

The comment of Nicholson addresses an important issue in application of oxygen triple isotope composition of dissolved O₂ as a tracer of gross O₂ production (GOP) by marine photosynthesis, the method developed by Luz and Barkan (2000; 2005; 2009). Specifically, Nicholson suggests a correction of the isotopic composition of photosynthetic O₂, δ¹⁷Op, recently derived by Kaiser (2011). Historically, the ¹⁷O excess in photosynthetic O₂ has been defined through several, somewhat different from each other, mathematical formulations (for details, see Kaiser, 2011). These formulations were based on certain approximations, and while the deviation from the exact expression were small (PROKOPENKO et al., 2011), applying approximated formulations in the triple O isotopic mass balance of dissolved O₂ resulted in an error of the calculated values of GOP. Recently, Kaiser (2011) and Prokopenko et al. (2011) derived an exact formulation for quantifying the GOP. The new formulation was based on δ¹⁷O and δ¹⁸O rather than approximated expressions for the ¹⁷O excess. However, the new formulation required a precise knowledge of δ¹⁷Op and δ¹⁸Op (p stands for photosynthetic O₂) composition of the photosynthetic end member, used in the mass balance calculations. The value of δ¹⁷Op was not known precisely at the time when Kaiser (2011) has written his paper, thus it was derived by Kaiser (KAISER, 2011) from the previously published δ¹⁸Op and definition of ¹⁷O excess, ¹⁷Δ (ANGERT et al., 2003; LUZ and BARKAN, 2005):

$${}^{17}\Delta \cdot 10^{-6} = [\ln(\delta^{17}\text{Op}/1000+1) - \lambda \cdot \ln(\delta^{18}\text{Op}/1000+1)] \quad (1)$$

where ¹⁷Δ=249 is the ¹⁷O excess in photosynthetic O₂ relative to atmospheric O₂ previously reported by Luz and Barkan (2000, 2005). The value of λ in equation (1) is the focus of the current comment by Nicholson. λ_r for respiration only, where λ_r = (1 - α¹⁷)/(1 - α¹⁸)=0.5179, was determined experimentally by Angert et al. (2003) and Luz and Barkan (2005). On the other hand, Angert et al. (2003) and Luz and Barkan (2005) argued that since the atmospheric O₂ is in the steady state with O₂ produced by marine photosynthesis, when comparing atmospheric O₂ and photosynthetic O₂, a λ_{st} (λ for steady state) should be used, where λ_{st} = ln(α¹⁷)/ln(α¹⁸)=0.5154 in equation (1). Applying λ_r=0.5179 in equation (1) results in value of δ¹⁷Op ~ 0.050 ‰ lighter than δ¹⁷Op calculated with λ_{st}=0.5154. Nicholson (2011) showed that the ~0.050‰ lighter δ¹⁷Op, obtained with λ_r=0.5179 results in a larger discrepancy between the exact and approximated formulations than δ¹⁷Op obtained with λ_{st} = 0.5154 and argued that λ_{st} should have been used instead.

Using an example, provided by the other Referees of the current comment, if δ¹⁸Op = -20.003 ‰ (for further details, see Eisenstadt et al., 2010, Luz and Barkan, 2011 and Barkan and Luz, 2011 and the Referee comments by Luz and Barkan on the current manuscript), then corresponding the δ¹⁷Op = -10.112 ‰ (instead of δ¹⁷O = -10.164 ‰, as would have been obtained if λ_r = 0.5179 were used). If δ¹⁷Op = - 10.112 ‰ is used instead of δ¹⁷Op = - 10.164‰, it decreases the discrepancy between the exact and approximated formulations from ~ -35% to ~ + 5 to + 15%. Similar results were obtained in the example shown by Nicholson for δ¹⁸Op= - 22.835 ‰ and corresponding δ¹⁷Op values of -11.646‰ and -11.588 ‰.

I agree with the logic of Nicholson, arguing for using the steady state λ_{st} value. However, I found one problem with using $\lambda_{st} \neq \lambda_r$: subsequent respiration of the photosynthetic O_2 leads to changes in $^{17}\Delta$ values, if $\lambda_{st} = 0.5154$ is used in equation (1) applied to steady state, while $\lambda_r = 0.5179$ is used in defining $^{17}\Delta$ excess in dissolved O_2 (calculated using equation (1) and Rayleigh fractionation associated with respiration of ^{17}O and ^{18}O). In fact, I calculate that if the initial isotopic composition of $\delta^{18}O = -20.003\text{‰}$, and $\delta^{17}O = -10.112\text{‰}$ (as suggested by Luz and Barkan in the Referee comments) (or $\delta^{18}O_p = -22.835\text{‰}$ and $\delta^{17}O_p = -11.588\text{‰}$, example given by Nicholson), then respiration of this photosynthetic O_2 to the final atmospheric values of 0‰ would result in $^{17}\Delta = 0.299\text{‰}$ ($\delta^{18}O = 0\text{‰}$, $\delta^{17}O = 0.299\text{‰}$) steadily increasing from $0.249\text{‰} = 249$ per meg (or 249 ppm as suggested by Kaiser (2011)), which is the currently accepted value, as $\delta^{18}O$ increases due to respiration. On the other hand, if $\delta^{17}O = -10.164\text{‰}$ is used (as obtained from equation (1) with $\lambda_r = 0.5179$), the subsequent respiration of this photosynthetic O_2 does not result in changes of $^{17}\Delta$ value, as respiration progresses. In other words, using the λ_{st} for calculating the $\delta^{17}O_p$ seems to result in a non-conservative behavior of $^{17}\Delta$ excess during subsequent respiration, while by definition, $^{17}\Delta$ should not be affected by respiration (Luz and Barkan, 2000, Luz and Barkan, 2005).

I am really curious to see this issue addressed in the final published version of the Nicholson comment. I recommend this manuscript for publication, as it further improves and clarifies the application of the elegant and innovative method of oxygen triple isotopes for quantifying GOP.

References:

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