

# Triple Isotopic Composition of Oxygen in Water from Ice Cores

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## Key Words

Delta V, MAT 253, isotope ratio mass spectrometry, water stable isotopes, hydrological cycle, climate, ice core

## Introduction

Stable isotopes of water are largely used for various studies of climate and hydrological cycle. With this aim, the worldwide distribution of water isotopes is described through the database established by the Global Network for Isotopes in Precipitation (GNIP), a joint venture of the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO).<sup>1</sup> This database is essential for understanding the processes leading to variations in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in precipitation at seasonal and inter-annual timescales at different latitudes, i.e. the strong influences of both integrated precipitation along the trajectory and source evaporation for the low latitudes<sup>2</sup> and a much direct influence of temperature on both  $\delta^{18}\text{O}$  and  $\delta\text{D}$  for temperate to polar regions.<sup>3</sup>

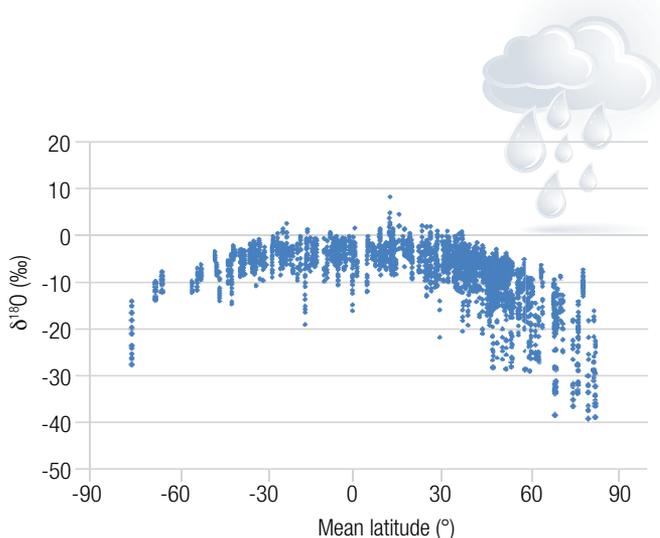


Figure 1. Mean latitude (°).

While  $\delta\text{D}$  and  $\delta^{18}\text{O}$  show the same first order variations on meteoric water samples with variations in  $\delta\text{D}$  being 8 times larger than  $\delta^{18}\text{O}$  variations, the combination of both in the d-excess ( $\text{d-excess} = \delta\text{D} - 8 * \delta^{18}\text{O}$ ) is strongly related to relative humidity at evaporation or during re-evaporation in low latitudes regions. Then, recent analytical developments have made it possible to measure the triple isotopic composition of oxygen in water with high precision. In meteoric water samples,  $\ln(\delta^{17}\text{O}+1)$  varies as 0.528 time  $\ln(\delta^{18}\text{O}+1)$ .<sup>5</sup> The  $^{17}\text{O}$ -excess has thus been defined as  $^{17}\text{O-excess} = \ln(\delta^{17}\text{O}+1) - 0.528 * \ln(\delta^{18}\text{O}+1)$ . As for d-excess, this parameter has been shown to be strongly dependent on relative humidity at evaporation and is thus a strong added parameter for all studies related to climate and hydrological cycle. In this note, we concentrate on the study of  $\delta^{18}\text{O}$ , d-excess and especially the added value of  $^{17}\text{O}$ -excess in polar ice cores for constraining the relationship between climate and water cycle organization. We present the basis for this research and the importance of the standard calibration of this new parameter not only for laboratory inter-comparison but also comparison with modeling outputs.

## Potential Reconstruction of Recent and Past Relative Humidity in Air Masses Using Water Isotopes ( $\delta^{18}\text{O}$ , d-excess, $^{17}\text{O}$ -excess)

Water isotopic measurements,  $\delta^{18}\text{O}$  and  $\delta\text{D}$ , are performed on polar ice cores since more than 40 years. At first order,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of polar ice cores relate to variations of past temperature at the drilling site. In addition to the temperature reconstruction and following the observation at lower latitudes, the combination of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in the second order parameter d-excess was expected to bring strong constraints on the humidity in the main region of evaporation.<sup>6</sup> It has since been shown that d-excess in Polar Regions is actually influenced by temperature in the evaporative and precipitation regions and relative humidity in the evaporative regions. The temperature affects differently  $\delta\text{D}$  and  $\delta^{18}\text{O}$  along the trajectory of a water sample from the source region of evaporation to the site region of condensation. Because of this, d-excess of snow is strongly imprinted by temperature. This undeciphered temperature influence is the main drawback to apply the d-excess as a powerful humidity proxy. On the contrary, temperature affects similarly  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  along the trajectory of a water mass from evaporation to precipitation so that  $^{17}\text{O}$ -excess in polar ice is expected to

be much less sensitive to temperature.<sup>7</sup> As a consequence,  $^{17}\text{O}$ -excess in polar ice cores should be a more direct tracer of relative humidity of the source region of evaporation.

