

Stable oxygen isotopes in hydrology

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The $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of meteoric water provide new insights on present and past hydrology. Global meteoric water define a tight straight line (GMWL) in the $\ln(\delta^{17}\text{O} + 1)$ vs. $\ln(\delta^{18}\text{O} + 1)$ plot. The slope of the GMWL (0.528) results, as expected, from precipitation forming in isotope equilibrium during cooling of air masses. When VSMOW is used as a reference, the GMWL has a positive intercept of the $\ln(\delta^{17}\text{O} + 1)$ axis showing that meteoric waters have an excess of ^{17}O with respect to seawater. This ^{17}O -excess of a given water sample is defined as:

$$^{17}\text{O-excess} = \ln(\delta^{17}\text{O} + 1) - 0.528 \cdot \ln(\delta^{18}\text{O} + 1)$$

The ^{17}O -excess is analogous to the well known deuterium excess and is the result of molecular diffusion fractionation of evaporating water vapor through air. The diffusion effect is inversely correlated with relative humidity (RH), and thus ^{17}O -excess increases when RH over the evaporation site goes low. Yet, in contrast to deuterium excess, ^{17}O -excess is independent of the evaporation temperature and is only influenced by RH. This makes ^{17}O -excess a unique tracer useful for obtaining quantitative information on past relative humidity over the ocean, and thus for evaluating the links between climate and the hydrologic cycle.

I will give examples and explanations of variations in ^{17}O -excess in recent liquid precipitation, atmospheric moisture and polar ice. I will also discuss variations over glacial interglacial time scales in Antarctica and in the equatorial region.

The isotopic composition of atmospheric oxygen

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One of the very early discoveries in isotope geochemistry was that atmospheric oxygen is enriched in ^{18}O with respect to seawater [1]. This enrichment was named Dole effect. By the mid 50' it became clear that the main driving force causing the Dole effect is respiration that favours ^{16}O over ^{18}O . It was also demonstrated that photosynthesis produces oxygen close in isotopic composition to the substrate water [2]. Yet, the Dole effect, whose magnitude is almost 24 ‰ [3], cannot be explained exclusively by respiratory fractionation. Over the past four decades the consensus has been that evapotranspiration that enriches leaf water in heavy isotopes [4], enhances the Dole effect through the production of ^{18}O enriched O_2 in leaves of land vegetation. In this consensus, the respiratory fractionation on land has been taken to be about 18 ‰. This assumption, however, was proven wrong by our group [5, 6]. We showed that slow oxygen-gas diffusion in roots and soils reduces the effective respiratory fractionation, and globally, fractionation by soil respiration, which consumes most of the land production of O_2 , is about 14 ‰. This relatively small fractionation compensates for the evapotranspiration enhancement, and overall, the magnitude of the terrestrial component of the Dole effects remains relatively small, thus leaving the global effect unexplained. Our recent experiments [7], using $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios, show that marine photosynthesis produces O_2 that is enriched by several ‰ with respect to seawater. This new discovery solves the long standing question about the magnitude of the global Dole effect.

[1] Dole (1935) *J. Am. Chem. Soc.* **57**, 2731. [2] Lane & Dole (1956) *Science* **123**, 574-576. [3] Barkan & Luz (2005) *RCM* **19**, 3737-3742. [4] Dongmann (1974) *Radiat. Environ. Biophys.* **11**, 219-225. [5] Angert & Luz (2001) *GCA* **65**, 1697- 1703. [6] Angert *et al.* (2003) *GBC* **17**, 1030-1043. [7] Barkan *et al.* (2009) *GCA*, this volume.