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

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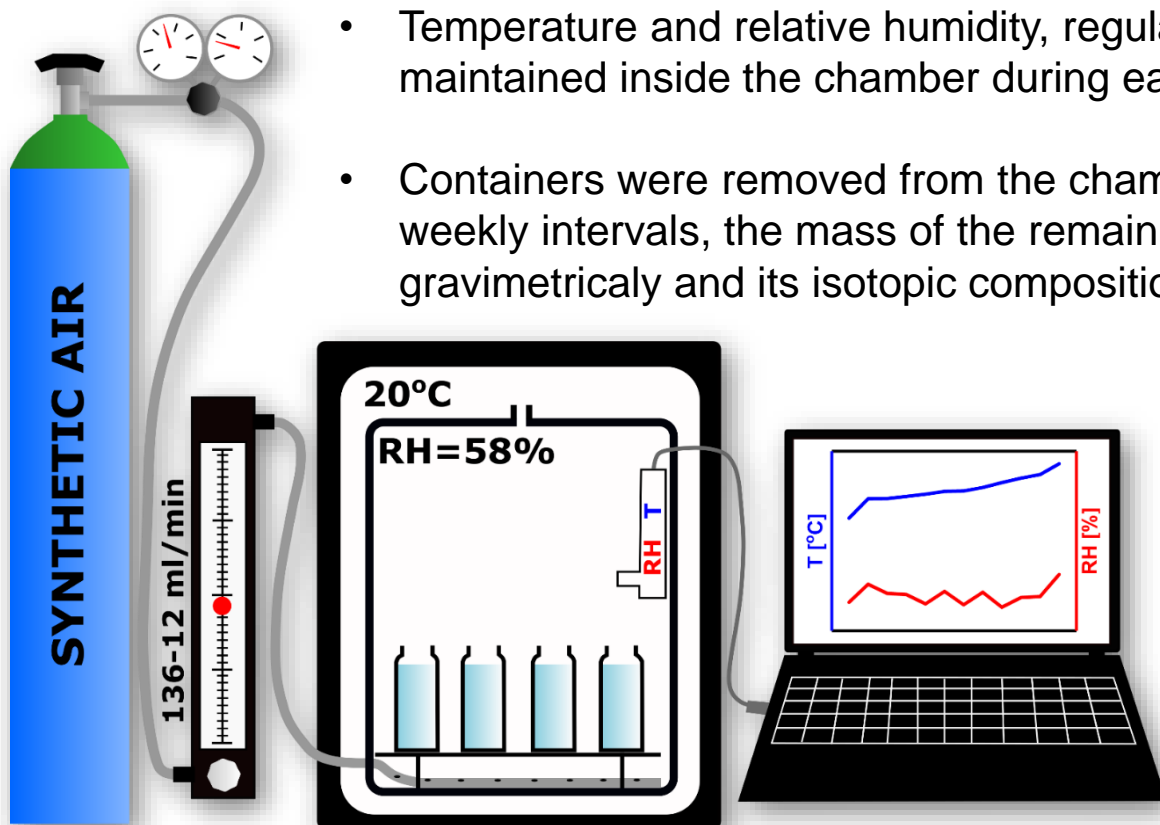
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GOALS:

1. Determination of kinetic fractionation (ε_{kin}) for $^1\text{H}_2^{17}\text{O}$ isotopologue
2. Investigating the dependence of kinetic fractionation (ε_{kin}) on the relative humidity and temperature for three isotopologues of water ($^1\text{H}^2\text{H}^{16}\text{O}$, $^1\text{H}_2^{18}\text{O}$, $^1\text{H}_2^{17}\text{O}$)

EXPERIMENTAL SET-UP

- Twelve containers (volume 20 ml), filled with defined mass of deionized water of known isotope composition were placed inside thermostated chamber
- Temperature and relative humidity, regulated by the flow of carrier gas, were maintained inside the chamber during each experiment
- Containers were removed from the chamber one by one in approximately weekly intervals, the mass of the remaining water was measured gravimetrically and its isotopic composition was analysed



- Isotope analyses ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$) were performed using Picarro L2140-i laser spectrometer
- Raw data were corrected for memory effect and short-term drift and calibrated against USGS47 and USGS48 standards [2]



