Triple isotope effects accompanying evaporation of water: new insights from dedicated laboratory experiments

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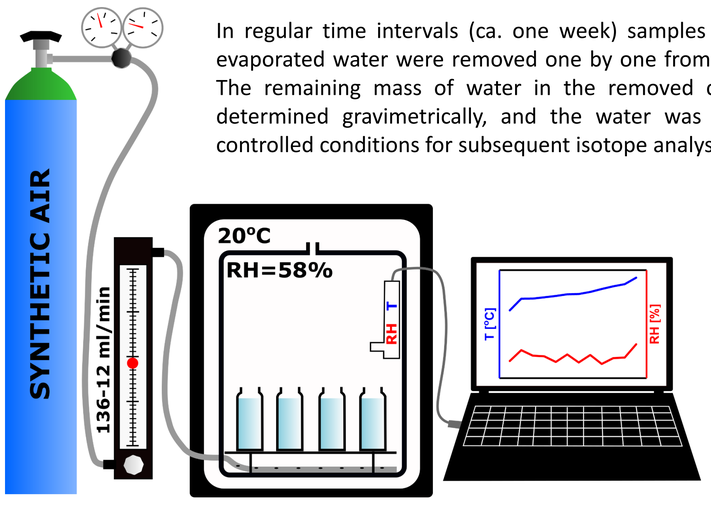
INTRODUCTION

Stable isotopes of hydrogen and oxygen (^{2}H and ^{18}O) have often been used for quantification of water budgets of lakes and other surface water bodies, in particular for the assessment of underground components of those budgets which are very difficult to quantify using classical hydrological methods [1]. Recent advances in laser spectroscopy resulted in the construction of commercial laser analysers capable of simultaneous analyses of ^{2}H, ^{18}O and ^{17}O content in water, with measurement uncertainties comparable ($\delta^{18}O$) or surpassing ($\delta^{2}H$) those routinely achieved by off-line sample preparation methods combined with conventional IRMS technique [2,3]. This opens up the doors for improving reliability of isotope-aided budgets of surface water bodies by adding third isotope tracer (^{17}O). This, however, requires good knowledge of triple isotope effects accompanying evaporation of water, in particular the kinetic isotope effect related to evaporation of $^{1}H_2{}^{17}O$ isotopologue.

Here we present the results of a dedicated laboratory experiment aimed at quantification of triple isotope effects accompanying evaporation of water. The experiment presented here hes been designed to achieve fully developed laminar layer at the water-atmosphere interface. The main goal of the experiment was to verify the Craig and Gordon conceptual model of evaporation [4] postulating existence of isotope equilibrium conditions at the interface and a laminar layer on top of it, where transport is controlled entirely by molecular diffusion. Above this laminar layer, non-fractionating turbulent transport occurs. Transport of water isotopologues through the laminar layer is associated with kinetic fractionation factor. So far, for $^{1}H_2{}^{17}O$ isotopologue the kinetic fractionation was determined by only one laboratory [5]. Our goal was to measure it using entirely different experimental set-up.

METHODS

Identical containers with predefined mass of water of known isotopic composition were placed in an isolated chamber with controlled parameters during the experiment (temperature, relative humidity, flow of synthetic air).



In regular time intervals (ca. one week) samples with partially evaporated water were removed one by one from the chamber. The remaining mass of water in the removed container was determined gravimetrically, and the water was stored under controlled conditions for subsequent isotope analyses.



Isotope analyses ($\delta^{2}H$, $\delta^{18}O$, $\delta^{17}O$) were conducted with the aid of Picarro L2140-*i* laser spectrometer. Four injections per sample were performed. Raw analytical data were corrected for memory effect and in-the-run drift of the instrument and were calibrated against two reference standard waters (USGS47 and USGS48) [3].

Isotope evolution of water during evaporation into dry atmopshere (as realized in the experiment) can be described by the Rayleigh formula, with two parameters controlling this evolution: (i) the remaining fraction of water, and (ii) the effective fractionation factor.

$$\Delta\delta = F^{\frac{1}{\alpha_{eff}}-1} - 1 \qquad (1)$$

$$\alpha_{eff} = \alpha_{eq}(T) \cdot \alpha_{kin} \qquad (2)$$

Δδ – fractional change of the δ the value of evaporating water,
F – remaining fraction of evaporating water,
α – fractionation factor: ***eq*** – equilibrium, ***kin*** – kinetic; ***eff*** – effective,
T – temperature,

