

EXPLORING POTENTIAL ANTHROPOGENIC CHANGES IN THE DOLE-MORITA EFFECT

U. Seibt¹, JA Berry¹, M Battle², JP Severinghaus³

¹ *Department of Global Ecology, Carnegie Institution of Washington, Stanford CA, USA*

² *Department of Physics and Astronomy, Bowdoin College, Brunswick, Maine, USA*

³ *Scripps Institution of Oceanography, La Jolla CA, USA*

ABSTRACT

The Dole-Morita effect (DME) describes the $\delta^{18}\text{O}$ enrichment of atmospheric O_2 with respect to ocean water [Dole 1935, Morita 1935]. The magnitude of the DME ($23.8 \pm 0.1\text{‰}$ at present, Horibe *et al.* [1973]) varies over geologic time scales, and might have changed as a result of human activity. Such variations are preserved in the air enclosed in polar firn and ice. Here, we explore the potential effects of human activity on the DME. We estimate that global changes in the land biosphere may have led to a decrease in the DME in the order of 0.07‰ over the last 150 years. We then predict profiles of $\delta^{18}\text{O}\text{-O}_2$ in firn air resulting from a range of atmospheric scenarios using a model [Severinghaus and Battle, submitted] and compare the simulated profiles to measurements of air samples extracted from polar firn.

PRE-INDUSTRIAL ISOTOPIC MASS BALANCE

The DME is the result of isotope effects on photosynthesis and respiration. Respiration discriminates against $^{18}\text{O}^{16}\text{O}$ by $\approx 20\text{‰}$, resulting in $\delta^{18}\text{O}$ enrichment of the remaining atmospheric O_2 . Photosynthesis produces O_2 with a $\delta^{18}\text{O}$ signature corresponding to that of the water used to make O_2 . Because on the global scale, foliage water is enriched by 5 to 7‰ compared to ocean water, the $\delta^{18}\text{O}$ of O_2 released during land and ocean photosynthesis are different. The DME has been summarized as an isotopic mass balance calculated from a global model [Hoffmann *et al.* 2004]:

$$\text{DME} = (P_o D_o + P_t D_t) / (P_o + P_t) - \varepsilon_{\text{st}}$$

where P_o , P_t , D_o and D_t are oceanic and terrestrial gross O_2 fluxes and partial DME's (i.e. resulting from only ocean or land O_2 exchange), and ε_{st} is a small stratospheric contribution. The two partial DME's differ by 10‰ in this estimate, making the DME sensitive to variations in the ratio of gross O_2 exchange with land and ocean biospheres. We use this model as a starting point, and adopt their gross O_2 fluxes (P_o : 7.6 , P_t : 16.7 Pmol/year) and D_t value (26.9‰), with a small change in the ocean DME. To accommodate changed calibration of the DME (Friedman and O'Neil [1977], applied to the value reported by Kroopnick and Craig [1972]), we increase their D_o value (17‰) to 18.3‰ to give a total DME of 23.8‰ for our global pre-industrial mass balance.

POTENTIAL ANTHROPOGENIC CHANGES

Taking the above as an initial condition, we consider the consequences of the following plausible anthropogenic changes in the terrestrial oxygen cycle from pre- to post-industrial times: (1) 3% of terrestrial respiratory O_2 release replaced by biomass burning, decreasing the overall fractionation during O_2 uptake, (2) 5% decrease in global terrestrial GPP due to land cover change [DeFries *et al.* 1999], (3) 100 ppm increase in atmospheric CO_2 mole fraction, leading to a decrease in global photorespiration, (4) 10% decrease in stomatal conductance resulting from CO_2 increases and partially offsetting photorespiratory decreases, (5) 5% decrease in the O_2 flux weighted ^{18}O enrichment of foliage water due to higher contributions of ^{18}O depleted northern mid-latitude biomes. The ocean fluxes and partial DME were left unchanged. Given sufficient time, these changes would create a new steady state DME that would be 0.7‰ lower than the pre-industrial value, with photorespiration accounting for $\approx 2/3$ of the total change. This puts potential anthropogenic changes in the same order of magnitude as the DME variations of 0.5 to 0.8‰ over the last 400 kyears determined from ice core and marine sediment analyses (for example, Bender *et al.* 1994). In addition, the turnover time of atmospheric O_2 might have increased by \approx

200 years due to the decrease in gross O₂ fluxes from pre- to post-industrial times. We assume that the transient change over 150 years corresponds to $\approx 1/10$ of the steady state difference reached after the turnover time of approximately 1500 years. This suggests a small (but potentially detectable) decrease in the order of $0.07 \pm 0.02\%$ in atmospheric $\delta^{18}\text{O}-\text{O}_2$ over the last 150 years as a result of human activity.