CONCEPTUAL MODEL

The results of the experiment were interpreted in the framework of the Craig-Gordon conceptual model of evaporation [3]:

- isotope equilibrium conditions at the interface → **equilibrium fractionation**

$$\alpha_{eq} = \alpha_{eq}(T)$$

- laminar sublayer on top of the interface, where transport is controlled by **molecular diffusion**

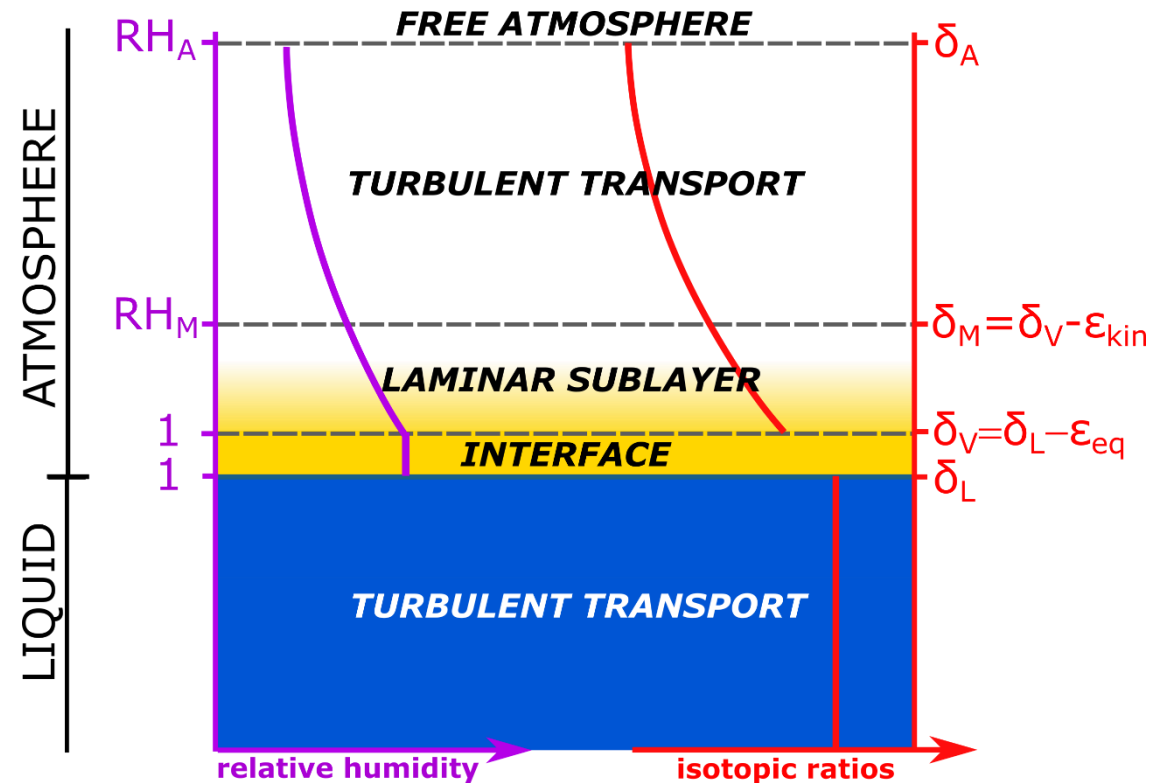
$$\varepsilon_{kin} = n \cdot \varepsilon_{diff}(1 - RH)$$

ε – isotopic fractionation (*kin* – kinetic, *diff* – diffusive), $\varepsilon = \alpha - 1$;

n – turbulence parameter ($0.5 < n < 1$)

RH – relative humidity

- non-fractionating turbulent transport** above the laminar sublayer



CONCEPTUAL MODEL

Isotopic evolution of water during evaporation into the dry atmosphere can be described by the following Rayleigh formula [5]:

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

$\Delta\delta$ – change in isotopic composition of the evaporating water, expressed with respect to its initial isotopic composition,

F – remaining fraction of water,

α_{eff} – effective fractionation factor $\alpha_{eff} = \alpha_{eq}(T) \cdot \alpha_{kin}$