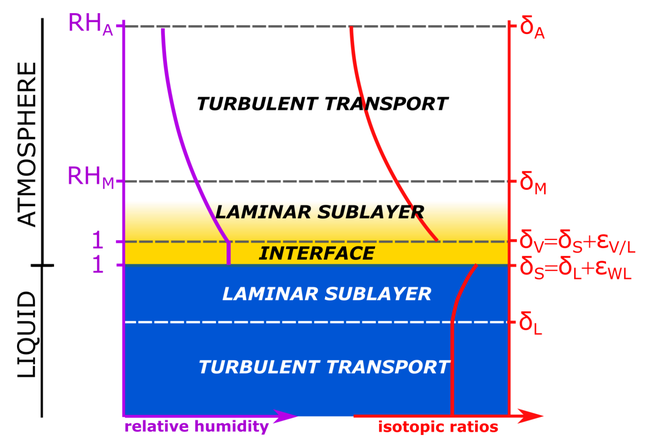
ASSUMPTIONS

1. Fractionation factor *α* is constant during process
2. Reservoir is well mixed (homogeneous)
3. The removed portions of water are small with respect to the mass of all water in the system

The results of the experiment were interpreted in the framework of the Craig-Gordon conceptual model of evaporation [4].

$$\varepsilon_{kin} = n \cdot \varepsilon_{diff}(1 - RH) \qquad (3)$$

ε – isotopic enrichment (***kin*** – kinetic, ***diff*** – diffusive), ***ε = α – 1***;
n – turbulence parameter (0.5 < n < 1); ***RH*** – relative humidity



