

## Author response to short comment from Dr. J. Kaiser

I thank Dr. Kaiser for his thoughtful comments regarding my paper. Below, I respond to his comments, which are repeated in blue type. My responses are in black. Since the initial submission of my paper (and publishing of Kaiser's), previously unavailable data has been published in two papers (Barkan and Luz, 2011; Luz and Barkan, 2011). In my opinion, these new data bolster my interpretation of earlier measurements and the case I present in my paper. I include and put in context these new observations in the revised version of this manuscript.

Nicholson's comment and Luz' review are both suffering from a misinterpretation of my initial paper. Both imply that I had concluded that previous estimates of gross O<sub>2</sub> production are too low. Luz even considers this to be "a major conclusion". I would like to emphasise that, in my initial paper, I have not drawn any conclusions with respect to the magnitude of production estimates based on different calculation parameters and calculation methods. In particular, what I considered as the "base case" should not be misconstrued as a "best case". Based on the available data, I have not been able to construct a "best case". I requested from Boaz Luz the original data of the 2000 measurements of the isotopic composition of photosynthetically oxygen produced at steady-state, but was unsuccessful in obtaining them. I therefore had to rely on a more indirect reconstruction of what the isotopic composition might likely have been. This was only possible in the case of *Acropora*. I also presented an alternative derivation based on the isotopic composition of water. This is discussed in Section 5 of the initial paper, as well as the choice of "base case" values. A recent correction of the earlier measurements of the isotopic composition of water by the Luz group (as referenced in Luz' comment) allows the derivation based on these values to be revisited. It appears to partially resolve some of the discrepancies I highlighted in my initial paper. Thus, it actually responds to one of the actual conclusions in my initial paper, i.e. the need to remeasure several of the input parameters for the oxygen triple isotope method. The main point of my initial paper was to present a consistent and accurate way of calculating gross production from oxygen triple isotope measurements, which I have dubbed the "dual delta method".

I agree that the 'dual delta' method proposed by Kaiser (2011) and Prokopenko et al. (2011) introduces an improved, and more precise way to calculate gross oxygen production. The equation introduced is mathematically correct and avoids a number of the approximations made by previous methods. This is an important advance.

However, this 'dual delta' method requires a number of parameters be known, including  $^{17}\delta_P$ ,  $^{18}\delta_P$ ,  $^{17}\epsilon_R$  and  $^{18}\epsilon_R$ . If these terms are not properly related to one another, even a small discrepancy in one can cause a large bias in GOP

calculated using the 'dual delta' method.

This shows, among other things, that the way the triple isotope excess ( $^{17}\Delta$ ) is defined is irrelevant for the work with oxygen triple isotopes. In contrast to what is implied by Nicholson and Luz, there is no such thing as a "correct" coefficient for the definition of  $^{17}\Delta$ , or indeed the functional relationship between  $^{17}\delta$  and  $^{18}\delta$  itself.

While I agree that there is no "correct" coefficient to define  $^{17}\Delta$ , there is a correct equation that relates the quantity measured by Luz and Barkan (2000) (249 ppm) to  $^{17}\delta_P$  and  $^{18}\delta_P$ . This relationship is shown in my eq. (4) and (5). I argue that the usage of 249 ppm in the original paper in formulating the base case is not correct.

Other major aspects of the paper include a study of the systematic uncertainties in the derived gross production / O<sub>2</sub> influx ratio (termed g) due to the choice of calculation parameters as well as studies of how the choice of parameters and calculation methods may lead to systematically different results in practice. I will submit a formal reply to Nicholson's comment soon. Independently, a Corrigendum will be published to correct some minor errors in the initial paper, including the implicit choice of  $\gamma_R = 0.5205$  by Juranek and Quay (2010) rather than 0.518 as I had assumed. This implicit choice was confirmed by personal communication with Ellie Laurie Juranek.

General comments in response:

To clarify, I do not think that the "base case" need to represent the "best case" scenario. My argument is that the "base case" scenario as presented by Kaiser is not internally inconsistent, and thus cannot be fairly compared to the calculation methods of previous studies. By internally consistent, I mean that the quantities  $^{18}\delta_P$ ,  $^{17}\delta_P$ ,  $\gamma_R$ ,  $^{18}\epsilon_R$  and  $^{17}\Delta^{BSS}$  must be appropriately related to one another. In Kaiser's base case, I do not believe that he has correctly related the observed ( $^{17}\Delta^{BSS} = 249$  ppm) to his calculated  $^{17}\delta_P$ .

Equations (4) and (5) of my paper (repeated below) outline the appropriate relationship between these terms:

$$^{17}\Delta^{BSS} = \ln(1 + ^{17}\delta) - \lambda_{BSS} \ln(1 + ^{18}\delta) \quad \text{where} \quad \lambda_{BSS} = \frac{\ln(^{17}\alpha_R)}{\ln(^{18}\alpha_R)} = \frac{\ln(1 + \gamma_R ^{18}\epsilon_R)}{\ln(1 + ^{18}\epsilon_R)}$$

Notice that to calculate  $^{17}\delta_P$  the slope that should be used ( $\lambda_{BSS}$ ) depends on the assumed values of  $\gamma_R$  and  $\epsilon_R$ . For any choice of  $\gamma_R \approx 0.5$  and  $\epsilon_R \approx -20\%$ ,  $\lambda_{BSS}$  will

be roughly 0.0025 less than  $\gamma_R$ . Because for the base case, Kaiser effectively uses a value of 0.5179 for both  $\lambda$  and  $\gamma_R$ , his base case is internally inconsistent.

The iterative method for calculating GOP (Hendricks et al., 2004) has this same required relationship between  $\gamma_R$  and  $\lambda$ . While the  $\gamma_R$  used in these studies varied, each of the studies that employed the iterative method (Hendricks et al., 2004; Juranek and Quay, 2010; Reuer et al., 2007) used a  $\lambda$  that was about 0.0025 less than  $\gamma_R$  (see Kaiser, Table 3 and the Corrigendum for Juranek and Quay's  $\gamma_R$ ).

There is a ~30% offset in GOP between Kaiser's base case and all previous study methods (see: Kaiser (2011) Fig. 3, Corrigendum version). This offset is due to Kaiser's choice of  $\lambda = \gamma_R$  in his base case, and not due to anything inherent about the various equations being used. The magnitude of this offset in calculated GOP, due to a small change in one parameter, highlights how important it is in the 'dual delta' to consistently define all the necessary terms.

As to the question of what "best case" values are, given currently available data, I have added a new section to the revised paper that uses new results ((Barkan and Luz, 2011; Luz and Barkan, 2011) to calculate a "best estimate" of what parameters should be. In this section I show that the original measurement of ( $^{17}\Delta^{\text{BSS}} = 249$  ppm) is consistent with new measurements of  $^{17}\Delta_{\text{sw}}$  and recent observations of fractionation during photosynthesis (Barkan and Luz, 2011; Eisenstadt et al., 2010). Kaiser's 'base case' however, has a  $^{17}\text{O}$  excess that is about 50 ppm too low. Potential future applications of the 'dual delta' method with the too low value of  $^{17}\delta_p$  would lead to an overestimate of GOP by ~30%.