

We thank the two reviewers for their time and valuable comments that were taken into account as detailed in the following.

### Response to Referee 2:

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  $^{17}\text{O}$ -excess is not clearly located at 16.2 ka (as it is really indicated by  $\delta\text{D}$ ), the interpretation that the trend in  $^{17}\text{O}$ -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  $^{17}\text{O}$ -excess data itself as mentioned in my most major comment below.

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

>> Done

My biggest issue with the study is the analytical methods from line 102 to 108 for the CoF3 based water fluorination and  $^{17}\text{O}$  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  $^{17}\text{O}$ -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  $^{17}\text{O}$ -excess through scale distortion.

>> The method for water  $^{17}\text{O}$ -excess measurements through fluorination was already described in several papers (all details are given in Barkan and Luz, 2005) but we agree with the reviewer that it is important to detail again here the methodology, especially since we improved precision compared to previous studies at LSCE using a new mass spectrometer (MAT 253).

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?

>> MAT 253

2: How is the sample being introduced to the mass spec.

>> To reach the 5 ppm precision, we use the mass spectrometer in dual inlet mode and hence introduce the sample in gas phase (pure oxygen) through the classical sample bellow of the mass spectrometer. The sample is run (measured) against a standard (pure commercial oxygen).

3: What is the composition of the in-house reference relative to the samples (raw data would do) ?

>> The in-house references are several water standards calibrated every 3 years with respect to SMOW and SLAP provided by IAEA. For this study, we used in-house standards

with the following isotopic composition: NEEM ( $\delta^{18}\text{O} = -33.56 \text{ ‰}$ ;  $^{17}\text{O}$ -excess = 32 ppm); OC ( $\delta^{18}\text{O} = -54.05 \text{ ‰}$ ;  $^{17}\text{O}$ -excess = 12 ppm); ROSS ( $\delta^{18}\text{O} = -18.64 \text{ ‰}$ ;  $^{17}\text{O}$ -excess = 37 ppm)

4: Some basics about the CoF<sub>3</sub> technique. (He carrier gas?, source of the CoF<sub>3</sub> for purity questions, reaction temperature etc.)

>> We used the published procedure: He carrier gas is purified through a trap of liquid nitrogen (-196°C); CoF<sub>3</sub> is bought by Sigma-Aldrich following numerous tests by several producers (Sigma-Aldrich CoF<sub>3</sub> gives the best reproducibility and precision according to the species measured by the mass spectrometer); the temperature reaction is 370°C.

5: How is the resulting O<sub>2</sub> gas purified?

>> The purification is done through a molecular sieve trap immersed in liquid nitrogen. Tests of GC purification were also performed during the development of the line at LSCE but did not improve the precision. Indeed, a systematic correction to a V-SMOW – SLAP scale is performed.

Every two-three weeks, three in-house standards bracketing the d18O and d17O values of the samples are run on the fluorination line. These standards are then used to put the d18O and d17O values on the V-SMOW – SLAP scale following procedure described in Schoenemann et al. (2013) and Landais et al. (2013). Then, everyday, only one in-house standard is run to check the day to day stability of the whole system (line + mass spectrometer) but this house standard is not used alone for shifting the d17O and d18O data, a full scale compression on the V-SMOW – SLAP scale is performed.

This will be explained better in the new manuscript and we propose the following paragraphs:

“In order to perform  $^{17}\text{O}$ -excess measurements on water samples at LSCE, we follow the method described in details in (Barkan and Luz, 2005). In short, for each sample, 2 mL of water are injected in a helium flow purified by passing through a trap immersed in liquid nitrogen. Water vapor then reacts with CoF<sub>3</sub> (producer Sigma-Aldrich) in a nickel tube heated at 370°C to produce oxygen and fluorhydric acid which is trapped in liquid nitrogen at the outlet of the nickel tube. Oxygen is first trapped in a molecular sieve tube immersed in liquid nitrogen and then separated from helium and purified through 2 cycles of warming (+30°C) and cooling (-196°C) of the tube with molecular sieves. The oxygen is finally trapped in a manifold immersed in liquid helium. After warming the manifold at least 40 minutes at room temperature, the triple isotopic composition of produced oxygen is injected in the mass spectrometer (MAT 253) and measured by dual inlet against a reference O<sub>2</sub> gas (2 runs of 20 measurements).

Every day, at least one home standard is run with the batch of samples to check the stability of the fluorination line and mass spectrometer and a series of 3 water home standards, whose  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values are calibrated on the SMOW – SLAP scale following Schoenemann et al. (2013), is run at least every month. For this study, the SMOW – SLAP calibrated home standards have  $\delta^{18}\text{O}$  values of respectively -18.64 ‰, -33.56 ‰ and -54.05 ‰, hence bracketing the  $\delta^{18}\text{O}$  values of the measured samples. The comparison of the measured and SMOW-SLAP calibrated  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$  values then enable calibrating the  $\delta^{18}\text{O}$  and  $^{17}\text{O}$ -excess values of the NGRIP samples of this study following the method described in (Schoenemann et al., 2013; Landais et al., 2014). The resulting mean uncertainty is of 5 ppm (1  $\sigma$ ) for the  $^{17}\text{O}$ -excess measurements of this study and we note that the use of the MAT 253 mass spectrometer gave much more stable results than a Delta V+ instrument used for previous studies at LSCE (e.g. Landais et al., 2012).”

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 CoF<sub>3</sub> 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  $^{17}\text{O}$ -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  $\text{NF}_3$  but also non-isobar impurities which can generate pressure baseline type effects via scattering. The errors in  $^{17}\text{O}$ -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  $^{17}\text{O}$ -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.

>> See answer above.

Line 139-140 This is true enough that seawater  $^{17}\text{O}$ -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.

>> We actually cannot claim for sure that  $^{17}\text{O}$ -excess of seawater remains constant over the last deglaciation, no data can demonstrate it with the sufficient accuracy yet. What we want to emphasize is that the water cycle processes will not create an artificial  $^{17}\text{O}$ -excess signal linked to the seawater  $\delta_{18\text{O}}$  change of 1 permil over the last deglaciation as it is the case for  $\delta$ -excess. If  $^{17}\text{O}$ -excess of seawater is modified, this modification will be conserved in the meteoric water  $^{17}\text{O}$ -excess. This was indeed not very clear and we propose to clarify as follows:

“Because of its logarithmic definition,  $^{17}\text{O}$ -excess is not sensitive to changes in  $\delta_{18\text{O}_{\text{sea water}}}$  given that the  $^{17}\text{O}$ -excess of global sea water remains constant with time. As a consequence, a change in sea water isotopic composition will only be transmitted to the  $^{17}\text{O}$ -excess of the precipitation if the  $^{17}\text{O}$ -excess of the evaporated sea-water is modified.”

Line 197 “Rhodes 2915” is cited.

>> Oups... Indeed, i is not correct and the “9” should be changed in “0”, thank you for pointing it.

As a minor point: In a general sense, I feel there is too much interpretation in the Result part:

>> We will try to better equilibrate this part and it goes along with more details in the methodology part answering the comment of reviewer 2 above.