Combined measurements of  $\delta^{18}\text{O}$ , d-excess and  $^{17}\text{O}$ -excess with isotopic modeling have been performed over 3 seasonal cycles (2003 – 2005) using snow from a surface snow pit at the Greenland drilling site of NEEM (77°27'N 51°3.6'W). The 3 parameters exhibit clear seasonal cycles (Figure 2) with  $\delta^{18}\text{O}$  variations paralleling the local temperature variations, d-excess marking a clear maximum during fall and  $^{17}\text{O}$ -excess being anti-correlated with  $\delta^{18}\text{O}$  variations. The interpretation of these parameters has been performed using an isotopic model forced by observed principle climate parameters of tropical North Atlantic Ocean source region (32–42°N, 25–40°W) and the local Greenland climatic conditions. The d-excess variations are well explained by the oceanic temperatures exhibiting a maximum during fall of each year, while  $^{17}\text{O}$  excess is anti-correlated to relative humidity in the tropical Atlantic Ocean region. These variations can well be explained by the isotopic models that predict a 1 ppm decrease of  $^{17}\text{O}$ -excess for a 1% increase in relative humidity at evaporation.

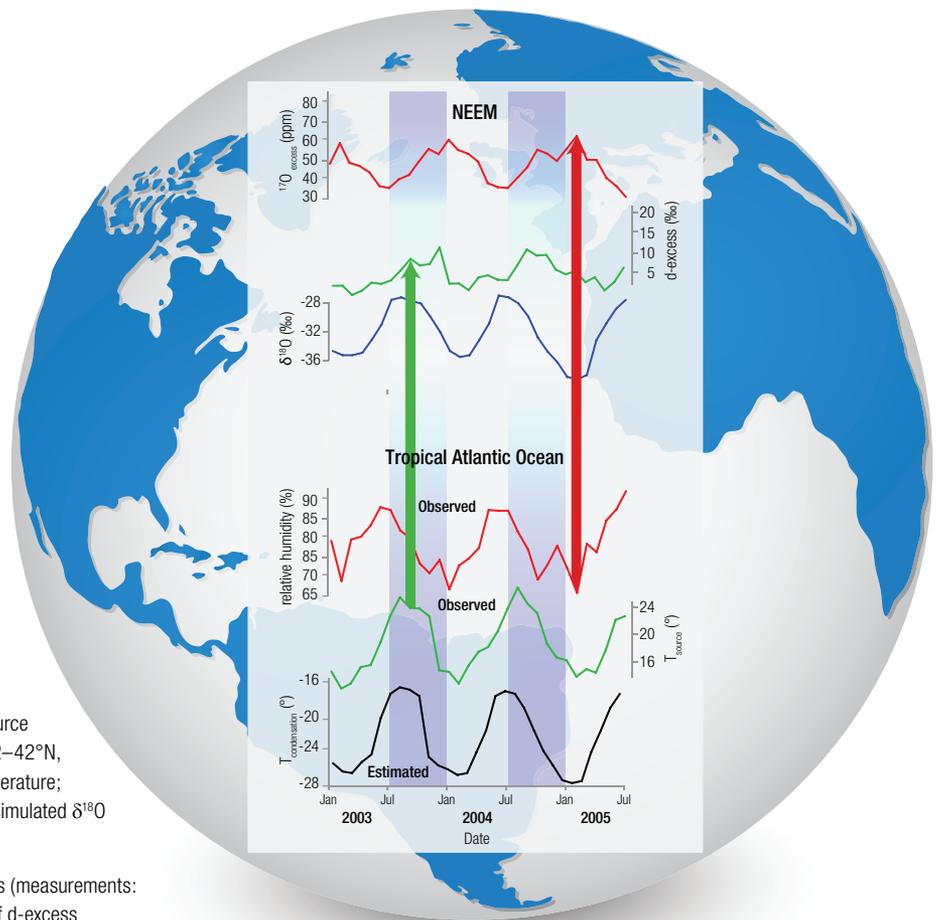


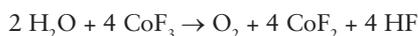
Figure 2. Comparison of measured and modeled isotopic composition of water over three seasonal cycles at NEEM (Greenland).

