Biological influences on isotopic ordering in O_2

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Quantifying marine gross primary production (GPP) is of critical importance for addressing the impacts of anthropogenic climate change on ocean ecosystems. Comparisons of results from primary productivity indicator methods as ^{14}C and $^{17}\Delta$ differ by a factor of ~2 [1]. Known issues with these methods include difficulties in scaling from in-vitro bottle experiments and error introduced by vital effects [2]. These uncertainties and others potentially introduce large errors into global estimates of GPP.

The bond geochemistry of molecular oxygen could be utilized as a new tracer of marine GPP. The relative proportions of rare multiply-substituted isotopologues $^{18}O^{18}O$ and $^{17}O^{18}O$ (measured as Δ_{36} and Δ_{35} values that quantify departures from stochastic bond order) are independent of the bulk isotopic composition of the reservoir. Values of Δ_{36} and Δ_{35} in atmospheric O_2 are ~2‰ and ~1‰ respectively, reflecting gas-phase isotopic equilibration through $O(^3P) + O_2$ isotope exchange reactions [3]. Oxygenic photosynthesis creates new O_2 bonds and thus imparts a unique Δ_{36} biosphere signature, but the rapidity of photochemistry in the free atmosphere removes this effect. However, in places where photosynthesis occurs removed from the free atmosphere, such as in the marine photic zone, the Δ_{36} biosphere signature should remain intact.

We will present results from a closed-system terrarium experiment that monitored the evolution of Δ_{36} and the bulk isotopic composition of O_2 altered by photosynthesis and respiration. After 30 days of diurnal light/dark cycles, Δ_{36} approached a value of 0‰. For 5 months, Δ_{36} remained at 0‰ even as the community structure and bulk isotopic composition changed profoundly. This result suggests that the biosphere can remove atmospheric Δ_{36} signatures from O_2 when mixing with the atmosphere is limited. Measurements of photic-zone Δ_{36} could therefore potentially be used as a tracer of marine GPP and biological oxygen cycling.

[1] Quay *et al* (2010) *Global Biogeochem. Cy.* **24,** GB3014 [2] Bender *et al* (1998) *Deep-Sea Res. Pt. I* **46**, 637-654 [3] Yeung *et al* (2012) *J. Geophys. Res.* **117**, D18306