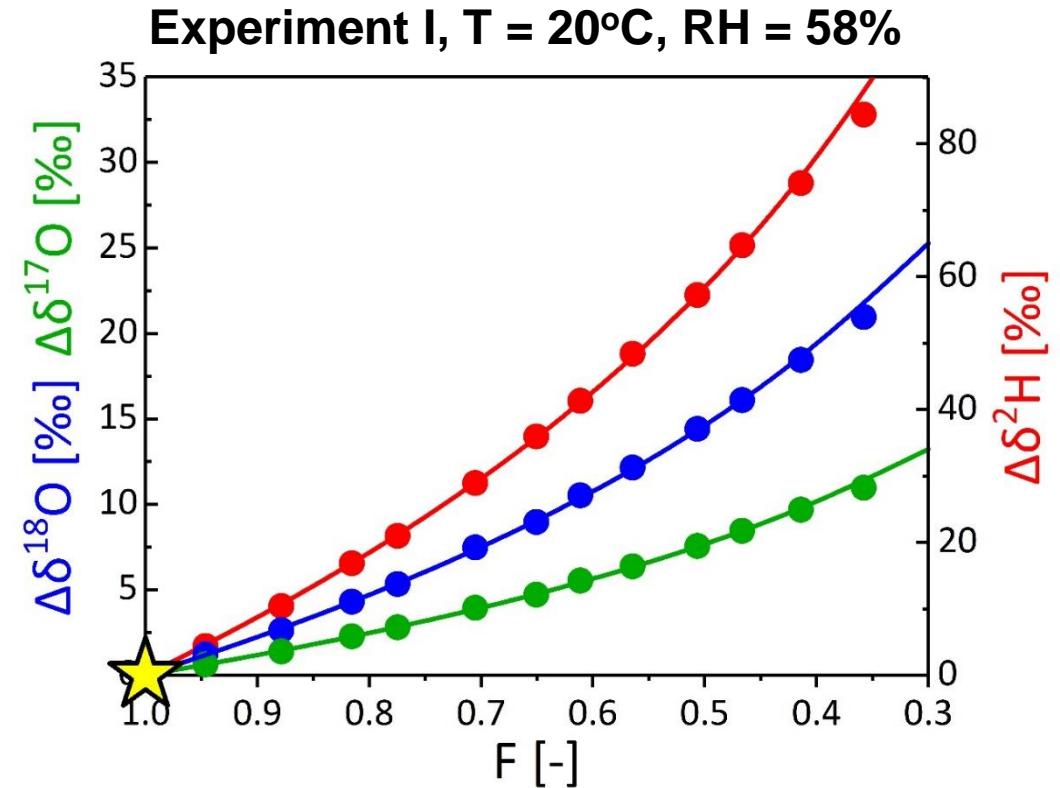
eq – equilibrium, kin – kinetic, eff – effective

ASSUMPTIONS

1. Effective fractionation factor α_{eff} is constant during process
2. Reservoir of evaporating water is well mixed
3. The removed portions of water are small with respect to the total mass of water in the system

RESULTS

- ① $\Delta\delta = F^{\alpha_{eff}} - 1$
- ② $\alpha_{eff} = \alpha_{eq}(T) \cdot \alpha_{kin}$
- ③ $\varepsilon_{kin} = n \cdot \varepsilon_{diff}(1 - RH)$
 $\alpha_{kin}^{\parallel} - 1$



- The relationship ① was fitted to the analytical results obtained for all three isotopes ($\Delta\delta$ and F values), with α_{eff} as fitting parameter
- From equation ② α_{kin} was calculated for each isotope, with equilibrium fractionation factors α_{eq} calculated from known empirical relationships for ^2H and ^{18}O , for the temperature of the experiment. For ^{17}O equilibrium fractionation the following relationship was used: $^{17}\alpha_{eq} = ^{18}\alpha_{eq}^{0.529}$.
- From equation ③ the value of turbulence parameter 'n' was obtained separately for each isotope system (^2H , ^{18}O , ^{17}O) using literature values for diffusive fractionation (ε_{diff}) [1,4], and the mean value of relative humidity measured during the experiment (RH=58%).

