

## ***Interactive comment on “Quantifying molecular oxygen isotope variations during a Heinrich Stadial” by C. Reutenauer et al.***

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Review of Reutenauer et al., “molecular oxygen isotope”..

This is a useful, important work, which brings together a large variety of observations and compares them to a fairly detailed global-scale model to test our understanding of the processes that control the isotopic composition of atmospheric dioxygen.

The task is not an easy one due to the complexity of the topic, and I think the authors have mostly done a laudable job in bringing off a difficult comparison between model and data. The main finding is that the increases in the d18O of precipitation in the tropics during Heinrich Stadials, already well known from low-latitude cave records, are the main cause of the increase in the d18O of atmospheric dioxygen. Other hypothesized

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causes, such as decreased relative humidity with attendant increases in leaf-water evaporative enrichment, and increases in the respiratory fractionation in soils, appear to be minor according to the results.

I have a number of suggestions of ways to improve the manuscript, but overall I believe this paper should be published in CP as it makes a substantial contribution to understanding the relative importance of these various effects, after major revisions.

1) One important improvement can be made in the magnitude of isotopically-relevant O<sub>2</sub> production, which of course also must match respiratory consumption. 11 Pmol O<sub>2</sub>/yr seems much too small to me, given that many plants produce O<sub>2</sub> without engaging the carbon fixation apparatus, for example during times of stress. The plants are able to produce ATP by absorbing photons and creating O<sub>2</sub>. Thus my guess is that by scaling O<sub>2</sub> production to carbon uptake we have badly underestimated the true O<sub>2</sub> production and destruction. Furthermore, even within the carbon fixation framework, I think we have underestimated the amount of photorespiration. Most plant physiology experiments are done under ideal, well-watered, nutrient-replete conditions. In the real world, drought stress is common, and plants often photorespire at these times because of closure of stomata to preclude water loss. In the oligotrophic subtropical surface oceans, nutrient limitation seems to drive picoplankton to produce O<sub>2</sub> without fixing carbon and nitrogen, and so O<sub>2</sub> production by the marine realm has also been underestimated. Based on the rapidity of the changes we see in the d18O<sub>atm</sub> record in ice cores, a total O<sub>2</sub> production figure of 40 Pmol per yr seems more likely, with perhaps half of that from the terrestrial biosphere. So instead of 11 Pmol I would guess that it is more like 20 Pmol. I don't have the relevant literature at my fingertips but the authors can find it by searching on the names of colleagues such as Joe Berry of the Carnegie Institution of Washington, Boaz Luz, and Graham Farquhar.

2) A second improvement can be made in explicitly treating the effect of poor exchange between wet soil air and atmosphere, as described by Angert et al. in several papers, and its connection to water saturation of the soil. Water saturated soils are known

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to be very poor at transmitting oxygen from the sites of respiration back to the atmosphere. For this reason actual soil respiration in wet soils has a much weaker effect on  $d_{18}O_{atm}$  than would be estimated from the enzymatic fractionation itself. This effect can be understood via the following thought experiment: imagine a liter of air taken from the atmosphere in a flask, then the valve is closed. Then respiratory fractionation consumes all the oxygen in the flask. When the valve is reopened, only nitrogen and argon diffuse back out to the atmosphere. This flask has therefore made no contribution to  $d_{18}O_{atm}$ . In other words, a back flux of isotopically enriched oxygen to the atmosphere, the residual left over after partial respiratory consumption, is necessary to make an effect on  $d_{18}O_{atm}$ . If this back flux does not exist, no effect on the atmosphere occurs.

Therefore during strong monsoon intervals, some large fraction of respiratory isotope enrichment goes unrealized as a  $d_{18}O_{atm}$  contributor due to the waterlogged soils in these climates. During a Heinrich event, these zones dry out and the soils become well aerated, greatly increasing the respiratory contribution to  $d_{18}O_{atm}$ . In my opinion the authors have not adequately evaluated this "Angert" mechanism. I was surprised that the authors found a small effect of opposite sign to this hypothesis, in fact a reduction in the isotopic enrichment during Heinrich events from soil respiration. This is probably wrong and needs to be re-evaluated, since Heinrich events are times when waterlogged soils dry out and start having a stronger impact on  $d_{18}O$ .

3) A third area that could be improved is the precipitation isotopic match between data and model. For example, the model produces 1.6‰ changes at DO events in Greenland, but the data show 4‰ changes. This is not really satisfactory, even though the authors say it is acceptable. While Greenland is not important for  $O_2$  production, there are other somewhat more troubling mismatches between data and model in the low latitudes and the authors seem to wave away these issues. A more candid and realistic discussion of these model shortcomings would boost the effectiveness of the paper.

