

## Reply to reviewers' comments

Dear Dr. Loutre

We thank yourself and the reviewers and for constructive comments and are happy to resubmit our revised manuscript. We have addressed the all concerns raised by three anonymous reviewers and provide replies to each reviewer comment below.

### *Reviewer 1:*

Both Reviewers 1 and 3 commented on the dating of the ice core.

- Reviewer 1 highlighted the difficulty in picking annual layers on Figure 6 (now Fig. 4). The  $\delta D$  record has been re-plotted to aid viewing and annual layers are indicated. Furthermore, the back-diffused  $\delta D$  time series is plotted for comparison and  $NO_3^-$  is also included because of its use in identifying annual layers.
- As recommended by both Reviewers 1 and 3, an additional figure has been added to the Appendix (Fig. A4) to demonstrate the effect of back-diffusion on the  $\delta D$  record.
- Tritium content was determined for only 6 samples because this analysis was conducted to verify the approach to annual layer counting chosen as we had little information about expected accumulation rates (Pg. 9, line 22). The annual layer count model was not adjusted to match our measured tritium maximum value to the tritium peak in precipitation (Fig. 2) because aliasing could have occurred as a result of low sample resolution.
- In relation to the Mt Tambora eruption age marker, Reviewer 1 queried the presence of peaks in Tl, Pb and Bi relative to Al at other timings (Fig. 3). These spikes were not identified as significant volcanic deposition for one of two reasons: i) they constitute only one isolated sample, whilst deposition from the Tambora eruption causes elevated values for > 8 samples, or ii) Tl, Pb and Bi do not also show enrichment relative to other terrestrial elements (La and Mn) as well as to Al.
- The discussion of Pb pollution providing a possible age tie point has been removed from Section 3.2, along with plot comparing MES Pb record to Law Dome (previously Fig. 4).
- To constrain the dating error below the age tie point of the Tambora eruption (61.1 m depth) the Dansgaard-Johnsen ice flow model used to predict the depth-age relationship was run with various values of accumulation rate as now reported in Section 3.3 (Pg. 10, line 32) and Appendix C (Pg. 29).
- A mis-communication between co-authors regarding the accumulation rate employed in the flow model has been revealed. An accumulation rate estimate of  $0.252 \text{ m w.e. yr}^{-1}$  had been used previously. The correct value is  $0.23 \text{ m w.e. yr}^{-1}$ , which is the mean of 1950-2006 values. As a consequence the age of the core at 120m is now younger by 145 yr (Pg. 10, line 29).
- In response to concerns voiced by Reviewer 1, Section 1 has been modified in order to set the MES climate record in a context of existing knowledge about the Little Ice Age, both globally and in Antarctica. The direct reference to the bi-polar seesaw, which operates during glacial periods, has been removed and an additional reference pertaining to the hypothesis of thermohaline circulation influence on the Little Ice Age has been added (Pg. 3, line 24).

- Several additional statistical analyses have now been conducted on the ICP-MS dataset. As noted by the reviewers, our trace element data are not normally distributed so statistical methods not susceptible to biasing from outlying points are used (notched boxplots Fig. 8 and MCD estimator-based correlations Fig. 7A).
- Monthly mean concentrations for several additional lithophile elements have been added to Figure 5 to show that even though the seasonal cycle is not statistically significant (as noted by Reviewer 1), as a result of large amplitude fluctuations, the timing of deposition is a consistent feature of all the lithophile element records (Pg. 13, line 23).
- The error on the  $\delta D$ -temperature slope from Steig et al. (1998) has been added (pg. 17, line 29) and the resulting uncertainty on Little Ice Age cooling is given in text and abstract.
- The high mean  $Ca^{2+}$  concentration in IC procedural blanks is linked to the elution of Ni originating from the ice core melter disk in a region very close to  $Ca^{2+}$  on the CS-12A column (Osterberg et al., 2006) (Appendix B, Pg. 26, line 9).
- Verification of the d-excess shift at ~1600 AD is addressed below in the reply to Reviewer 3.

*Reviewer 2:*

- As suggested by Reviewer 2 further statistical analysis has been performed on the trace element dataset (see Figs. 8 and 7, Table 2). PCA could not be conducted on this dataset because the data are not normally distributed.
- Comparison of trace element concentrations measured in this study and those measured in inland Antarctica is included (Pg. 15, line 3). Additionally, we compare detection limits achieved using our quadrupole ICP-MS instrument to those achieved using sector-field ICP-MS instruments (Appendix B, Table A1).
- Data from this study will be uploaded to the iceREADER database <http://icereader.org/icereader/index.jsp>.

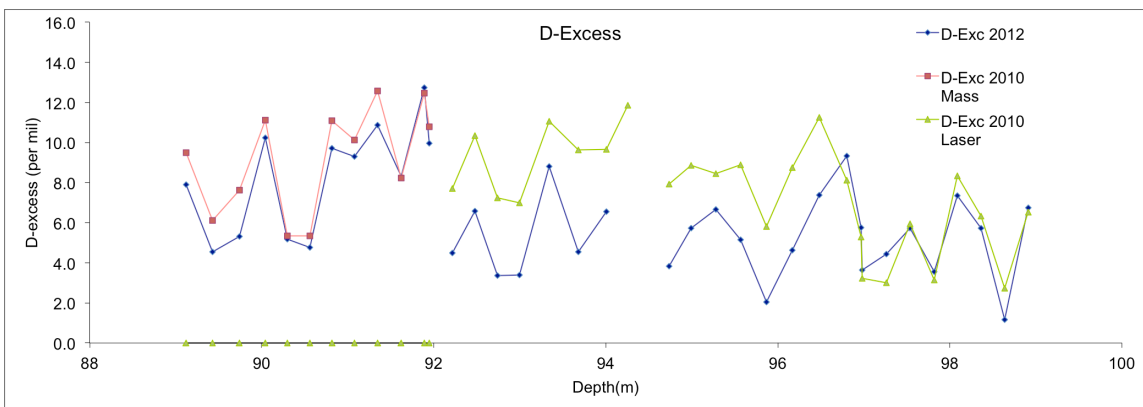
*Reviewer 3:*

Both Reviewers 1 and 3 expressed reservations about the stable isotope record.