RESULTS

Experiment I, T = 20°C, RH = 58%

Isotope	ϵ_{kin} [‰] (experimental)	Turbulence parameter 'n'	ϵ_{diff} [‰] (ref. [1,4])
^2H	3.9	0.37	25.1
^{18}O	11.3	0.94	28.5
^{17}O	5.8	0.94	14.6

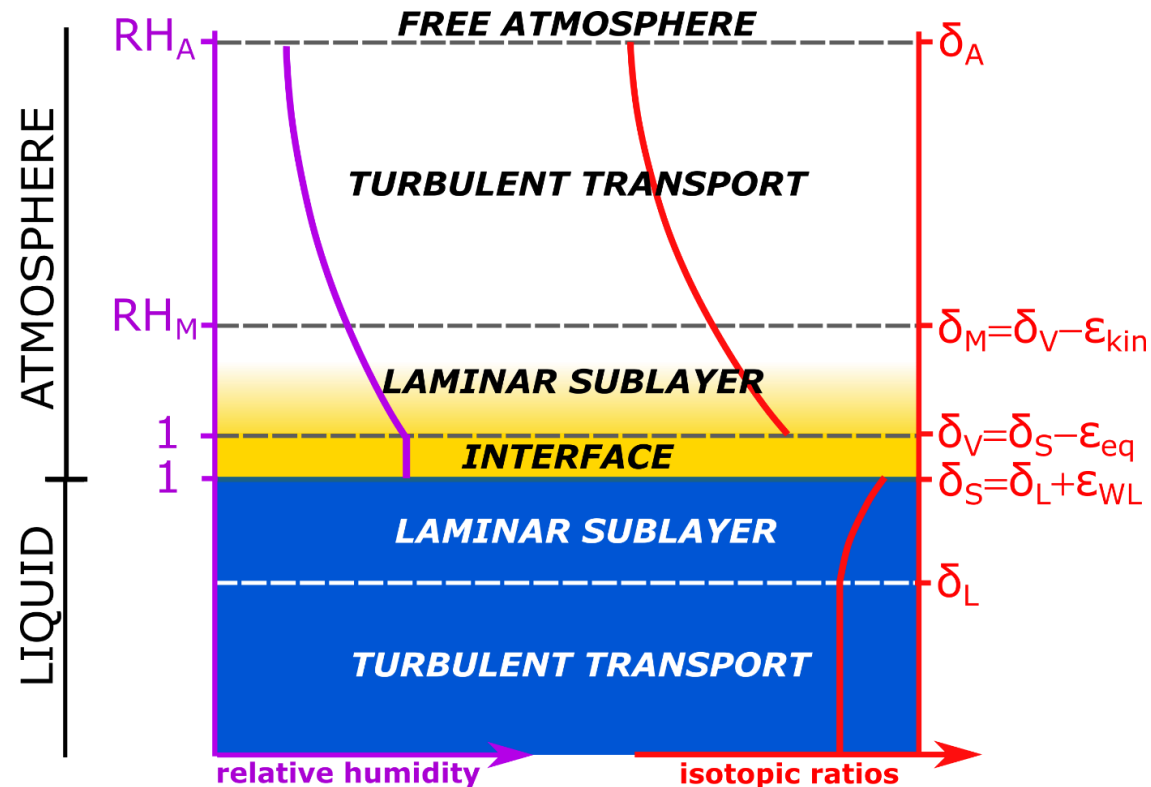
Turbulence parameter 'n' is quantifying apparent reduction of diffusive fractionation occurring in the laminar sublayer due to impact of turbulent transport which is not fractionating (micro eddies reaching the interface and returning to turbulent atmosphere).

Turbulence parameter should have the same value for each isotopic system.
However, it is not!

REVISED CONCEPTUAL MODEL

THE EVAPORATING RESERVOIR IS NOT ISOPICALLY HOMOGENEOUS

Due to preferential loss of light isotopes to the vapor interface (equilibrium isotope fractionation), thin laminar sublayer at the liquid interface is becoming enriched in heavy water isotopologues. With time, a steady-state diffusion profile is developing, with isotope enrichments at 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 diffusive fractionations (ϵ_{diff}) for the given RH value, occurring within gaseous laminar sublayer adjacent to the vapor interface.

