

The isotopic mass dependence of respiratory O₂ consumption revisited and implications for primary productivity estimates

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Molecular oxygen (O₂) acts as a terminal electron acceptor in the electron-transport chain. Its isotopic composition has been an indispensable tool for tracing primary productivity (PP) and carbon cycling in aquatic environments. The oxygen triple-isotope system, in particular (i.e., the ¹⁸O/¹⁶O and ¹⁷O/¹⁶O ratios in O₂), has provided many marine and global PP estimates [1].

One of the foundations of this approach is the use of a constant mass-dependent relationship for isotope fractionation during natural community respiration [2]. PP estimates are extremely sensitive to its precise value [1]. Historically, it has been determined empirically and rationalized by assuming the fractionation-controlling step is adiabatic [3]. Recent laboratory experiments [4] and analytical improvements [5], however, question the accuracy of the earlier data and imply that the conceptual understanding may also need revision.

We argue that electron transfer to O₂, a diabatic process that “commits” heme-copper oxidases to catalysis [6], influences the isotopic mass dependence of respiratory O₂ consumption. Theory for outer-sphere electron transfer [7] predicts that it exhibits a unique mass dependence that deviates significantly from the canonical triple-oxygen relationship and also leads to enrichments in the proportions of ¹⁸O¹⁸O and ¹⁷O¹⁸O in O₂. We present laboratory and field evidence for the importance of electron-transfer isotope effects in natural systems. If these inferences are correct, PP estimates will be affected.

[1] Juranek & Quay *Annu. Rev. Mar. Sci.* **5** (2013) 503-524.
[2] Luz & Barkan *GCA* **69** (2005) 1099-1110. [3] Young et al. *GCA* **66** (2002) 1095-1104. [4] Stolper et al. *GCA* **240** (2018) 152-172. [5] Yeung et al. *RCMS* **32** (2018) 1811-1821. [6] Verkholsky et al. *Nature* **380** (1996) 268-270. [7] Buhks et al. *J. Phys. Chem.* **85** (1981) 3763-3766.