CFC-12 from firn air spanning the entire atmospheric history of this gas. This should be mentioned and perhaps used in the analysis because their firn air had very fine resolution in time, was also from the southern hemisphere and the uncertainties in the reconstructed record were estimated.

We included a reference to the CFC-12 measurements of Sturrock et al. (2002) in firn air in the Introduction where we discuss the atmospheric history of this gas. We do not think inclusion of their data would add to the manuscript since all available information on the atmospheric history of this gas are in agreement and suggest that the southern hemisphere mixing ratio of CFC-12 was at or below detection limits prior to 1940's.

Responses to minor points

- Diffusive permeability of firn is replaced with diffusivity in firn.
- The text now reads the CFC-12 mixing ratio.
- Table now reads deepest firn air sample.
- The sentence in question reads “. . .to eliminate the micro-cracks that may exist close to the drilling surface” and implies that the procedure would only eliminate micro-cracks that exist close to the drilling surface. The micro-cracks are not visible in a casual inspection. This is quite evident in the text with the next sentence starting with “The visible cracks. . .”.

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- It is stated in the beginning of section 3.1 that a more detailed description of analytical methods is provided in a publication by Aydin et al. (2007).
- Intent can be used as a synonymous noun to intention.
- SS spelled out as stainless steel.
- Deleted “either”.
- Inserted “the” before ECD.
- The citation of Sturrock et al. (2002; see discussion above) was added to the last paragraph of the Introduction, rather than the last paragraph of Section 4 where the CFC-12 levels in SPRESSO samples are discussed.
- The sentence regarding the rejected samples from WAIS-D is rephrased: “Results from 4 ice samples (143.6 m, 162.6 m, 199.3 m, and 232.0 m) out of a total of 57 from the WAIS-D 05A core are not included in the analyses because CFC-12 measurements in pre- or post-shred blanks indicated leaks into the extraction chamber.”
- We included “(moles of air in sample)” where appropriate in section 5.

Suggested changes to the manuscript The changes in the Conclusions are in addition to the changes proposed in our responses to referee #1.

Abstract

In this study, we report measurements of CFC-12 (CCl<sub>2</sub>F<sub>2</sub>) in firn air and in air extracted from shallow ice cores from three Antarctic sites. The firn air data are consistent with the known atmospheric history of CFC-12. In contrast, some of the ice core samples collected near the firn-ice transition exhibit anomalously high CFC-12 levels. Together, the ice core and firn air data provide evidence for the presence of modern air entrapped in the shallow ice core samples that likely contained open pores at the time of collection. We propose that this is due to closure of open pores after drilling, entrapping modern air and resulting in elevated CFC-12 mixing ratios. Our results re-

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veal that open porosity can exist below the maximum depth at which firn air samples can be collected, particularly at sites with lower accumulation rates. CFC-12 measurements demonstrate that post-drilling closure of open pores can lead to a change in the composition of bubble air in shallow ice cores through purely physical processes. The results have implications for investigations involving trace gas composition of bubbles in shallow ice cores collected near the firn-ice transition.

### 3.1 Ice core analysis (UCI)

We included a sentence in the second paragraph of this section to clarify sample size and sample selection, although this was not among the referee suggestions. The sentence reads: "The size of the ice samples were typically ~15 cm long (10-18 cm range), from gas sample specific cuts to minimize inclusion of the outer layer of the core that contacts the drill during recovery."

### Conclusions

Through an examination of firn air and ice core samples, this study presents evidence from three Antarctic sites for the presence of unexpectedly high CFC-12 levels in some ice core samples near the firn-ice transition region. It is highly unlikely that the observations can be attributed to in situ production or analysis artifacts because CFC-12 levels are undetectable in deeper ice, and firn air profiles are consistent with the known history of industrial production of this compound. At Siple Dome, exposure to a highly enriched source of CFC-12 is required to explain the elevated levels. This may also be the case at WAIS-D and South Pole, but it is not required to explain the observations. The most likely explanation for the observations is the entrapment of modern air after the collection of the ice cores, likely due to closure of open pores that exist at the time of recovery.

Most ice coring sites are at high elevation and the cores are subjected to higher barometric pressures than the in situ equilibrium pressure of the air inside the open pores after being transported off the drilling site. We hypothesize that modern air rich in CFC-

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12 can get incorporated into the core by moving through the existing channels, driven by gradients in  $\Delta P$  induced flow or via turbulent diffusion. The open pores must later close, possibly due to successional sublimation and recrystallization. The laboratory analysis of SPRESSO, Siple Dome, and WAIS-D samples were completed roughly within 3 y, 7 y, and 2 y after their drilling, apparently providing sufficient time for this process to occur.

A notable result from this study is that at the two sites with slower accumulation rates (Siple Dome and South Pole), open porosity seems to persist well below the depth at which firn air can no longer be extracted from a borehole. The accuracy of empirical relationships between closed porosity and density seem to be site specific and appear to be less reliable at sites with lower accumulation rates. At all three study sites, the extent of post-coring entrapment appears to increase rapidly once above the FSTD. Air extracted from ice core samples collected from above the FSTD should be assumed to contain some fraction of modern air at most drilling sites. One notable exception could be sites with very high accumulation rates. Etheridge et al. (1996, 1998) and MacFarling Meure et al. (2006) compared CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O measurements in air from the deepest 5 m of the firn with measurements in ice core bubbles at Law Dome, Antarctica and did not observe any discrepancies attributable to the processes we discuss here. The accumulation rate at Law Dome was about 6 times higher than the WAIS-D site at 1.2 m/y (ice equivalent), consistent with our hypothesis that the alteration of ice core trace compositions due to post-coring entrapment of modern air may be inversely related to accumulation rate. It should also be noted that the very fast accumulation at Law Dome enables selective analysis of samples from denser winter layers, in which the bubble close-off occurs at shallower depths than the summer layers (Etheridge et al., 1992, 1996; Martinerie et al., 1992). The sample requirements of our analysis and the accumulation rates at the study sites preclude such selective sampling.

The results of this study have no implications for the ice core gas records derived from

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analysis of deep ice core samples, or the majority of the shallow ice cores samples that do not contain any open porosity at the time of collection. We detected no CFC-12 in deeper sections of the cores at any of the study sites, indicating that anomalous gas measurements close to the firn-ice transition do not categorically invalidate measurements from an entire ice core. However, analyses of shallow ice core samples that may contain open pores at the time of collection should be interpreted with caution. Sowers et al. (1989) saw evidence that during storage, the elemental composition of N<sub>2</sub>, O<sub>2</sub>, and Ar in shallow ice cores may change. Our data show that post-coring entrapment can occur, implying that at sites with low to medium accumulation rates, it may not be possible to establish continuity between trace gas measurements in firn air and shallow ice cores. Further studies are needed to better quantify the magnitude of the entrapment. The anthropogenically produced CFC, HCFC, and HFC compounds may be ideal for such studies because they are nonreactive and have well defined atmospheric histories.

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 1631, 2010.

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