

Interactive comment on “Planetary fertility during the past 400 ka based on the triple isotope composition of O₂ in trapped gases from the Vostok ice core” by T. Blunier et al.

J. Kaiser (Referee)

j.kaiser@uea.ac.uk

Received and published: 22 May 2012

Blunier et al. use O₂ isotopologue measurements of air extracted from the Vostok ice core to constrain paleo-productivity on land and in the ocean. They use a box model for their calculations, which requires a large number of parameters (Tables 1 and 2). A formal uncertainty analysis is not presented, but according to the paper, the main factors contributing to the uncertainty, next to the analytical uncertainty itself, are relative humidity and the fraction of C₄ plants. Relative humidity is constrained by the 17O excess of water, but measurements of its value are inconsistent across different ice cores. Since the mass balance calculation is very sensitive to relative humidity, the

C421

results have significant uncertainties and additional estimates of paleo-production of the land biosphere from the literature are invoked to reduce these uncertainties.

The authors are to be highly commended for this major effort, which despite the uncertainties, is a valuable contribution to answer the question how productivity changed between glacial and interglacial times.

My main concern with the paper in its present form is the lack of an uncertainty analysis or sensitivity study into how the measurement uncertainty in $\delta(18\text{O})$ and $\delta(17\text{O})$ [or 17O excess] as well as parameters other than relative humidity and C₄ fraction propagate into the calculated productivities. In 2011, a number of new measurements of some of these parameters have been published and it is currently unclear to what extent the proposed changes might affect the results in the present paper. A corresponding analysis should be added to the discussion, drawing in the new measurements, as detailed below.

1) Barkan and Luz revised their measurement of $\delta(17\text{O})$ in VSMOW rel. to Air-O₂ from -11.93 to -11.88 ‰ (Barkan, E., and Luz, B.: The relationships among the three stable isotopes of oxygen in air, seawater and marine photosynthesis, *Rapid Commun. Mass Spectrom.*, 25, 2367-2369, 10.1002/rcm.5125, 2011.) How does this affect the results? Note that these revised measurements contradict with results from Kaiser and Abe (Kaiser, J., and Abe, O.: Reply to Nicholson's comment on "Consistent calculation of aquatic gross production from oxygen triple isotope measurements" by Kaiser (2011), *Biogeosciences Discuss.*, 8, 10517-10541, 10.5194/bgd-8-10517-2011, 2011.)

2) Luz and Barkan (2011) suggest that there is isotopic fractionation during photosynthesis (of about 4 ‰ for 18epsilon) and that the marine (surface) Dole effect is in fact $(23.7 \pm 1.8) \text{‰}$. How does this affect the results?

3) The bulk air stratosphere-troposphere exchange flux may have changed when temperature and CO₂ mole fraction of the atmosphere changed (Rind, D., Lerner, J.,

C422

McLinden, C., and Perlwitz, J.: Stratospheric ozone during the Last Glacial Maximum, *Geophys. Res. Lett.*, 36, 2009.) How much does an increase or decrease of perhaps 20 % affect the results?

I'd also like to suggest that the used terminology regarding 17O is potentially confusing and should be revised. E.g., it would be better to refer to 17Δ simply as 17Δ , or perhaps 17O excess. Use of the word "anomaly" opens up large number of questions, such as what isotope composition is "normal" (which may vary in modern and glacial times), effects of different mass-dependent processes on 17Δ , mixing etc. Really, 17Δ is a convenient definition to facilitate easier discussion of small quantities and I would suggest it to avoid terms such as "anomaly" and "mass-independent fractionation" as far as possible. In particular, the term "fractionation" refers to a process (or isotope effect associated with it), not a delta value (which is measured relative to an arbitrary standard).

Have all co-authors agreed to the publication of this paper? The affiliation of Bruce Barnett has changed - I think he is at Duke University now. von Fischer is spelled with "sch". Is his affiliation correct?