RESULTS

$$\epsilon_{kin} = n(\epsilon_{diff} - \epsilon_{wl})(1 - RH)$$



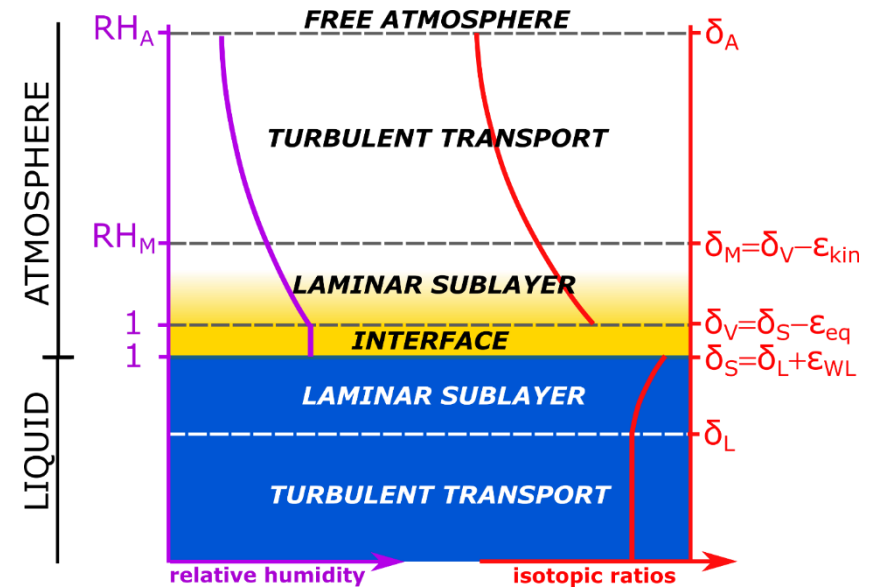
$$\begin{aligned} \frac{{}^2\epsilon_{kin}}{(1 - RH)} &= 9.3 = n \cdot (25.1 - {}^2\epsilon_{wl}) \\ \frac{{}^{18}\epsilon_{kin}}{(1 - RH)} &= 26.9 = n \cdot (28.5 - {}^{18}\epsilon_{wl}) \\ \frac{{}^{17}\epsilon_{kin}}{(1 - RH)} &= 13.9 = n \cdot ({}^{17}\epsilon_{diff} - {}^{17}\epsilon_{wl}) \end{aligned}$$



$$\begin{aligned} n &= 1.009 \pm 0.10 \\ {}^2\epsilon_{WL} &= 15.9 \pm 1.0\text{‰} \\ {}^{18}\epsilon_{WL} &= 1.81 \pm 0.12\text{‰} \\ {}^{17}\epsilon_{WL} &= 0.96 \pm 0.06\text{‰} \\ {}^{17}\epsilon_{diff} &= 14.76 \pm 0.26\text{‰} \end{aligned}$$



${}^{17}\epsilon_{diff} = 14.60 \pm 0.30\text{‰}$
 [Barkan E. Luz B. Rapid Commun. Mass Spectrom., 2007(21) 2999-3005.]



