

A period of inverse Dole effect after Marinoan deglaciation

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The Earth's Dole effect (DE), known as the ¹⁸O enrichment in atmospheric O₂ with respect to ocean water, is determined by fluxes of photosynthesis, respiration, troposphere-stratosphere gas exchange, and hydrological process (evaporation, precipitation, and evapotranspiration). It consists of three components: marine DE, terrestrial DE, and stratospheric isotopic effect (1). The magnitude of the current DE is 23.88‰ (2), which has had a limited variation (i.e. ±0.2‰) dating back to 130 kyrs before present, a time of global glacial-interglacial cycles (1). DE beyond the ice-core record is not known due to the lack of reliable proxies. It is expected, however, that magnitude of DE must have changed in Earth history, especially during periods of rapid and extreme hydrosphere, biosphere, and atmosphere transitions.

Recent triple oxygen isotope studies (3, 4) on barite or carbonate associated sulfate indicate that atmospheric O₂ had distinct non-mass-dependent ¹⁷O anomalies ($\Delta^{17}\text{O}$), implying that the $\delta^{18}\text{O}(\text{O}_2)$ was also abnormal. Building upon our earlier 4-box, quick-response, and dynamic model on the evolution of $\Delta^{17}\text{O}(\text{O}_2)$ (6), we added into model variables of $\delta^{18}\text{O}(\text{CO}_2)$ and kinetic isotope effects associated with O₂ consumption to examine the evolution of the $\delta^{18}\text{O}(\text{O}_2)$. Our modeling result shows that there exists a positive correlation between $\Delta^{17}\text{O}(\text{O}_2)$ and $\delta^{18}\text{O}(\text{O}_2)$ and that the greatly enhanced stratospheric isotope effect by ultra-high $p\text{CO}_2$ together with relatively low $p\text{O}_2$ result in an inverse Dole effect at the immediate aftermath of the Marinoan glacial meltdown. The inverse effect is largely due to the extremely low $\delta^{18}\text{O}$ value (down to -19‰) of the stratospheric O₂. We found that this conclusion is in general consistent with the observed sulfate $\delta^{18}\text{O}$ data, although the translation between $\delta^{18}\text{O}(\text{O}_2)$ and $\delta^{18}\text{O}(\text{SO}_4)$ is not straightforward due to a dynamic evolution of atmospheric O₂, complexity of oxidation pathways, and degrees of mixing with existing sulfate pools. Our result provides another independent test of the proposed "snowball" Earth condition at 635 million years ago.

[1] Bender *et al* (1994) *GBC*, **8**, 363-376 [2] Luz and Barkan (2011) *GBC*, **25**, GB3001. [3] Bao *et al* (2008) *Nature*, **453**, 504-506 [4] Bao *et al* (2009) *Science*, **323**, 119-122 [5] Hoffmann *et al* (2004) *GBC*, **18**, GB1008. [6] Cao and Bao (2013) *PNAS*, **110**, 14546-14550