

Interactive comment on “An improved method for delta ¹⁵N measurements in icecores” by F. S. Mani et al.

F. S. Mani et al.

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Response to Todd Sowers Comments

The reviews from Todd Sowers were very positive and encouraging, especially as he was one of the early mentors in this field of d15N measurements and realised the effect of oxygen on d15N measurements. We would like to thank the reviewer for recognising this technique as an important tool in evaluating small signals in Antarctica.

The reviewer had some questions and the response are given below in bold

I do have some questions that, when addressed, should improve the manuscript. First, the d15N profile from Berkner Island firn air is unusual. In every d15N profile from numerous sites that I have seen, d15N shows a shallow enrichment due to the previous

winter cold bump still apparent in the firn. This normally occurs around 15m. Below about 20m, $\delta^{15}\text{N}$ increase in a linear fashion owing to gravitational fractionation. In fact, the linear nature of this purely diffusive region is normally used to extrapolate to the surface to determine the depth of the convective zone below the surface. There does not appear to be any samples between 25 and 50 meters that would normally be used to establish the convective region. I may have missed this but I think few words could be added to address this issue and the significance of the $\delta^{15}\text{N}$ profile at Berkner Island in terms of firn air transport (lock-in, convective?)

I do agree with the reviewer's comments and I have added a few lines about the significance of the $\delta^{15}\text{N}$ profile at Berkner Island. However we did not intend to discuss this in great details and present the full firn profile, as it has been already published and discussed in great detail in Landais et al., 2006b . The primary purpose to present only part of the firn profile here is to cross check with the published firn data to validate the method and also to highlight that the $\delta^{15}\text{N}$ of the early Holocene ice agrees well with what was observed at the bottom of the firn at the same site.

The following lines were added to the caption of Fig 2.

The firn profile obtained is comparable to published firn data (Landais et al., 2006b) and shows similar patterns. The $\delta^{15}\text{N}$ measured was close to zero in the first few meters of the firn column. This is typical of the convective zone as it represents the isotopic composition of the contemporary air. In the diffusive zone the $\delta^{15}\text{N}$ increased with increasing depth until it reached the lock-in-depth zone. The lock-in-depth is characterized by constant $\delta^{15}\text{N}$ values and remains constant through close-off depth, where bubbles close-off, capturing the isotopic signal at the bottom of the firn and preserving it in the ice.

Secondly, I am somewhat concerned about the two air samplings yielding $\delta^{15}\text{N}$ values that differ by 0.03 (Table 3). This is a huge difference given the two days that separate

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the two samplings. This is troubling and really needs an explanation. If real, then there are some very large sources/sinks of atmospheric N₂ with very anomalous $\delta^{15}\text{N}$ values. If real, this could be potentially be a unique tracer of nitrogen dynamics that we have not access to till now. If this is an artefact, it goes without saying that the utility of the method would not gain us additional information about paleo temperature swings recorded in ice core bubbles.

It was during the initial phase of the experiments when these air samples were measured. As much as I would like to say that we have found a unique tracer of nitrogen dynamics in the atmosphere, we also assume that atmospheric $\delta^{15}\text{N}$ is constant for our measurements. Most of the studies refer to Marriotti (1983), who concluded that atmospheric $\delta^{15}\text{N}$ is constant but his precision was about ± 0.03 per mil. The deviation of 0.03 per mil between these two air samples could be mainly due to drift in the isotopic composition of the working standard in the bellows. We discuss this in the last paragraph in section 2.4 on Normalization to Atmospheric N₂ isotopic composition. The samples collected on 21/03/07 were measured when the reference bellows were almost fully compressed and thus the working reference gas was slightly enriched by 0.03 per mil as described in section 2.4. Thus the measured $\delta^{15}\text{N}$ of air with respect to the reference gas is 0.03 per mil lighter. It is certainly not an artefact of the method, it is something we realised and took into account when making measurements and particularly when making measurements in ice cores. We analysed outside air samples almost everyday to take into account of any drift in the isotopic composition of the reference either in the tank or in the reference bellows. Samples measured on any particular day were normalized using the air ratios analysed on that day, hence the data is not compromised. Generally the isotopic composition of the gas in the bellows does not change over a week or so and this has been investigated several times. This was clearly illustrated when we measured 7 air samples on 7 consecutive days with the same reference in the bellow and the standard deviation of the measurements was 0.003 per mil. However we always

observed that when the reference bellows was almost fully compressed then the ratios of the samples becomes lighter. This was easily rectified by evacuating the reference bellow and filling it with fresh reference gas from the tank. Normally it is difficult to assess where this threshold position of the reference bellow was. When the reference or the working standard in the bellow started to drift then we loaded fresh reference into the bellow. The ideal solution to this would be filling the reference bellow with the fresh working standard every time when a sample is measured but it would be an awful waste of the custom-made working standard, especially when we knew that its composition is retained in the bellow for days.

Furthermore, the air values presented in table 3 are 29/28 ratios in air samples with respect to the working standard. Hence it is not the variation in outside air, but could be a drift in the working standard in the reference bellow.

