

Interactive comment on “Ice core evidence for decoupling between mid-latitude atmospheric water cycle and Greenland temperature during the last deglaciation” by Amaëlle Landais et al.

Anonymous Referee #2

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I think this a great study which is appropriate for the journal. My background is in triple-oxygen from a perspective outside of the hydrology community so I will stick to this. Although the change in 17O-excess is not clearly located at 16.2 ka (as it is really indicated by dD), the interpretation that the trend in 17O-excess over this time period is due to an increase in the relative humidity of the source region through HS1 seems valid. I have no issues with the interpretation and most everything seems to be consistent with previous work. I do have some question on the 17O-excess data itself as mentioned in my most major comment below.

Line 78: The definitions for $\delta^{18}\text{O}$, 17O-excess and D-excess should be given at first

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occurrence.

My biggest issue with the study is the analytical methods from line 102 to 108 for the CoF3 based water fluorination and ^{17}O calibration. The methods for this are insufficient. The methods as is simply state that the reaction is done and gives a citation for Barkan and Luz 2005. High precision ^{17}O -excess measurements require extreme care in gas handling, the right mass-spec setup and consistent methodology. Some errors in gas handling can generate incorrect values at the 100 ppm level, let alone at the 5 ppm level reported as precision. Impure gas in particular can even yield a false measured relationship between $\delta^{18}\text{O}$ and ^{17}O -excess through scale distortion. The minimum things that would need to be known to trust the data in no particular order and not intended to be exhaustive are: 1: What mass-spec is being used? 2: How is the sample being introduced to the mass spec. 3: What is the composition of the in-house reference relative to the samples (raw data would do). 4: Some basics about the CoF3 technique. (He carrier gas?, source of the CoF3 for purity questions, reaction temperature etc.) 5: How is the resulting O_2 gas purified? This last point is in particular critical. Sample purification is something that for a long time went overlooked because there was no need to push precision, but to get down to sub-10 ppm with any hope of being similarly accurate seems to require GC purification of the gas. This includes CoF3 lines. If there is no GC purification to remove residual impurities, then I think some in the community would be inclined to not trust the ^{17}O -excess results to the detail needed for the submitted study. These impurities may be things that would clearly cause issues with the measurement, such as the mass 33 isobar generating NF_3 but also non-isobar impurities which can generate pressure baseline type effects via scattering. The errors in ^{17}O -excess induced by these impurities roughly scale with the $\delta^{18}\text{O}$ (or $\delta^{17}\text{O}$) so correcting for these can not be done by simply shifting the results but can be accounted for by applying a scale compression correction such as VSMOW-SLAP assuming that the impurity is a constant.

Related to this, how was, or was, the ^{17}O -excess data scaled? Is VSMOW-SLAP



being used? It is stated on line 106 that “home” standards, which I guess should be “in-house” standards, spanning the SMOW-SLAP scale are run on a regular basis, but it is not clear if these have been calibrated to VSMOW-VSLAP2, or any other scaling. It might be this was intended by the Schoenemann et al. 2013 citation, which with the current language seems out of place. The reported values do seem like they plot in the correct region for being calibrated to VSMOW-SLAP.

Line 139-140 This is true enough that seawater 17O -excess remains constant, at least in the recent past. However, this is an artifact of the 0.528 slope in the definition (and the value assigned to SLAP) in addition to the logarithmic form. There should be a citation here that amounts to essentially saying average glacial water falls on a 0.528 slope from modern seawater. Zach Sharp and company had a recent study in *Geochemical Perspectives Letters* which has data this could be calculated from.

Line 197 “Rhodes 2915” is cited.

As a minor point: In a general sense, I feel there is too much interpretation in the Results section. These instances (e.g. line 185) should be moved to the discussion.

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