(Bottom) From top to bottom: seasonal variations of the source relative humidity (a tropical north Atlantic source region, 32–42°N, 25–40°W); seasonal variations of the source surface temperature; temperature of condensation (NEEM) adjusted so that the simulated  $\delta^{18}\text{O}$  evolution (right panel) fits the measured  $\delta^{18}\text{O}$  evolution.

(Top) From top to bottom: seasonal variations of  $^{17}\text{O}$  excess (measurements: dark thin line; model: light thick line); seasonal variations of d-excess (measurements: thin line; model: dark line); seasonal variations of  $\delta^{18}\text{O}$  (measurements: thin line; model: dark line).

## Preparation of Water for $^{17}\text{O}$ Excess Determination and Standards

In order to analyze the triple isotopic composition of oxygen by dual inlet method on Isotope Ratio Mass Spectrometry (IRMS), water molecules shall first be transformed in oxygen. The conversion is achieved through a fluorination reaction with cobalt fluorine so that:



A final precision of 5 ppm on the  $^{17}\text{O}$ -excess of water with a Thermo Scientific<sup>TM</sup> Delta XL<sup>TM</sup> IRMS is best obtained following the experimental method first displayed by Barkan and Luz.<sup>9</sup> Firstly, 2  $\mu\text{l}$  water is injected in a constant helium flow, vaporized and converted to  $\text{O}_2$  within a nickel tube containing  $\text{CoF}_3$  at 370 °C. Directly after the nickel tube HF and  $\text{CoF}_2$  are trapped while oxygen is recovered in a molecular sieve (1/8" stainless steel tube) using two serial liquid nitrogen traps. Supernatant and entrapped helium is removed by heating and refreezing the  $\text{O}_2$  trap at -190 °C. Each of the  $\text{O}_2$  samples is transferred again to a 1/4" stainless steel coldfinger at -270 °C which is part of a home-made manifold (10 samples). In a second step and after a 40 min warming at room temperature, the home-made manifold is connected with the Thermo Scientific Delta V<sup>TM</sup> IRMS or Thermo Scientific MAT 253<sup>TM</sup> IRMS. Simultaneous measurements of the signals on masses 32, 33 and 34 are done. Each sample is measured through a sequence of two runs of 16 dual inlet measurements, lasting approximately one hour on a whole. The pressure is classically adjusted to obtain a signal for mass 32 of 12 V on the Delta V IRMS and 6 V on the MAT 253 IRMS.

The standard for dual inlet measurements of pure oxygen is a flask of pure oxygen from a commercial bottle (5.0). Our measurements are calculated versus V-SMOW. For this, we have performed fluorination and measurements of  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  of our internal water standards (Table 1) in parallel to international standards provided by IAEA (V-SMOW2, GISP2, SLAP2). From this calibration of our standards and inter-calibration with other institutes,<sup>10</sup> we run at least 1 internal standard in our series of 10 samples every day to check the stability of our measurements.

## Calibration of $^{17}\text{O}$ of Water Samples for Correct Interpretation of $^{17}\text{O}$ -Excess

Calibration issue is key for  $^{17}\text{O}$ -excess measurements because of the very small signals, of the order of ~10 ppm, that are measured over a large range of  $\delta^{18}\text{O}$  in meteoric water, up to ~ 15‰ in leaf water and down to -60‰ in ice cores from the East Antarctic plateau. To deal with this large variety of isotopic signatures, two international water standards are classically used, VSMOW with a  $\delta^{18}\text{O}$  of 0‰ and SLAP with a  $\delta^{18}\text{O}$  of around -55.5‰. The  $^{17}\text{O}$ -excess of VSMOW is assigned to 0 ppm by definition but  $^{17}\text{O}$ -excess of SLAP has never been determined in an absolute way. After showing uncertainties linked with the experimental procedure, we explain below what drove the consensus of taking a value of 0 ppm for  $^{17}\text{O}$ -excess of SLAP which is the international accepted calibration value.