Taking heed of the reviewers comment on this issue I would like to add a line in the caption for table 3 that would clarify any doubts the readers might have.

The air values shown are expressed with respect to the working standard, which exhibit a drift in its isotopic composition towards enriched ^{15}N values as the gas depletes. Hence the apparent 0.03 per mil change in air composition with respect to the working standard

It would be nice to discuss the origin of the $^{15}\text{N}/^{14}\text{N}$ ratio of your working standard. I am surprised to see such a large difference between the results with and without O_2 in table 3 and the fact that the values deviate so much from the zero as they are the effectively the internationally recognized standard for such measurements.

The origin of the working standard was given in the text. The working standard was a mixture prepared from commercially available Ultra-pure (oxygen free) nitrogen and argon in the ratio of 78:1 ($\text{N}_2:\text{Ar}$). The large variation was because our working standard was devoid of any oxygen hence any variations observed was due to the presence of

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O₂ in the sample. We deliberately designed this experiment to see the effect of O₂ on $\delta^{15}\text{N}$ and offer a plausible explanation.

Response to Anonymous Referee 4

We are thankful to the reviewer for his comments about the manuscript, which have been taken into account to improve the paper. We note that the reviewer recognised the manuscript as a potentially useful addition to the existing method of nitrogen isotope measurements in ice cores and a worthwhile contribution in highlighting that carbon monoxide forms in the source which could interfere with $\delta^{15}\text{N}$.

We are grateful to the reviewer for pointing out missing references and several errors in the manuscript, which have now been rectified. The reviewer also stated that the manuscript does not adequately demonstrate the experimental results that underpin its conclusion. We have responded specifically to this point by carrying further experiments using N₂:¹⁸O¹⁸O mixtures. To confirm our finding that O₂ reacts in mass spectrometer to form CO, which have masses 28 and 29, we have subsequently carried out an experiment in which we stripped the oxygen from air samples and then added aliquots of ¹⁸O₂. The reaction of ¹²C or ¹³C with ¹⁸O would not interfere with mass 28 and 29. The new results show that air samples with ¹⁸O₂ did not show any large increase in $\delta^{15}\text{N}$ and also showed a larger peak at $m/z = 30$, which confirms the formation of ¹²C¹⁸O in the source. These results and discussions are now added in the manuscript and is a novel experimental strategy to confirm that CO forms in the source via reaction of carbon and oxygen and interferes with $\delta^{15}\text{N}$ measurements. Sowers et al., 1989 recognised the contribution of CO⁺ ions to $m/z = 29$ and 30, which is formed from the degeneration of CO₂ in the source and consequently applied corrections based on the CO₂ content of the sample.

The referee gave detailed requirements for a future publication, which have all been addressed below:

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Point 1// Done.

Kobashi et al., (2007, 2008) has been cited in the text and table as suggested by the referee. We had over-looked the Kobashi et al., (2007) work during the manuscript preparation and Kobashi et al., 2008 work was obviously not published when the manuscript was submitted in December 2007. We have now included these references in the paper.

In the introduction on page 152 line 10 now reads There is data however, to suggest that oxygen present in the analyte gas may also affect the accuracy and precision of the $\delta^{15}\text{N}$ measurement. For example, Kobashi et al.,(2007, 2008) referred to a technique in which oxygen was removed from the sample. The authors obtained a pooled standard deviation of 0.004 per mil for $\delta^{15}\text{N}$. Kobashi et al., 2007 stated that oxygen was removed because $^{18}\text{O}^{18}\text{O}$ interferes with ^{36}Ar and therefore affects $\delta^{40}\text{Ar}$ but did not explain how it affects the $\delta^{15}\text{N}$ measurement or how it improves $\delta^{15}\text{N}$ precision.

Kobashi's work has now been acknowledged in table 1 as well.

Point 2// Done

The sentence before this erroneous statement is changed so that it is true. Page 161 line 12 now reads// *This direct method for $\delta^{15}\text{N}$ measurements could be useful in assessing the magnitudes of temperature changes for the succession of abrupt climate events during Marine Isotopic Stage 3 in Antarctic ice cores* //

Point 3// Done

Pg. 151 In 19 now reads// *To date, Caillon et al., (2001) is the only study that utilized the $\delta^{15}\text{N}$ and $\delta^{40}\text{Ar}$ method to identify thermal signal during the last glacial period at the Vostok site in Antarctic. They evaluated the thermal signal during the MIS 5b/5c transition. This is probably the largest transition documented in the Vostok deuterium profile during the last glacial period. They also used the*

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isotopic data and methane concentration data to evaluate the phase relationship between Antarctic and Greenland climates (Caillon et al., (2003a)). Another classic example of the application of isotopes of trapped gases in the Antarctic ice core was during termination III about 240, 000 years BP, where Caillon et al., (2003b) used argon isotopes to identify thermal diffusion and indirect gravitational settling.