POTENTIAL FIRN AIR CHANGES

Firn air at a given depth exchanges with the air above and below by molecular diffusion. Changes in the composition of the atmosphere propagate downwards through the firn such that the mean age of the air in the firn increases with depth and could carry a record of changes in the DME. We used data on $\delta^{15}\text{N}$, $\delta(\text{O}_2/\text{N}_2)$ and $\delta^{18}\text{O}-\text{O}_2$ of air samples collected from the firn at South Pole (Battle et al. 1996). We also re-analysed a subset of these samples. For the re-analyses, the laboratory precision of $\delta^{18}\text{O}-\text{O}_2$ measurements was 0.01% using conventional isotope ratio mass spectrometry with minor modifications. The original dataset was adjusted to give the best fit with the re-analysed data. We interpret the data using a newly developed model [Severinghaus and Battle, submitted] in which the firn air composition changes as a result of gravitation, molecular diffusion, convective mixing in the upper 15 m, and the sealing of air bubbles in the bottom 7 m of the firn column. The model was parameterised for the 120 m deep firn column at South Pole and run for 200 years, with the following atmospheric change scenarios prescribed as boundary conditions at the surface of the firn: (a) no change, (b) linear increase or (c) decrease of $\delta^{18}\text{O}-\text{O}_2$ by 0.05 to 0.1% over the last 150 years, i.e. starting in 1850. The model has not been fully evaluated for $\delta^{18}\text{O}-\text{O}_2$ yet, but was found to adequately reproduce the depth profiles for several other gases ($\delta^{15}\text{N}$, $\delta(\text{O}_2/\text{N}_2)$, $\delta(\text{Ar}/\text{N}_2)$) analysed on the same samples.

The observed and simulated firn air profiles show nearly linear enrichment in $\delta^{18}\text{O}-\text{O}_2$ with depth in the middle part of the profile (≈ 40 to 110 m), as expected from gravitational effects and molecular diffusion. Artefacts associated with convective mixing or bubble formation are small in this region of the profile. Assuming a decrease of 0.05% over 150 years gave the same slope as the observations ($10.65 \pm 0.1 \cdot 10^{-3} \%$ /m). However, the current analytical uncertainties put limits on this determination of DME changes ($0.05 \pm 0.1\%$ decrease) related to human activity.

The approach described above presents a challenge for mass spectrometric analyses. For example, the firn air $\delta^{18}\text{O}-\text{O}_2$ values at 115 m depth differ by 6 and $13 \cdot 10^{-3}\%$ between the scenarios. The analytical precision required to resolve such differences needs to be at least $1 \cdot 10^{-3}\%$. One way to achieve this would be to repeat laboratory analyses of air samples. For example, a standard error of $0.6 \cdot 10^{-3}\%$ could be achieved with ≈ 70 repeated analyses at 5 or 25 at $3 \cdot 10^{-3}\%$ standard deviation. In light of the automated procedures currently being developed, it seems possible to quantify DME changes within the next few years. Finding out if and how much the Dole-Morita effect has been affected by human activity will add to our understanding of its current value and what drives its variations over longer time scales.

REFERENCES

- Battle M, M Bender, T Sowers, PP Tans, *Nature* 383, 231-235, 1996.
Bender M, T Sowers, L Labeyrie, *Global Biogeochemical Cycles* 8, 363-376, 1994.
DeFries RS, CB Field, I Fung, GJ Collatz, L Bounoua, *Global Biogeochemical Cycles* 13, 803-815, 1999.
Dole M, *Journal of the American Chemical Society* 57, 2731, 1935.
Friedman I, JR O'Neil, *U.S. Geological Survey Professional Paper* 440-KK, Data of Geochemistry, 1977.
Hoffmann G, M Cuntz et al., *Global Biogeochemical Cycles* 18, 2004.
Horibe Y, K Shigehar, Y Takakuwa, *Journal of Geophysical Research* 78, 2625-2629, 1973.
Kroopnick P, H Craig, *Science* 175, 54, 1972.
Morita N, *Journal of the Chemical Society of Japan* 56, 1291, 1935.
Severinghaus JP, M Battle, submitted.
Severinghaus JP, A Grachev, M Battle, *Geochemistry, Geophysics, Geosystems* 2, 2001.