Quantity symbols should be used, e.g. instead of $18\text{O}/16\text{O}$, use $n(18\text{O})/n(16\text{O})$ or $R(18\text{O}/16\text{O})$. Also, $x(\text{CO}_2)$ or $y(\text{CO}_2)$ instead of CO_2 to indicate mixing ratios.

Specific comments: 436/5 + 436/10: This is contradictory/unclear. It is correct that the slope of $\ln(1+\delta^{17}\text{O})$ vs. $\ln(1+\delta^{18}\text{O})$ in stratospheric CO_2 is 1.7. This is transferred to O_2 via isotope exchange. It is less obvious (and unlikely) that there is non-mass dependent fractionation during the exchange. Both sentences should be rephrased. Perhaps the word "mass-independent" could simply be deleted in both cases.

436/12: Would 17O excess be a more appropriate term than anomaly?

436/12: Replace "analysis" by "use" or something similar to avoid confusion with the

C423

actual measurement process.

436/14 and 437/23: A single isotope cannot be fractionated.

437/23: I don't think the exchange is "anomalous". More likely, the 17O excess is transferred from O_3 to $\text{O}(1\text{D})$ and then to CO_2 (e.g. Shaheen, R., Janssen, C., and Röckmann, T.: Investigations of the photochemical isotope equilibrium between O_2 , CO_2 and O_3 , *Atmos. Chem. Phys.*, 7, 495-509, 2007; and references therein). The section needs to be rewritten to ensure accurate description of the atmospheric chemistry involved.

437/25: Mass-dependent fractionation is described in $\ln(1+\delta)$ space. What is the reference for these delta values? Actually, $\delta^{17}\text{O}$ (12.08 ‰ vs. VSMOW) is more than 0.5 $\delta^{18}\text{O}$ ($0.5 \times 23.88 \text{ ‰} = 11.94 \text{ ‰}$ Barkan and Luz, 2005).

438/1: Mass-independent anomaly is a tautology. Perhaps use " 17O excess"?

438/17: Luz and Barkan (2011; Luz, B., and Barkan, E.: The isotopic composition of atmospheric oxygen, *Global Biogeochem. Cycles*, 25, GB3001, 10.1029/2010gb003883, 2011) should be cited here.

439/21: To show clearly that this is a definition a triple equal (identity) sign ($\hat{=}$) should be preferred.

439/23: It should be clarified that the data are reported to oxygen in modern air.

439/23: The sentence "It is an approximation for the exact ratio of $17\text{O}/18\text{O}$ fractionation during processes influencing the isotopic composition of O_2 in air (Luz and Barkan, 2005)." should be deleted because the choice of λ is explained better in the next paragraph.

439/24: As it stands, $\Delta^{17}\text{O}$ should be replaced by 17Δ and the equal ($=$) sign be replaced by an approximately equal (\approx) sign to show that is an approximation. Alternatively, if this sentence is meant to say that another definition was used then it

C424

should be rephrased and the equal sign be replaced by an identity sign ($\hat{=}$). Any definition would be acceptable, since $\delta^{17}\text{O}$ is essentially used as a (mathematically convenient) tracer rather than reflecting a physically observable quantity. In any case, a better choice of symbols would be helpful, e.g. using indices, to differentiate better between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$.