Point 4 There seems to be some misunderstanding here, all samples were integrated for the same number of times/cycles and not for different integration periods as the reviewer suggests. The machine precision was set to be 0.006 per mill and if the precision was lower than this then the instrument would reject the run, after executing the whole sequence of sample-reference cycle, and re-analyse the same sample in the bellows. There were very few cases where the machine precision was > 0.006 per mill. Where this occurred it was usually due to either instrument instability or the sample gas not equilibrated sufficiently between the bellows and the capillaries. This would lead to a drift in the measured $\delta^{15}\text{N}$ values and precision was > 0.006 per mill over a single run. Thus this test was designed to eliminate non-random sources of error and not improve the random precision. However if the repeated run again gave a precision >0.006 per mil then the $\delta^{15}\text{N}$ value obtained was considered in the analysis and therefore would not introduce any bias in the calculation. The runs were never prematurely stopped and each sample was run for the same number of integration cycles.

Point 5 The reviewer indicates that we have mistakenly made a comparison between samples containing oxygen and the standard gas which is a pure nitrogen/argon mixture. On the contrary the comparison is deliberate and specific. We wanted to understand the source of the effect and the implications with respect to high precision measurements on samples where incomplete removal of oxygen may have occurred. We find that measurable enrichments in the apparent $\delta^{15}\text{N}$ are observed with oxygen concentrations in the analyte gas that

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are 10^4 times lower than in air.

The comparison, over a range of oxygen partial pressures was designed to try and help identify the cause of the shift in measured 29/28 isotopic composition. Our preliminary results indicate that the functional dependency of change in $\delta^{15}\text{N}$ on the oxygen partial pressure is of the form change in $\delta^{15}\text{N}$ is directly proportional to $p(\text{O}_2)^{1/2}$. This is a new result and indicates that reactions between C and O₂ in the source of the mass spectrometer may be important. This is a new finding. We have also confirmed the observation with the new results using 18O₂-N₂ mixture as the analyte gas.

It is true that other researchers have identified this apparent shift in delta 15N with varying oxygen content of the sample and have made empirical corrections for this so-called "chemical slope". The correction factor lies between 0 and 0.004 per mil per per mil change in $\delta(\text{O}_2/\text{N}_2)$ and the total magnitude of the correction in Greenland ice cores is in the order of 0.01 per mil (Sowers et al., 1989). This is combined with a correction to account for CO₂ produced by ion induced decomposition of CO₂ in the source. The magnitude of this correction is on the order of 0.02 per mil. Combined corrections are 0.3 per mil and represent as much as 30% or more of likely recorded isotopic shifts in Antarctic ice.

Hence our desire to investigate an alternative approach in which successive corrections for chemical effects; are not required.

A few lines about the chemical slope; and appropriate references about this effect, as suggested by the reviewer, are now given in the text.

Page 160, line 20 now reads... *It is well known that different amount of oxygen in the sample and in the standard gas causes an artefact in the measured $\delta^{15}\text{N}$ composition, often described as the "chemical slope". To date, laboratories applied empirical chemical slope; corrections to $\delta^{15}\text{N}$ (Sowers et al., (1989), Headley and Severinghaus (2007)). The origin of this effect, however, was not*

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very well understood but our study elucidates the chemistry of this effect in the mass spectrometer source.

Point 6 Pressure below 20 Pa was not used to test the integrity of the o-ring seals because at any given time during the extraction the vapour pressure in the extraction vessel does not fall below 20 Pa, which are typical vapour pressure over ice at -30 degrees Celsius. The seals were tested by leaving for period of 24 hours under static vacuum and observing no rise in pressure indicating, for this method, there are no significant leaks.

Additional results An additional paragraph was added to manuscript explaining the test and results confirming our finding that CO is produced in the source and interferes with del15N measurements.

The paragraph is added on pg 160 beginning on line 15.

To confirm our finding we extracted five ambient air samples as described above, removing oxygen, and then adding approximately 20% 18O18O gas (98% purity, CK Gases Ltd) to two air samples. Any CO production in the source would contribute to $m/z = 30$ and $m/z = 31$, and not 28 and 29 as with oxygen of natural isotopic abundance and will therefore not affect $\delta^{15}N$ measurements. The $\delta^{15}N$ composition measured with respect to the reference gas for air stripped of oxygen gave an average value of 0.845. The two samples enriched with 18O18O gas gave values of 0.878 per mil and 0.923 per mil respectively. We did not observe any large enrichments in $\delta^{15}N$, compared to the 0.8 1 per mil enrichment observed in the case of samples containing 16O16O. The small enrichment in measured $\delta^{15}N$ obtained for samples containing 18O18O (0.03 to 0.08 per mil) may result from the fact that the as supplied 18O18O contained 1% 16O. Further we measured the 30/28 ratio for N2; 18O18O gas mixtures and obtained a value of 5.43×10^{-4} . The expected 30/28 ratio for pure is 1.37×10^{-5} . The large increase in the 30/28 ratio (40x) is due to formation of $^{12}C^{18}O$.

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