Some other points:

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4) Why aren't the time series of the model output shown, for direct comparison with the ice core  $d_{18}O_{atm}$  data? Just curious. It would strengthen the paper.

5) It would be useful to show a zonally-averaged  $d_{18}O$  of terrestrial precipitation curve versus latitude from the model, both pre- and post-Heinrich, so the viewer can see how the  $d_{18}O$  changes. This  $d_{18}O$  zonal average should be a weighted average, weighted by terrestrial photosynthetic production of  $O_2$ , so that it is most relevant to the question at hand. Of course, the weighting will change as the rainfall changes and the photosynthetic production changes. A second plot should show the latitudinal variation of  $O_2$  production, so that the reader can see that it is concentrated in the tropics. On a third plot, the total terrestrial rainfall amount both pre- and post- should also be shown. This way it is clear to the reader that the total rainfall shifts south during a Heinrich event, and at the same time becomes isotopically heavier. It is also an interesting question, whether the total amount of rainfall on land becomes less during a HS. The total amount of rainfall on both ocean and land is tightly constrained to equal the amount of evaporation, but no such constraint applies to the land fraction. So it is quite possible that more rain fell over the ocean at HS, compared with D/O Stadial conditions.

6) The maps of isotopic composition of rainfall aren't very useful. It would be better if the color scale was adjusted so that the most relevant range of values are more finely graduated. As it stands most of the interesting parts of the tropics are all one color.

7) I was surprised to see no reference to the controversial David Battisti hypothesis. This idea is that rainfall amount does not change at cave sites like Hulu Cave, but rather the  $d_{18}O$  of precipitation changes without change in rainfall amount. What does your model say about this hypothesis?

More detailed comments:

Page 2282, line 24 "effusion processes. . ." This is incorrect. Harmon Craig and Michael Bender erroneously used this term long ago and it has unfortunately stuck. Effusion

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is a different process, having to do with Graham's Law of Effusion, in which a gas is fractionated by passing through orifices smaller than the mean free path length, which is about 1 micron at atmospheric pressure. Because the light isotope has a higher velocity than the heavy isotope, in inverse proportion to the square root of the masses, the light isotope is enriched by a factor of the square root of the ratio of the masses. This process was used, for example, to enrich uranium isotopes during the second world war.

Current understanding of the bubble close-off fractionation in glacial firn is that permeation of the gases through the ice lattice surrounding an overpressurized bubble is responsible for the fractionation (Severinghaus and Battle, 2006; Huber et al., 2006).

Instead of transport through orifices of 1 micron, the permeation mostly occurs by breaking of bonds in the ice lattice, for gases like O<sub>2</sub> and N<sub>2</sub>. So it should be called "a permeation process" or just "permeation through the ice lattice", or 'ice permeation fractionation'.

Page 2283, line 1. Rather than "infer.." this should probably read "have thus been explored as possible constraints on biospheric productivity", since no truly successful inference has been made yet.

Page 2283, line 13. Should be "d18O<sub>atm</sub> variations actually reflect in large part..." because it is the variability that is dominated by meteoric water. The absolute value of d18O<sub>atm</sub> (+24 per mil on the VSMOW scale) is dominated by respiratory fractionation, in contrast.

Page 2283, line 14. "latter" not "later"

Page 2284, line 16. "Millennial-scale climate variability is perhaps best known from the Greenland ice cores, where it is manifested in the stable water isotopes of ice. During the last glacial period, these cores show 25 Dansgaard-Oeschger (DO) events..."

Page 2284, line 4. This is not really an accurate history, to say that "the supposed

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key role of the ocean stems in part from the presence of ice rafted debris...". The original papers on Heinrich events (by Bond, for example) stated very clearly that the Heinrich events came out into an ocean that was already in a cold, stadial state. Subsequent analyses have confirmed this timing relationship. So it was always known, right from the beginning of the discussions on Heinrich events, that Stadials were NOT caused by Heinrich events. Rather, the thinking at that time was that the stadials and DO events were a manifestation of a bistable nonlinear system in which the coupled ocean-atmosphere circulation could jump between two quasi-stable modes (Broecker and Denton, 1989). Today's thinking on this has not changed very much, and such bistability can indeed be found in a wide range of ocean circulation models. [Many IPCC-class coupled ocean-atmosphere general circulation models cannot reproduce this bistability, which is widely seen in simpler models, but this fact is viewed by most workers in the field as a model defect rather than as an indication of how the real ocean circulation operates. The model defect is likely due to the computational limitations inherent in representing the non-geostrophic (frictional) hydraulics of the bottom-hugging overflow currents on the Greenland-Scotland ridge. In the real world, these currents allow dense water to sink much deeper (to 3000 m) than they can in the model, and so the model produces a too-shallow AMOC that is also not subject to hysteresis, bifurcation, and bistability.]