440, 1st paragraph: This section confounds definitions of $\delta^{17}\text{O}$ with expectations for mass-dependent relationships under certain conditions. I am not sure whether the chosen definition "works best" or that the coefficient of 0.516 is "optimal". It would be sufficient to say that a coefficient of 0. reflects the expected relationship between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ for mitochondrial respiration fractionation with $\alpha - 1 = 0.518$ * ($\alpha - 1$) in steady-state with production, perhaps referencing Angert, A., Rachmilevitch, S., Barkan, E., and Luz, B.: Effects of photorespiration, the cytochrome pathway, and the alternative pathway on the triple isotopic composition of O_2 , *Global Biogeochem. Cycles*, 17, 1030, doi:10.1029/2002GB001933, 2003. As the authors observe, there is no single mass-dependent fractionation line and other MDF processes can create non-zero $\delta^{17}\text{O}$ values. $\delta^{17}\text{O}$ is therefore more akin to a mathematically convenient tracer, rather than an actual observable, which is also reflected by the separate treatment of ^{17}O and ^{18}O in the model. Consequently, the linear definition of $\delta^{17}\text{O}$ may actually be preferable because it behaves conservatively with respect to mixing. I've discussed this in Kaiser, J.: Technical note: Consistent calculation of aquatic gross production from oxygen triple isotope measurements, *Biogeosciences*, 8, 1793-1811, 10.5194/bg-8-1793-2011, 2011 and Kaiser, J., and Abe, O.: Reply to Nicholson's comment on "Consistent calculation of aquatic gross production from oxygen triple isotope measurements" by Kaiser (2011), *Biogeosciences Discuss.*, 8, 10517-10541, 10.5194/bgd-8-10517-2011, 2011.

440/22: The meaning of "per meg" should be explained. In Kaiser (2011), I pointed out that the symbol "ppm" for 10^{-6} is more widely accepted by international bodies and more widely known in general.

C425

441/23: The following sentences are potentially confusing because of the terms "anomalous" and "mass independent fractionation": "However, this standard is itself anomalous: the $\delta^{17}\text{O}$ of air O_2 is lowered by 170 per meg vs. SMOW using values found by Barkan 25 and Luz (2005). As mass-independent fractionation decreases, $\delta^{17}\text{O}$ of O_2 with respect to modern air increases, reaching +170 per meg when there is no mass independent fractionation." Since modern Air- O_2 is defined as reference in Eq. (1), it is unclear where the reference to SMOW [which should actually be VSMOW] comes from. Obviously, this is because the isotopic composition of seawater is at the basis of that of photosynthetic O_2 , however this has not been explained at this stage. It would be sufficient to say that as CO_2 decreases during glacial times, there is less preferential transfer of ^{17}O from O_2 to CO_2 in the stratosphere and correspondingly, O_2 is left more ^{17}O (and ^{18}O -rich).

Note that the value of 170 ppm is given as 173 ppm in Barkan and Luz (2011); Barkan, E., and Luz, B.: The relationships among the three stable isotopes of oxygen in air, seawater and marine photosynthesis, *Rapid Commun. Mass Spectrom.*, 25, 2367-2369, 10.1002/rcm.5125, 2011. In any case, the same paper has revised the value to 223 ppm, as mentioned above.

442/4: Do you mean present-day air?

442/9: What are the uncertainties of these values?

442/19: Do you mean present-day air?

443/5: What do you mean by "ultimate"? Ts the terms biogeochemical and hydrological cycle imply that there is no beginning or end.

443/16: Luz and Barkan (2011; Luz, B., and Barkan, E.: The isotopic composition of atmospheric oxygen, *Global Biogeochem. Cycles*, 25, GB3001, 10.1029/2010gb003883, 2011) suggest there is isotopic fractionation during photosynthesis and Equation (2) should be updated to reflect this possibility.

C426

445/3: O₂ should be deleted after "mol" because it is not a unit. The unit "mol" does not have an "e" at the end.

446/18: This is not a fact, but an assumption.

447/21: Is the Bender et al. (2000) reference correct? What ratio did you use?

447/23: Seawater is depleted in ¹⁷O by 5 ppm relative to VSMOW (Luz, B., and Barkan, E.: Variations of ¹⁷O/¹⁶O and ¹⁸O/¹⁶O in meteoric waters, *Geochim. Cosmochim. Acta*, 74, 6276-6286, DOI: 10.1016/j.gca.2010.08.016, 2010.).

449: What are the uncertainties of the global mean humidity and the leaf water isotope composition?

450/25: Again, the term "anomaly" might create improper expectations; "¹⁷O excess" would be more neutral.