The first step in our calibration effort was to measure the dispersion of SLAP vs SMOW values when measuring  $^{17}\text{O}$ -excess on different instruments. Due to the recent shortage of VSMOW and SLAP at IAEA, VSMOW2 and SLAP2 were run on the fluorination line and their triple isotopic composition measured on two IRMS at LSCE in a dual inlet mode. For both the MAT 253 and the Delta V IRMS, the obtained raw  $\delta^{18}\text{O}$  values for SLAP2 vs VSMOW2 were very close with  $\delta^{18}\text{O}$  of ~-55‰. However, we have noted a significant difference in the  $\delta^{17}\text{O}$  values leading to a raw measurement of  $^{17}\text{O}$ -excess for SLAP2 vs VSMOW2 of +26 ppm on the Delta V IRMS and -30 ppm on the MAT 253 IRMS (Table 1). The same effect is observed when running two different pure oxygen gases with a  $\delta^{18}\text{O}$  difference of ~ 52.6‰ on the dual inlet system of the two IRMS (Table 1). Measurements performed with internal water standard with  $\delta^{18}\text{O}$  value intermediate between VSMOW and SLAP have also shown increasing  $^{17}\text{O}$ -excess differences when the difference in  $\delta^{18}\text{O}$  increases between the two oxygen samples (Table 1). The high robustness and stability of the MAT 253 and the Delta V instruments approves the ability to recognize this effect over months for a given filament and rarely changed source tuning.

Table 1. Measurements of the triple isotopic composition of oxygen on two different mass spectrometers. The 5 first lines correspond to analyses of home water standards after conversion to  $\text{O}_2$  by fluorination and the last line corresponds to measurements performed on pure  $\text{O}$  gas.

	Raw $\delta^{18}\text{O}$ (‰)	Raw $^{17}\text{O}$ -excess (ppm) Delta V	Raw $^{17}\text{O}$ -excess (ppm) MAT 253
SLAP2 vs V-SMOW2	-55.051	26	-30
Talos2 vs V-SMOW2	-38.823	35	-1
D57 vs VSMOW2	-32.513	39	11
ROSS 4 vs VSMOW2	-18.658	41	31
EPB5 vs VSMOW2	-6.317	18	19
$\text{O}_2$ -high vs $\text{O}_2$ -low	52.648	-481	-433

Given the above observations, the calibration of measurements vs. the two extreme standards V-SMOW and SLAP is essential and can easily be done using a linear correction because of the robustness of the two IRMS. The  $^{17}\text{O}$ -excess value of SLAP2 has been assigned to 0 ppm because of its nature to fit to the average of the different measurements.<sup>12</sup> Additionally, 0 ppm of the  $^{17}\text{O}$ -excess of SLAP keeps data and modeling outputs logic.<sup>13</sup>

All laboratories measuring  $^{17}\text{O}$ -excess now use this value of 0 ppm for SLAP so that we have an excellent coherency to compare all  $^{17}\text{O}$ -excess measurements produced worldwide. We are also very coherent to compare model and data since we have ensured that the experimental determination of fractionation coefficients, now used in AGCM equipped with water isotopes, has been determined on the internationally accepted reference scale of SMOW vs. SLAP both at HUJI for vapor liquid and kinetic fractionation coefficients<sup>14</sup> and at LSCE for vapor – solid fractionation coefficients.<sup>15</sup>

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### Conclusion

The triple isotopic composition of oxygen in water is a complementary tool for the study of the relationship between climate and water cycle. It has been proved to be extremely useful for inferring the variations of relative humidity at evaporation. Its measurement is now routinely performed in several institutes through the combination of a fluorination line for conversion of water to oxygen and dual inlet measurements in IRMS with an accuracy of 5 ppm. Still, we have demonstrated that for the large range of  $\delta^{18}\text{O}$  in meteoric water, measurements on different IRMS may provide  $^{17}\text{O}$  excess systematic shifts of up to 50 ppm which is the maximum amplitude of observed  $^{17}\text{O}$  excess variations. Such discrepancy makes the need for a correct two point calibration on each IRMS using VSMOW2 and SLAP2, in analogy to SMOW/SLAP corrections for  $\delta^{18}\text{O}$  of oxygen in water. This calibration is also essential for a meaningful comparison between isotopic modeling and measurements. This is the reason why a reference value of  $^{17}\text{O}$ -excess of 0 ppm is classically taken to be coherent with experimental determination of fractionation coefficients associated with the triple isotopic composition of oxygen.

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