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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.

Anonymous Referee #4

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This manuscript presents a potentially useful addition to the well-established tool of nitrogen isotope measurements in ice cores as a paleo-indicator of rapid surface temperature change. The authors point out that carbon monoxide can form in the mass spectrometer source if oxygen (O2) is present in the gas sample being analysed. Although this was pointed out by earlier authors in the 1950s and 1960s, it is worthwhile mentioning it again as it may have been forgotten. As discussed by Sowers et al. (1989) and many other subsequent publications, carbon monoxide interferes with the nitrogen isotope measurement because it has masses at 28, 29, 30 and other masses due to the various carbon and oxygen isotopes present in natural samples.

However, the manuscript in its current form does not adequately discuss prior work, nor does it adequately demonstrate the experimental results that underpin its conclu-

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sions, and therefore does not really add much of anything new in its present form. I believe there are also several outright errors, discussed below. Therefore, it should not be published at this stage. I would recommend that the authors read the relevant literature much more thoroughly, cite appropriate prior work, correct several erroneous statements regarding prior work, and carefully re-do their measurements with much greater care and with much larger numbers of replicate samples so that they present a more convincing case. When these steps are taken, the authors should re-submit the paper, and then I think it will be acceptable for publication.

Detailed requirements for a future publication:

1) The idea of improving precision of d15N measurements on ice core samples by removing O2 is not new. Kobashi et al. (2007) described exactly this technique, using hot copper to remove the oxygen in the air sample, followed by cryotrapping at 4 Kelvin. Kobashi et al obtained a pooled standard deviation (one sigma) of 0.004 per mil (n=232), somewhat better than than the authors report and with a much larger number of analyses. Therefore the authors must re-word their abstract and text to accurately reflect Kobashi et al.'s work. The full reference is:

Kobashi, T., Severinghaus, J.P., Brook, E.J., Barnola, J.-M., Grachev, A., Precise timing and characterization of abrupt climate change 8,200 years ago from air trapped in polar ice, Quaternary Science Reviews 26, 1212-1222 (2007).

Other publications discussing this technique include:

Kobashi, T., Severinghaus, J.P., Barnola, J.-M., 4ś1.5 C abrupt warming 11,270 yr ago identified from trapped air in Greenland ice, Earth and Planetary Science Letters 268, 397-407 (2008).

Kobashi, T., Greenland temperature, climate change, and human society during the last 11,600 years. PhD thesis, University of California, San Diego, 227 pp., (2007).

2) The statement on page 161 of Mani et al's manuscript that "Antarctic d15N signals

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have yet to be studied" is incorrect. Caillon et al. measured d15N in order to identify thermal signals at the MIS 5b/5c transition in the Vostok ice core. They reported a precision of 0.007 per mil, which translates to 0.004 per mil standard error. The full reference is:

Caillon, N., J.P. Severinghaus, J.-M. Barnola, J. Chappellaz, J. Jouzel, and F. Parrenin, Estimation of temperature change and of gas age- ice age difference, 108 kyr B.P., at Vostok, Antarctica. J. Geophys. Res. 106(D23), 31893-31901 (2001).

An additional work using these measurements is:

Caillon, N., J. Jouzel, J.P. Severinghaus, J. Chappellaz, and T. Blunier, A novel method to study the phase relationship between Antarctic and Greenland climate. Geophys. Res. Lett. 30(17), 1899, doi:10.1029/2003GL017838 (2003a).

Mani et al. also may wish to study Caillon's PhD thesis completed at the University of Paris under the direction of J. Jouzel, which is available through library sources.

3) Also, it is a bit misleading to the reader to imply that the technique of identifying thermal fractionation signals in ice cores has not been applied to Antarctica. Although this statement was not explicity made, it is the clear implication. In fact, Caillon et al. (2003b) used argon isotopes to identify thermal diffusion and indirect gravitational signals of Antarctic warming at Termination III. The argon isotopic technique relies on the same firn physics as the nitrogen technique, and so really should not be thought of as a separate technique, even though the laboratory analysis for argon is obviously different. The full reference for that work is:

Caillon, N., Severinghaus, J.P., Jouzel, J., Barnola, J.-M., Kang, J., and Lipenkov, V.Y., Timing of atmospheric CO2 and Antarctic temperature changes across Termination III, Science 299, 1728-1731 (2003).

4) The authors have perhaps mistakenly chosen to automatically analyze with further integration those runs in which the internal standard deviation (i.e., machine precision)

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was greater than 0.006 per mil. This is a practice that is not recommended for sound statistical reasons. In essence, some subsamples of a true underlying distribution will always, by chance, have less than the true (parametric) standard deviation. The mean of such an "accidentally precise" subsample, however, can be biased from the true mean of the distribution. Therefore, ending integration prematurely for these samples will introduce a small bias in the result. Instead, it is recommended practice that all samples have the same amount of integration.

5) The authors have mistakenly made a comparison, it seems, between samples containing oxygen and a standard gas devoid of oxygen. This comparison is not very meaningful, because it is well known that the presence of sample oxygen in differing amount from the standard gas causes an artifact in measurement of d15N. This sensitivity of measured isotopic ratios to the elemental abundance ratios in the sample is known in the literature as the "chemical slope" and is thought to result from ion-molecule reactions in the mass spectrometer source, although the detailed chemistry is not well understood. Sowers et al (1989) described this phenomenon and made empirical corrections for it. In many laboratories an empirical "chemical slope" correction is routinely made to d15N, d18O of O2, d40Ar/36Ar, and other isotopic ratios. The d15N correction was recently described in Headly and Severinghaus (2007), on page 7, paragraph 28. The full reference is:

Headly, M. A., and J. P. Severinghaus, A Method to Measure Kr/N2 Ratios in Air Bubbles Trapped in Ice Cores, and its Application in Reconstructing Past Mean Ocean Temperature, Journal of Geophysical Research –Atmospheres 112, D19105, doi:10.1029/2006JD008317 (2007).

This correction may also be described in several PhD theses, such as those by Landais, Caillon, Grachev, and Kobashi, although I do not have time to check. Mani et al. may wish to check these to insure that they adequately cite prior work.

6) The pressure used to test the integrity of the o-ring seal seems quite high, 20 Pa.

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Modern vacuum technology easily allows a pressure of 0.1 Pa or better, which would increase the sensitivity of the test. Why was such a pressure not used?

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