452/21: I think a new section heading might be appropriate here or a division of section 4.2 into two parts.

453/5: There is a contradiction here to 444/15, where the fraction of C₄ is stated as 27.5 %.

Table 1: I could not quite reproduce some of the figures in Table 1, based on the given references. The coefficient lambda should be renamed because it is already used in the definition of ¹⁷Delta (Eq. 1). Alternatively, lambda in Eq. 1 should perhaps be renamed lambda_ref (or omitted).

Mehler reaction: Helman et al. (2005) give gamma = 0.526. This results in ¹⁷eR = -5.681 ‰ not -5.685 ‰.

Photorespiration: Based on the assumption that for every two O₂ molecules converted by Rubisco, one is converted by glycolate oxidase (Tolberg, 1997 as cited in Helman et al. 2005), the weighted average should be -21.367 ‰ for ¹⁸eR and -10.932 ‰ for ¹⁷eR.

C427

Alternative oxidase: Based on gammaR = 0.5179 and ¹⁸e = -30 ‰. ¹⁷e should be -15.537 ‰.

For the weighted averages, I obtain ¹⁸eR = -18.020 ‰ for modern (rather than -17.998 ‰) and -18.320 ‰ for LGM (rather than -19.161 ‰). Similarly, for ¹⁷eR.

Fig. 2: This figure is difficult to read due to the 3D projection. It would be better to show a series of 2D projections or if quantitative interpretation was not desired, then these 2D projections should be included as an Appendix.

Fig. A1: I think doing a regression with interpolated data might give different results than using the sparser original data. What regression coefficients and R² values result if the original data are used instead? If there is any bias, what effect does this have on the productivity calculations?

Fig. A2: What are the regression coefficients and R² value?

Fig. A3: What are the regression coefficients and R² value? How do the results compare to the Benson and Krause (1979) measurement of the equilibrium isotope fractionation of O₂, see Benson, B. B., Krause, D., and Peterson, M. A.: The solubility and isotopic fractionation of gases in dilute aqueous solution. I. Oxygen, *J. Solution Chem.*, 8, 655-690, 1979.

Technical corrections: Throughout the manuscript incl. the title, the term "fertility" should be replaced by "productivity" because "fertility" has a connotation of potential production and is mainly used in agriculture. Also, "mass-independent" should be replaced with "non-mass dependent" (it does not follow a mass-dependent law and the fractionations for ¹⁷O/¹⁶O and ¹⁸O/¹⁶O are not equal, i.e. they are not mass-independent).

436/15, 438/18+19+20, 441/3, 452/24, 454/23+24, 458/9: Replace "kyr" with "ka" for consistency and as per international conventions.

442/23, 443/18, 444/8, 444/13, 445/3, 447/23, 449/24: Replace "yr" with "a" for consistency.

C428

tency and as per international conventions.

437/9: "Ocean and land ..."

437/18: Fractionation is a process, not a state; "mass-independent fractionation" should be replaced by $\delta^{17}O$ excess or a similar term.

437/18: Replace "is encoded" with "influences".

439/4: Replace "cc" by cm^3 or cubic centimetres.

439/5: "Louwers-Hapert"

439/13: "separated chromatographically to remove other gases, e.g. N_2

443/12+13: "isotopomer" should be replaced by "isotopologue"

443/18, 447/22: The unit should be " $mol\ a^{-1}$ ".

444/13: Is "burned" the right word?

448/21: The equation should be numbered.

449/14+28: Flux should have units of amount per time (mol/a).

449/18: "decreases"

449/23: Please define the symbol ppb or use SI units for the mole fraction ($nmol/mol$).

451/9: BP should be defined or spelled out.

453/7: "than modern"

455/23: "is" should be replaced by "would be"

456/21: Replace "fertile" by "productive and contain more chlorophyll"

459/10: The left hand side should be $10^3\ \epsilon$ or $\epsilon\text{‰}$.

Interactive comment on Clim. Past Discuss., 8, 435, 2012.

C429