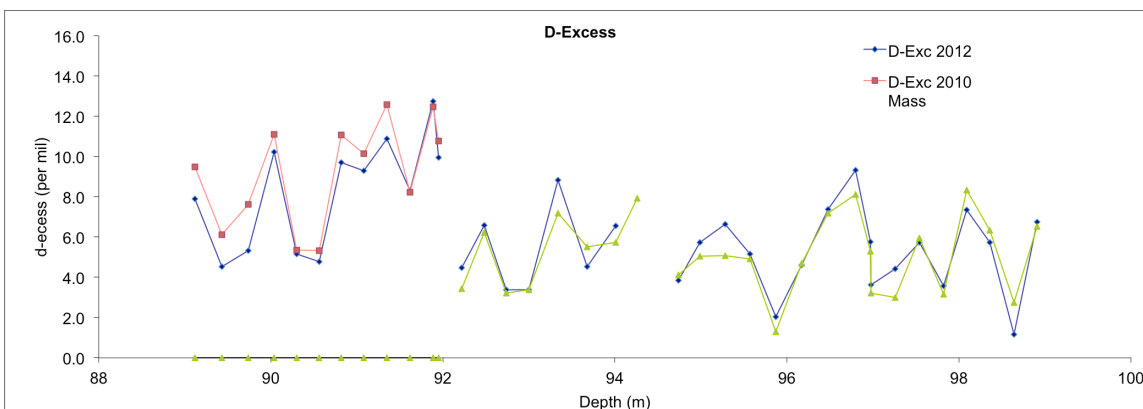
- Reviewer 3 queried the internal standards used for isotopic analysis. The calibration standards were listed incorrectly and this has been rectified – calibration is conducted using two standards that bracket the range of sample values and the third standard is used as an accuracy check (Pg. 6, lines 18-21). The Los Gatos data are corrected for memory effects by measuring each sample six times and

discarding early measurements that shows signs of memory effects (Pg. 6, lines 22-23).

- In accordance with the recommendation of Reviewer 3, additional stable isotopic analyses were conducted on samples from 89 to 99 m depth to confirm the existence of the d-excess shift observed at 96.6 m depth. Samples were analysed by mass spectrometer for both  $\delta D$  and  $\delta^{18}O$  in order to calculate d-excess values. The results are shown below (blue):



- These analyses allowed the identification of a section of ice core (92 to 96.6 m depth) for which the laser data (green) and the new mass spectrometer values (blue) showed particularly poor agreement (mean difference of 3.43‰). This section of the record comprises about 350 samples or one week's worth of analyses. It was recognized that during the week when this particular set of samples were analysed the internal standards produced slightly erroneous values, believed to result from re-bottling. However, an alternative set of standards, obtained directly from LGR, was also run at this time. Re-calibrating the data using results of these standards produces LGR d-excess values that show a much better match with the mass spectrometer values (mean difference of 0.72‰):



- Resolution of this issue meant that the adjustment of LGR data to mass spectrometer equivalent values needed to be recalculated. Appendix A (Pg. 22) demonstrates that an offset (albeit a smaller one) still exists between mass

spectrometer and LGR measurements and this is corrected for. This correction is referred to at several points through the manuscript (Pg. 6, line 28; Pg. 12, line 20-28; Pg. 19, line 5).

- The d-excess shift observed previously at 1590 AD coincided with a change in stable isotope calibration used and was therefore an artifact.
  - The d-excess record now shows a change of characteristics at 1658 AD but this is directly coincident with the instrument change and it is acknowledged that this is likely to be an artifact (Pg. 12, line 28).
  - The likelihood of winter snow ablation is stated in Section 3.1 (pg. 9, line 8). There are no weather station data from this site from which to determine accumulation distribution through the course of a year.
  - Uncertainty in the  $\delta D$  -temperature slope of 20% (Masson-Delmotte et al., 2008) is acknowledged to result from using a local  $\delta D$  -temperature slope from a different site and the effect of this is calculated (Pg. 18, line 5).
  - The possibility of a link between d-excess and cyclonic activity is tentatively proposed but the d-excess record isn't suitable for any conclusion to be reached (Pg.18, line 30).
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- It is now stated that summer Na maxima observed at MES are opposite to the pattern seen in inland Antarctica (pg. 13 line 17).
  - Reviewer 3 commented "the rapid decrease of lithophile elements, referred to in the text, is at different timings: Ce and Mn (less clear) high values cease before Al. The timing is different. Please, provide comments." We include discussion of why the Ce, Mn and Al show different behavior (Pg. 16, line 22 to pg. 17, line 10) and specifically address the end of the LIA period (Pg. 17, line 10).
  - The marine sediment cores referred to were dated by the extrapolation of accumulation rates (derived from Pb-210 measurements) calculated for the first 100 yr of the records. Dating errors are not quantified in the study of Leventer and Dunbar (1988) but all time ranges are referred to as 'approximate' (Pg. 19, line 27).
  - Reviewer 3's concerns about the dating were shared by Reviewer 1 and are addressed above.
  - Other technical comments are addressed. Tables 1 and 2 (now A1 and A2) have been moved to Appendix B, along with some analytical method details. The authors included the letters AD after each calendar year in the original submitted manuscript but these were removed by the journal.