DEPENDENCE OF ϵ_{kin} ON TEMPERATURE AND RELATIVE HUMIDITY

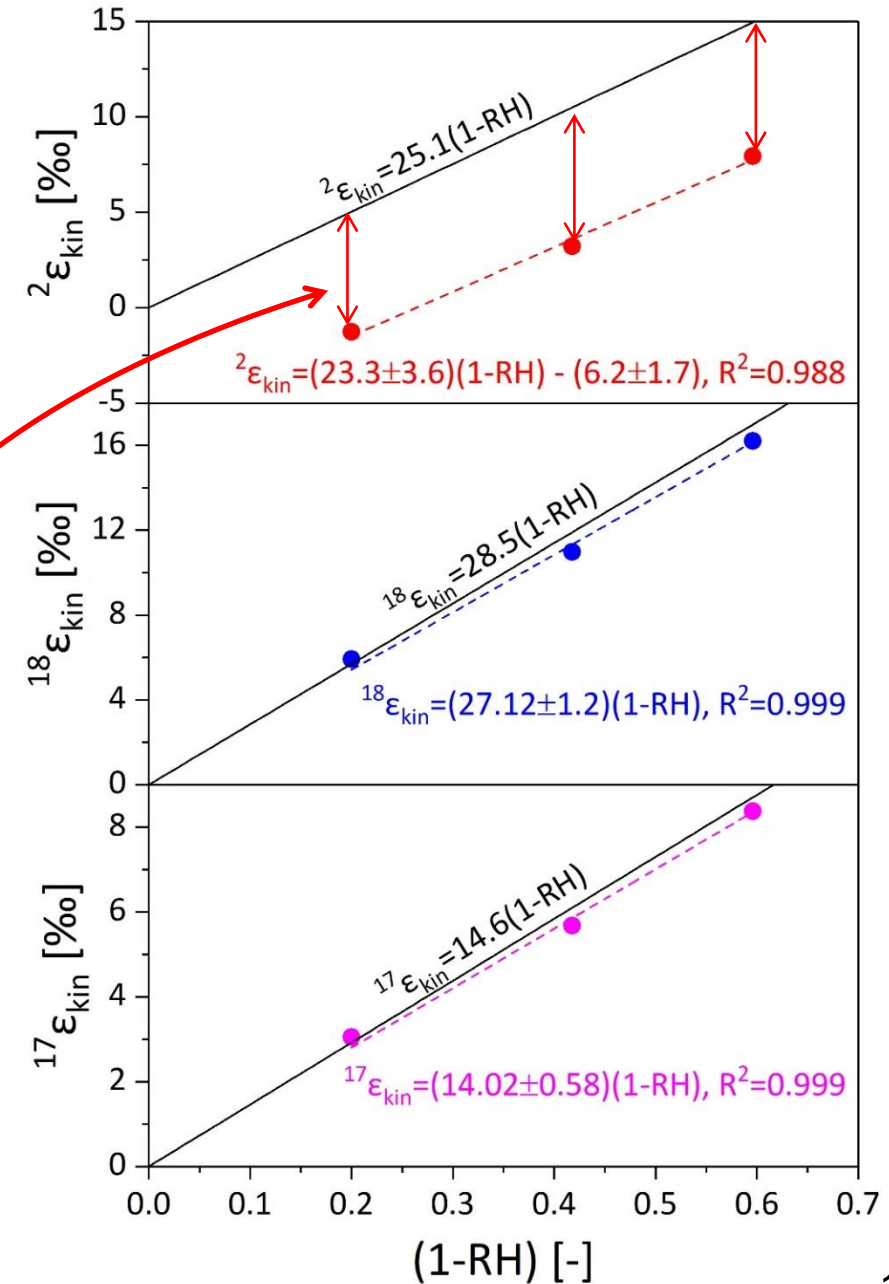
Experiments comprised two different temperatures ($T = 10^\circ\text{C}$ and 20°C) and three different relative humidities ($RH = 40, 58$ and 79%).

In the case of ^2H , the surface enrichment ϵ_{wl} is comparable to the diffusion enrichment ϵ_{diff} , which causes a significant, systematic deviation of experimental ϵ_{kin} from its value predicted by the model.

$$\begin{aligned}\epsilon_{kin} &= n(\epsilon_{diff} - \epsilon_{wl})(1 - RH) \\ &= n\epsilon_{diff}(1 - RH) - \underbrace{n\epsilon_{wl}(1 - RH)}_{\text{deviation}}\end{aligned}$$

Temperature dependence of ϵ_{kin}

	20°C	10°C
$^2\epsilon_{kin}$	3.2 ± 0.56	2.49 ± 0.78
$^{18}\epsilon_{kin}$	10.97 ± 0.22	10.91 ± 0.12
$^{17}\epsilon_{kin}$	5.68 ± 0.13	5.638 ± 0.070



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 ($^1\text{H}^2\text{H}^{16}\text{O}$, $^1\text{H}_2^{18}\text{O}$, $^1\text{H}_2^{17}\text{O}$) is included in the model, consistent results for all three isotope systems can be obtained.
- ③ The kinetic fractionation for $^1\text{H}_2^{17}\text{O}$ isotopologue derived from the experiment is equal to 14.76 ± 0.26 ‰, which agrees well with the value of 14.60 ± 0.30 reported by Barkan and Luz [1].
- ④ Within the quoted uncertainties, ε_{kin} does not depend on temperature of the evaporation process and shows linear dependence on the humidity deficit (1-RH)

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- [1] Barkan E., Luz B. Rapid Commun. Mass Spectrom., 2007(21) 2999-3005.
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