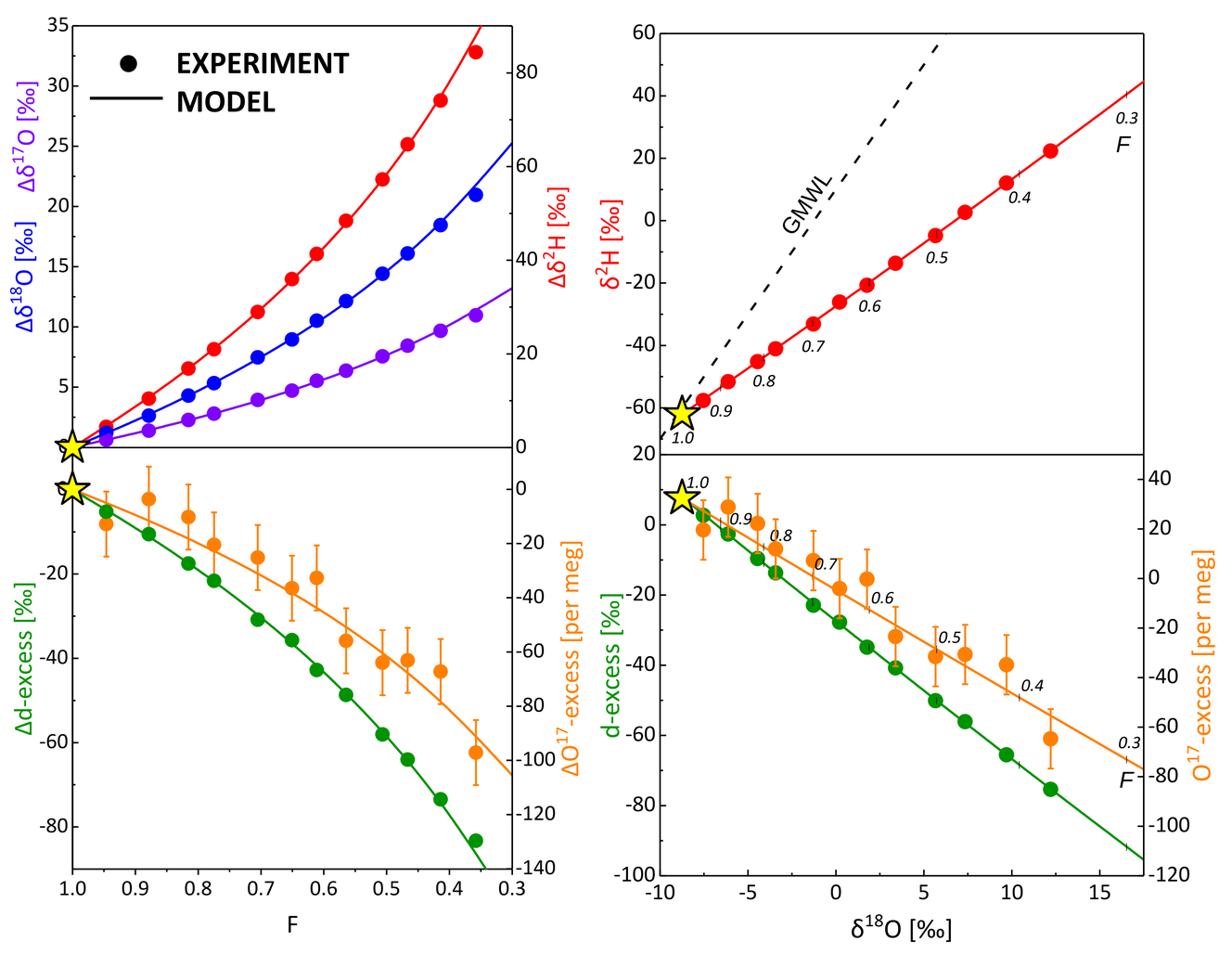
RESULTS

The relationship (1) was fitted to the analytical results obtained for all three isotopes (Δδ and F values), with α_{eff} as fitting parameter. Next, from equation (2) α_{kin} was calculated for each isotope, with the equilibrium fractionation coefficients derived for the temperature of the experiment from known empirical relationships for ^{2}H and ^{18}O [4], and from the relationship $^{17}\alpha_{eq} = {}^{18}\alpha_{eq}{}^{0.529}$ for ^{17}O. Then, from equation (3), the value of turbulence parameter n was obtained separately for each isotope system (^{2}H, ^{18}O, ^{17}O) using known diffusive fractionation factors (α_{diff}) and associated ε_{diff} values [5,6], and the mean value of relative humidity measured during the experiment (RH=58%). The results are summarised below.

Isotope	ε_{kin} [‰] (experiment)	Turbulence parameter 'n'	ε_{diff} [‰] (literature)
^{2}H	3.9	0.37	25.1 [6]
^{18}O	11.3	0.94	28.5 [6]
^{17}O	5.8	0.94	14.6 [5]

The parameter 'n' (turbulence parameter) is quantifying apparent reduction of the diffusive fractionation occuring in the laminar layer due to impact of turbulent transport which is not fractionating (micro eddies reaching the interface and returning to turbulent atmosphere) and should be the same for each isotope system. However, it is not!

MODEL VS. EXPERIMENT



HYPOTHESIS:

THE EVAPORATING RESERVOIR IS NOT ISOTOPICALLY HOMOGENEOUS

Due to preferential loss of light isotopes to the vapor interface (equilibrium fractionation), thin laminar layer at the liquid interface is becoming enriched in heavy water isotopologues. With time, a steady-state diffusion profile is developing, with isotope enrichments of the liquid interface (ε_{wl}) different for each isotope system. Isotope enrichment of the evaporating surface can be interpreted in the framework of the Craig Gordon model as apparent reduction of the kinetic fractionations for the given RH value, occuring within gaseous laminar layer adjacent to the vapor interface (ε_{diff}).

For the given RH value measured in the experiment, eq. (3) can be then re-written as a set of three equations:

$$\begin{cases} {}^{2}\varepsilon_{kin}/_{1-RH} = 9.3 = n \times (25.1 - {}^{2}\varepsilon_{WL}) \\ {}^{18}\varepsilon_{kin}/_{1-RH} = 26.9 = n \times (28.5 - {}^{18}\varepsilon_{WL}) \\ {}^{17}\varepsilon_{kin}/_{1-RH} = 13.9 = n \times ({}^{17}\varepsilon_{diff} - {}^{17}\varepsilon_{WL}) \end{cases}$$

Where: *n* – turbulence parameter (the same for all three isotope systems),
$^{17}\varepsilon_{diff}$ – diffusive fractionation for $^{1}H_2{}^{17}O$ isotopologue
$^{2}\varepsilon_{WL}$, $^{18}\varepsilon_{WL}$, $^{17}\varepsilon_{WL}$ – isotope enrichments at the liquid interface

With some additional information concerning relationship between $^{17}\varepsilon_{WL}$ and $^{18}\varepsilon_{WL}$ and between $^{2}\varepsilon_{WL}$ and $^{18}\varepsilon_{WL}$ (Rozanski et al. – in preparation) the above equations can be solved for n, $^{17}\varepsilon_{diff}$, $^{2}\varepsilon_{WL}$, $^{18}\varepsilon_{WL}$ and $^{17}\varepsilon_{WL}$. The results are summarized below:

n = 1.009 ± 0.024, $^{17}\varepsilon_{diff}$ = 14.76 ± 0.48‰, $^{2}\varepsilon_{WL}$ = 15.9 ± 2.4‰, $^{18}\varepsilon_{WL}$ = 1.81 ± 0.26‰, $^{17}\varepsilon_{WL}$ = 0.96 ± 0.14‰

CONCLUSIONS

1. **The assumption often used in the description of isotopic effects accompanying evaporation, which says that the liquid phase is isotopically homogeneous during the process, leads to conflicting results for all three isotope systems.**
2. **If surface enrichment of the liquid phase, different for each heavy isotopologue ($^{1}H^{2}H^{16}O$, $^{1}H_2{}^{18}O$, $^{1}H_2{}^{17}O$) is included in the model, consistent results for all three isotope systems can be obtained.**
3. **The kinetic fractionation for $^{1}H_2{}^{17}O$ isotopologue derived from the experiment is equal to 14.76 ± 0.48 ‰, which agrees well with the value of 14.60 ± 0.30 reported by Barkan and Luz [5].**

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