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Climate of the Past Discussions

Interactive comment on "An improved method for delta ^{15}N measurements in icecores" *by* F. S. Mani et al.

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This is a technical paper highlighting a method to obtain high precision d15N measurements in small air samples, without applying any corrections for CO+ ions nor for O2/N2 sensitivity of the ion source. As the referee points out, this method is valuable in measuring d15N in polar ice cores; indeed obtaining sufficiently high precision in d15N measurements has been a limiting factor in the application of this method of paleothermometry to Antarctic ice cores, where perturbations in d15N due to rapid temperature fluctuatons are expected to be much smaller than those reported from Greenland ice cores (Blunier et al., 2007). To date, there are no published reports of this particular method being employed in reconstructing paleo-temperatures in ice cores. Hence we feel strongly that a paper highlighting the methodological development should be

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recognized in its own right. Subsequently we will indeed publish results from Berkner Island, Antarctica obtained using this same technique. This forthcoming paper relies on additional isotopic measurements using more conventional measurements (made by additional coauthors), and will include a more extensive interpretation than would be appropriate in the current paper. We note that Climate of the Past supports the publication of such technical papers in its publication policy. Although the method description is based on that of Mariotti (1983) for free atmospheric samples, but it did not achieve a precision that was adequate for Antarctic ice core work (i.e. 0.025 per mil versus 0.006 in this work). Mariotti used silica gel for cryo-trapping the nitrogen that was isolated from air samples and initially we also used Si gel obtaining a similar precision of about 0.02 per mil. Further tests showed that the nitrogen was fractionated during the desorption stage (it became slightly enriched in 15N) and that this also induced a greater degree of variability in the measurements that cannot be fully explained at this stage. Hence we highlighted this fact as a precautionary measure for those planning high precision and accuracy d15N measurements. In addition to using helium cryo-pumping, as compared to Mariotti′s Si gel method, we also prepared and used a standard that was similar in gas composition to the extracted sample (so that if there were any other unknown isobaric effect it would cancel out) and we also controlled the flow through the furnace to efficiently strip all the O2. This latter step proved very critical as our results showed that even a very small amount of oxygen can significantly deteriorate the precision of the measurement. The precision was calculated from 9 replicates of ice core samples (these 9 pieces were not identical pieces but were from the same 55cm ice core from a climate stable period where d15N is assumed to be invariant) and the value of 0.006 per mil is 1 standard deviation (sd) of the 9 sample measured on the instrument. This value of 0.006 per mil takes into account any variability induced during the extraction procedure, any instrumental and reference drift. This is the most realistic way to estimate the precision (1 sd) of the entire method including extraction and analysis. We used 20 grams of the sample for each measurement and we had sufficient sample volume for 3-4 measurements on the mass spectrometer. The internal

CPD
4, S23–S26, 2008

precision of the measurements was usually better than 0.006 per mil. It is important to note that we used 9 samples to define the precision of the procedure and that when measuring actual ice core d15N compositions we use a single 20g sample. Huber et al. (2006) and Landais et al. (2004) used only slightly less ice per measurement, and were able to measure O2/N2 ratio on the same sample, which we cannot do so having removed oxygen from the sample. The reviewer is correct that it would be possible to also measure d40Ar on the same sample by peak jumping, but then the precision of d40Ar would be very low. Hence Landias et al. (2004) state that they measured del40Ar on a separate ice sample using a further 40g of ice. Huber et al., 2006 approximated the error in estimation of rapid temperature changes to be $\pm$ 3 °C. This was estimated by using Monte Carlo simulations and derived primarily from the analytical uncertainty of the d15N measurements of $\pm$ 0.02 per mil ($\pm 2 \times$ 0.02 per mil /$\omega = \pm$ 2.9 °C, where ω is the thermal diffusion sensitivity, equating to a value of 0.014 per mil/°C at $-$50 °C). With our analytical uncertainty and using the similar approach we will be able to constrain the error to better than $\pm$1°C, hence it could prove very useful in detecting small climate signals recorded in Antarctic Ice cores. The referee commented on the influence of oxygen on d15N measurements and that we proposed that it can be corrected but not explained. There may be some misunderstanding here; we did not propose any correction because the enrichment in d15N is evidently so large that it cannot be corrected for whilst maintaining the precision of the measurement. However, we did identify the origin of this effect (see our Figure 3), which is the production of CO in the ion source especially by the tungsten filament, and this is further supported by published literature (Singleton et al., 1966 and Brion Stewart, 1968). Sowers et al., (1989) observed a similar effect of approximately the same order of magnitude but was unable to identify the origin of the effect. The referee suggests that the reference "Kobashi, T., Severinghaus, J. and J.M. Barnola, EPSL, in press " was not given in the manuscript. This particular paper appears to still be in press and not accessible. We would be very willing to inspect, and potentially incorporate a citation to this paper, in to a revised manuscript after we have had sight of this manuscript; and we would be

CPD
4, S23–S26, 2008

grateful if the authors could allow us to see a preprint.

Interactive comment on Clim. Past Discuss., 4, 149, 2008.