Author response to reviewer comments (M. Prokopenko, Referee)

I would like to thank Dr. Prokopenko for her valuable comments. I have repeated them here, and listed my responses in black text below each.

The comment of Nicholson addresses an important issue in application of oxygen triple isotope composition of dissolved O_2 as a tracer of gross O_2 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 O_2, $\delta^{17}Op$, recently derived by Kaiser (2011). Historically, the ^{17}O excess in photosynthetic O_2 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 O_2 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 $\delta^{17}O$ and $\delta^{18}O$ rather than approximated expressions for the ^{17}O excess. However, the new formulation required a precise knowledge of $\delta^{17}Op$ and $\delta^{18}Op$ (p stands for photosynthetic O_2) composition of the photosynthetic end member, used in the mass balance calculations. The value of $\delta^{17}Op$ 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 $\delta^{18}Op$ and definition of ^{17}O excess, $^{17}\Delta$ (ANGERT et al., 2003; LUZ and BARKAN, 2005):

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

where $^{17}\Delta=249$ is the ^{17}O excess in photosynthetic O_2 relative to atmospheric O_2 previously reported by Luz and Barkan (2000, 2005). The value of λ in equation (1) is the focus of the current comment by Nicholson. λr for respiration only, where $\lambda r = (1-\alpha_{17})/(1-\alpha_{18})=0.5179$, 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 O_2 is in the steady state with O_2 produced by marine photosynthesis, when comparing atmospheric O_2 and photosynthetic O_2, a λst (λ for steady state) should be used, where $\lambda st = \ln(\alpha_{17})/\ln(\alpha_{18})=0.5154$ in equation (1). Applying $\lambda r=0.5179$ in equation (1) results in value of $\delta^{17}Op \sim 0.050$ ‰ lighter than $\delta^{17}Op$ calculated with $\lambda st=0.5154$. Nicholson (2011) showed that the ~0.050‰ lighter $\delta^{17}Op$, obtained with $\lambda r=0.5179$ results in a larger discrepancy between the exact and approximated formulations than $\delta^{17}Op$ obtained with $\lambda st = 0.5154$ and argued that λst should have been used instead.

I agree.

Using an example, provided by the other Referees of the current comment, if $\delta^{18}Op = -20.003$ ‰ (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 $\delta_{17}O_p$ = -10.112 ‰ (instead of $\delta_{17}O$ = -10.164 ‰, as would have been obtained if λ_r = 0.5179 were used). If $\delta_{17}O_p$ = - 10.112 ‰ is used instead of $\delta_{17}O_p$ = - 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 $\delta_{18}O_p$= - 22.835 ‰ and corresponding $\delta_{17}O_p$ values of -11.646‰ and -11.588 ‰.

Yes, given recent results the values you quote are more accurate ($\delta^{18}O_p$ = -20.003 ‰ and $\delta^{17}O_p$ = -10.112 ‰). The effect is the same. See the new/revised section 4 of the paper which takes into account the new results you refer to (These results were not yet available at the time of original submission).

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 λ_{st} = 0.5154 is used in equation (1) applied to steady state, while λ_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 $_{18}O$).

The equation I use for λ_{st} (paper notation is λ_{BSS}) assumes P = R biological steady-state. This is representative of the conditions used to get the value $^{17}\Delta^{BSS}$ = 249 per meg (Luz and Barkan, 2000).

It is important to stress that I am not arguing that λ_{BSS} is the appropriate slope for representing all processes. It is the slope that is appropriate specifically for relating the 249 per meg measured by Luz and Barkan (2000) to $\delta^{17}O_P$ given the specific experimental conditions, which were approximately a biological steady-state system with (P=R).

The λ_{BSS} slope and the equations used to derive it, do not apply to a Rayleigh fractionation system with only respiration.

In fact, I calculate that if the initial isotopic composition of $\delta_{18}O$ = -20.003 ‰, and $\delta_{17}O$ = -10.112‰ (as suggested by Luz and Barkan in the Referee comments) (or $\delta_{18}O_p$ = -22.835‰ and $\delta_{17}O_p$ = -11.588‰, 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 ‰ ($\delta_{18}O$ = 0‰, $\delta_{17}O$ = 0.299 ‰) steadily increasing from 0.249‰ = 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.

I have added a new section that incorporates the latest new analytical results (Barkan and Luz, 2011; Luz and Barkan, 2011). Based on this new information, I present a 'best estimate' case with values of $\delta^{18}O$ = –20‰ and $\delta^{17}O$ = –10.112‰.

The ^{17}O anomaly for these values is $^{17}\Delta(\lambda = \lambda_{BSS} = 0.5154) = 249$ ppm which is equivalent to $^{17}\Delta(\lambda = \gamma_R = 0.5179) = 299.9$ ppm. If [O2] with this starting composition is respired (Rayleigh fractionated), it will conserve the value $^{17}\Delta(\lambda_{BSS} = 0.5179) = 300$ ppm and the composition will pass through $\delta^{18}O = -0$‰ and $\delta^{17}O = 0.2999$‰.
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The apparent issue highlights the need to use an appropriate definition of $^{17}\Delta$ depending on the case. $^{17}\Delta(\lambda = \lambda_{BSS})$ is the appropriate definition when comparing a system in biological steady state (P=R), while $^{17}\Delta(\lambda = \gamma_R)$ is appropriate when only respiration is acting.

On the other hand, if $\delta_{17}O = -10.164$ ‰ 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 affected by respiration (Luz and Barkan, 2000, Luz and Barkan, 2005).

Whether $^{17}\Delta$ changes depends on the slope (λ) used, not on what the starting $\delta^{17}O$ is. For the case of Rayleigh fractionation (respiration only), $^{17}\Delta(\lambda = \gamma_R = 0.5179)$ is conserved whether the starting composition is $\delta^{17}O = -10.112$‰ or whether it is $\delta^{18}O = -10.164$‰.

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.