Page 2285, line 9. "Even if IRD can be recorded..." this doesn't make sense – please fix. Perhaps you meant to say something else? "Even though IRD is present in each GS, not all GS contain a Heinrich event."?

Page 2285, line 12 should be Barker, not Baker

Page 2286, line 4. It is implied here that temperature records follow the Greenland signal, in speleothems. This is not correct, in that speleothems mainly record a rainfall signal, not a temperature signal.

Page 2286, line 8. The "ITCZ" is a term that is reserved by the atmospheric science

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community for situations over the ocean. Over land, it is advised to NOT use this term, because the dynamics of the rising air motion is quite different. Therefore many of us in the paleo community are now using the term “tropical rain belts” (e.g. Rhodes et al., Science 2015) for terrestrial air convergence zones with high rainfall. You can also say “through a shift in the ITCZ and its terrestrial equivalent, the tropical rain belt”.

Page 2286, line 15. Redundant use of “onset”

Page 2286, line 17. Spelling – should be “inflection” not inflexion

Page 2286, line 22. “. . .should provide added value. . .”

Page 2287, line 4. “repartition” is not widely understood in English – perhaps use “. . .water, vegetation redistribution, and productivity. . .”

Page 2287, line 12. Again, please do not use ITCZ. Instead, “. . .shifts in the tropical rain belt” is more accurate, because  $d_{18}O_{atm}$  is only affected by terrestrial precipitation, not marine precipitation.

Page 2287, line 14. “build up of atmospheric oxygen. . .” this means to most readers an increase in oxygen concentration. Instead you should say “The isotopic content of atmospheric oxygen is controlled by numerous processes, so we must consider. . .”

Page 2287, line 19 spelling – photosynthetically

Page 2287, line 19 to this list you should add a fourth category, soil aeration, because this strongly affects the effective respiratory fractionation – see papers by Alon Angert. In water-logged tropical soils in monsoon regions, the respiratory contribution to  $d_{18}O_{atm}$  is perhaps only half of what it is in temperate soils. The reason is that the backflux of isotopically enriched oxygen to the atmosphere is hampered by the poor diffusivity of oxygen in liquid water. Therefore the effective respiratory fractionation in monsoon regions may be quite reduced, adding to the depleted isotope signature in  $d_{18}O_{atm}$  from the monsoon meteoric water.

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Page 2287, line 22. “Assuming a steady state,  $d_{18}O_{atm}$  can thus be. . .”

Page 2288, line 7. “. . .because the  $CO_2$  level remains relatively stable (Bender. . .)” or other appropriate reference to the strat-trop  $CO_2$  isoflux

Page 2288, line 9. “. . .influence, in this first approach, for the. . .”

Page 2288, line 11. “. . .variations are largely driven by changes in the. . .” [these authors did not propose that precipitation  $d_{18}O$  was the sole control]

Page 2288, line 12. “. . .low-latitude hydrological cycle. . .”

Page 2288, line 22. “. . .as the leaf water.”

Page 2289, line 3. “. . .global production-weighted average isotopic composition of leaf water. . .”

Page 2289, line 13. “. . .is the temperature-dependent liquid-vapor equilibrium isotope effect (Majoube, 1971)”

Page 2290, line 3. “. . .leading  $^{18}O$  kinetic to values as low as 19‰ when using the Merlivat. . .”

Page 2290, line 5. “because higher values led to too high a global value for  $d_{18}O_{atm}$ .”

Page 2291, line 5. “. . .qualitatively agrees with paleoarchive reconstructions. . .”

Page 2291, line 10. “. . .followed the Lloyd and Farquhar. . .”

Page 2291, line 26 again, repartition is not a word widely recognized in English Page 2293, line 3. “leaf:, not leave

Page 2304, line 12. “. . .more important than. . .”

Page 2307, line 8. “low latitude water cycle. . .”

Page 2307, line 11. “. . .Rhodes et al.’s (2015) recent study suggests that. . . in the WAIS Divide ice core. . .”

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Page 2307, line 14. “Guillevic et al.’s (2014) ice core multi-proxy approach. . .”

Page 2307, line 18. “. . .is a valuable tool..”

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